THEORETICAL STUDIES OF ZEOLITES

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by

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ABSTRACT

The statistical thermodynamics of sorption in zeolites is studied. The multicomponent sorbate is regarded as a localized assembly of quasi-independent subsystems each contained in a sorption cavity of the microporous sorbent. Molecular exchange among the subsystems as well as between the assembly and the gas phase that is in thermodynamic equilibrium with the sorbate is allowed. Molecular statistics of the sorbate is worked out in detail with respect to a few representative ensembles.

In effecting thermodynamic association of theoretical results, a quasi-grand partition function is related to the sorption system which is in complete thermal and material but only in partial mechanical equilibrium with its surroundings. Fundamental thermodynamic equations of the sorbate are derived, and their conditions of integrability with respect to physical variables are interpreted in relation to 'surface effects' and certain operational restrictions connected with the sorption system. A study of small-system thermodynamics further helps to clarify the behaviour of individual subsystems, especially as regards fluctuations.

A quantitative theoretical study of the sorption of krypton and methane in Linde molecular sieve 5A is attempted. By means of analytic mathematics and Monte Carlo methods, statistical thermodynamic functions of the subsystems are calculated from relevant physical parameters. Some interesting features of the techniques used are also discussed. Interactions of the sorbate and sorbent, and in particular the effects due to exchangeable cations in the sorption cavities, are investigated. To indicate the degree of localization of the sorbate, probability distribution functions of the sorbate molecules within a specific subsystem, together with their distribution densities among all the subsystems are presented. Thermodynamic functions of the assembly are then calculated and compared with available experimental data. Finally, the usefulness of various approaches to the study of sorption in zeolites is assessed.

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CHAPTER 1

THEORETICAL STUDIES OF SORPTION IN ZEOLITES

1.1 INTRODUCTION

Zeolites are crystalline aluminosilicates of open structures with large sorption cavities which are interconnected by channels and openings of definite and uniform sizes. (Fischer & Meier 1965, Meier 1967) They are of general interest because of their crystal structures and mineralogy, their syntheses and modifications, their selective sorption and diffusion properties, their ion-exchange and molecular-sieve behaviours, and also their chromatographic and catalytic activities. In fact some of them already have important industrial applications. (Society of Chemical Industry Conference on Molecular Sieves, London, 1967)

Sorption properties of zeolites are determined by the geometry of their cavities, channels and openings, as well as by the chemical compositions of their aluminosilicate frameworks. Molecules having appropriate dimensions with respect to openings of the internal cavities can enter and be sorbed. (Barrer 1963, Kiselev 1965) As zeolites are microporous sorbents, in the study of their sorption properties the usual concept of 'surface adsorption' is, strictly speaking, inapplicable. Instead it should be more appropriate to consider the sorption as a filling of space volumes of the sorption cavities. Consequently in this case a detailed analysis of the sorption data may require some special theories other than those which have already proved successful in their application to sorption in other solids. (Bakaev 1966)

1.2 OUTLINE OF THE THESIS

The principal aim of this thesis is to study the sorption in zeolites from the standpoints of statistical mechanics, small-system thermodynamics and macroscopic thermodynamics. In particular an attempt is made to study the effects of microporosity of the sorbent on equilibrium properties of the sorbate.

Molecular statistics of the multicomponent sorbate in zeolite will be formally discussed in Chapter 2. There analytic expressions for the partition functions of some representative ensembles will be derived. In the theoretical model of interest the molecules sorbed in each cavity are considered as a quasi-independent subsystem for which statistical thermodynamic functions can be calculated. However, since the number of molecules in a subsystem is small, fluctuations in its statistical thermodynamic quantities can be relatively large. In consequence, not all of these functions have the significance of measurable thermodynamic quantities, and for each subsystem different ensembles of statistical mechanics are not necessarily equivalent. (Hill 1962)

It is certainly interesting to study the individual subsystems, especially as regards their fluctuations; so this will be attempted in Chapter 3. Chapter 4 is primarily concerned with the molecular statistical interpretation of certain measurable thermodynamic quantities that characterize the sorption. Thus thermodynamic association of theoretical results is made. The remaining chapters present details of pertinent mathematical techniques and evaluate the statistical thermodynamic quantities of interest from appropriate molecular and atomic parameters. In Chapters 7 and 8 calculations are carried out explicitly for the sorption of krypton and methane in Linde molecular sieve 5A. Some of these results are then compared with available experimental data.

1.3 STATISTICAL MECHANICAL APPROACH

The main object in studying statistical mechanics of the sorption in zeolites is to give it a molecular interpretation. Initially it is necessary to derive certain statistical thermodynamic functions that characterize a reasonable molecular model of the sorbate. To some of these can then be given the appropriate meanings of measurable thermodynamic quantities. (Hill 1956a) It is hoped that in this manner equilibrium experimental quantities could be conveniently related to the arrangements and properties of the individual atoms and molecules which compose the macroscopic system.

The zeolite sorbent is considered here as a large ordered assembly of distinguishable sorption cavities with identical structure. The sorbate molecules are chemically inert and are taken reversibly from the multicomponent gas phase that is in thermal and material equilibrium with the sorbed phase. Exchange of molecules among the cavities as well as between the whole assembly and the gas phase is permissible. (Bakaev 1966) In this open thermodynamic system complete and stable equilibrium is attained when the bulk chemical potential of each molecular species of the sorbate is identical in the two phases. (Guggenheim 1959) Nevertheless, from this fact it does not necessarily follow that the chemical potentials of the individual subsystems are thermodynamically well-defined and can thus be equated.

On the other hand each subsystem of relatively few molecules (up to about 16) in a single cavity is assumed to be quasi-independent. This means that its internal energy averaged over the relevant canonical ensemble is not an explicit function of the detailed distribution of other sorbate molecules in the neighbouring cavities. A theoretical treatment of the molecular statistical model described will be given in Chapter 2.

1.4 SMALL-SYSTEM THERMODYNAMIC APPROACH

It is of particular interest to study the sorption in zeolites from the point of view of small-system thermodynamics, for this should provide effective methods in analyzing, classifying and correlating equilibrium experimental data. As in macroscopic thermodynamics the primary object in studying the individual subsystems is to derive some equations that give useful interconnections between the thermodynamic functions characterizing them. However, since fluctuations in thermodynamic quantities can no longer be expected to be negligible, it is specifically required to derive those interconnections showing how the size of a subsystem does affect its intensive and extensive properties. (Hill 1963,1964) Of course there is no such effect in macroscopic thermodynamics.

Strictly speaking, ordinary thermodynamics applies only to the infinite limits of macroscopic systems. So it is useful to have a natural extension of its results to include an analysis of small subsystems, the behaviour of which should approach those of macroscopic thermodynamics in the appropriate large limits. Equations of macroscopic thermodynamics connect mean values of certain fluctuating extensive properties, such as the number of molecules in the system studied, its internal energy, entropy and free energies. Only the mean values are of real interest in this case because fluctuations about them are ordinarily so small that they are virtually the only possible results of any thermodynamic measurement. In contrast, for each of the small subsystems fluctuations cannot always be ignored: higher moments of the probability distribution functions of fluctuating extensive quantities are generally of interest as well as their mean values. Moreover, the higher moments are in fact related to derivatives of the mean values, so that in certain cases the derivatives could be conveniently estimated from fluctuations of appropriate quantities. Thus in Section 7.3 heat capacities of some specific subsystems will be calculated from fluctuations of their internal energies. In general, a hierarchy of thermodynamic equations can be derived which involve higher moments of the probability distribution functions of extensive properties; and these include the mean-value thermodynamic equations as the first members.

Chapter 3 deals primarily with small-system thermodynamics of the sorption in zeolites. Attempts will be made to understand the statistical thermodynamic behaviours of individual subsystems; and fluctuations of certain extensive quantities will also be studied. Evidently this approach can provide equations connecting some thermodynamic functions that characterize the subsystem, and such equations can subsequently be used to test the validity of a chosen molecular statistical model. Nevertheless it should be pointed out that, since in principle the magnitude of any thermodynamic function cannot be obtained by applying pure thermodynamics alone, the relevant quantities still have to be measured experimentally or else calculated from an appropriate theoretical model. In Chapter 7 certain thermodynamic functions for the subsystems of interest will be evaluated.

1.5 MACROSCOPIC THERMODYNAMIC APPROACH

Equilibrium thermodynamics of the sorption in zeolites will be studied in detail in Chapter 4. A purely thermodynamic study results in a set of formal relations between various equilibrium quantities associated with the sorption system. These relations are of course very general, since thermodynamic arguments do not depend directly on any molecular interpretation. When all the quantities that occur in a thermodynamic relation can be measured experimentally, this naturally provides a useful check of correctness and consistency of the physical interpretations and measurements. When all but one of these can be measured, again the relation can be applied to deduce the remaining quantity. In addition, a general thermodynamic theory can be used to determine which of the equilibrium quantities have to be measured or calculated in order to specify a particular system completely.

Admittedly, when thermodynamics is supplemented by statistical mechanics, it is no longer a general theory that is completely independent of the laws governing detailed behaviours of the atoms and molecules which constitute the sorbent and sorbate. But while it becomes less general it is nevertheless more informative, for the behaviours of individual sorption systems can now be quantitatively studied. (Wilson 1957a) Thus, in this thesis statistical mechanics and small-system thermodynamics will be used, wherever appropriate, to supplement the arguments based primarily on pure thermodynamics.

CHAPTER 2

STATISTICAL MECHANICS OF SORPTION IN ZEOLITES

2.1 NOTATION

In dealing with multicomponent systems it is particularly convenient to use the generalized set notation, since many formulae of statistical mechanics can thereby be written in the same general forms as those for a single-component system, and equations for the single-component system may themselves be written more concisely. In fact it turns out that many mathematical operations which are difficult to describe in standard notations may easily and systematically be presented in this specialized notation. (Mayer & Montroll 1941, McMillan & Mayer 1945, Meeron 1957, Friedman 1962a)

Let

B = the number of distinguishable sorption cavities of identical structure in the zeolite sorbent,
= the number of localized subsystems in the macroscopic thermodynamic system;

Δ_j = the space volume of the j th labelled cavity, where $j = 1,2,\ldots,B$;

σ = the number of components of the sorbate,
= the number of chemically inert molecular species constituting the sorbate;

N_s = the number of molecules of the s th component sorbed in all the B cavities,
where $s = 1,2,\ldots,\sigma$;

$\underset{\sim}{N}$ = $(N_1,N_2,\ldots,N_\sigma)$,
= the composition set of the sorbate in the system;

N = $N_1+N_2+\ldots+N_\sigma$,
= the total number of molecules in the B cavities;

$n_{s(j)}$ = the number of molecules of the s th component sorbed in the j th cavity;

n_s = the number of molecules of the s th component in any chosen subsystem, when its location in the assembly is clear from the context;

$\underset{\sim}{n}$ = $(n_1,n_2,\ldots,n_\sigma)$,
= the composition set of the sorbate in the subsystem;

n = $n_1+n_2+\ldots+n_\sigma$,
= its total number of molecules;

m_s = the molecular mass of the s th component;

$\underset{\sim}{m}$ = $(m_1,m_2,\ldots,m_\sigma)$,
= the molecular mass set of the sorbate;

$\underset{\sim}{r}_{is}$ = $\{is\}$, the position coordinates, with Cartesian components (x_{is},y_{is},z_{is}), of the i th molecule of the s th component;

$\underset{\sim}{p}_{is}$ = $[is]$, its momentum coordinates, with Cartesian components $(p_{xis},p_{yis},p_{zis})$;

$\{n_s\}$ = $\{1s\},\{2s\},\ldots,\{ns\}$,
= the coordinate set of the n_s molecules of the s th component in the chosen subsystem;

$[n_s] = [1s],[2s],\ldots,[ns]$,
= their momentum set;

$\{\underset{\sim}{n}\} = \{n_1\},\{n_2\},\ldots,\{n_\sigma\}$,
= the coordinate set of the n molecules of composition set $\underset{\sim}{n}$ in the subsystem;

$[\underset{\sim}{n}] = [n_1],[n_2],\ldots,[n_\sigma]$,
= their momentum set;

$\{N_s\} = \{1s\},\{2s\},\ldots,\{N_s s\}$,
= the coordinate set of the N_s molecules of the s th component in the macroscopic system;

$[N_s] = [1s],[2s],\ldots,[N_s s]$,
= their momentum set;

$\{\underset{\sim}{N}\} = \{N_1\},\{N_2\},\ldots,\{N_\sigma\}$,
= the coordinate set of the N molecules of composition set $\underset{\sim}{N}$ in the system;

$[\underset{\sim}{N}] = [N_1],[N_2],\ldots,[N_\sigma]$,
= the corresponding momentum set;

$B_{\underset{\sim}{n}}$ = the number of cavities in each of which n molecules of composition set $\underset{\sim}{n}$ are sorbed;

B_{is} = the number of cavities in each of which exactly i molecules of the s th component are sorbed together with any number of molecules of the other components;

$\underset{\sim}{B}_i$ = the set $(B_{i1},B_{i2},\ldots,B_{i\sigma})$;

S_s = the number of cavities with at least one molecule of the s th component sorbed in each;

$\underset{\sim}{S}$ = the set $(S_1,S_2,\ldots,S_\sigma)$;

N_{is} = the number of molecules of the s th component in all the B_{is} cavities;

$\underset{\sim}{N}_i$ = the set $(N_{i1}, N_{i2}, \ldots, N_{i\sigma})$.

It follows from the above definitions that

$$N_{is} = iB_{is} \tag{2.1.1}$$

$$S_s = B_{1s} + B_{2s} + \ldots + B_{N_s s} \tag{2.1.2}$$

$$\underset{\sim}{S} = \underset{\sim}{B}_1 + \underset{\sim}{B}_2 + \ldots + \underset{\sim}{B}_N \tag{2.1.3}$$

$$B = S_s + B_{0s} \tag{2.1.4}$$

$$\underset{\sim}{B} = \underset{\sim}{S} + \underset{\sim}{B}_0 \tag{2.1.5}$$

$$\begin{aligned} N_s &= N_{1s} + N_{2s} + \ldots + N_{N_s s} \\ &= B_{1s} + 2B_{2s} + \ldots + N_s B_{N_s s} \end{aligned} \tag{2.1.6}$$

and

$$\begin{aligned} \underset{\sim}{N} &= \underset{\sim}{N}_1 + \underset{\sim}{N}_2 + \ldots + \underset{\sim}{N}_N \\ &= \underset{\sim}{B}_1 + 2\underset{\sim}{B}_2 + \ldots + N\underset{\sim}{B}_N \end{aligned} \tag{2.1.7}$$

Let

μ_s = the chemical potential of molecules of the s th component of the σ-component gas phase that is in thermal and material equilibrium with the sorbate;

z_s = the corresponding activity,

and

λ_s = the corresponding absolute activity.

Clearly

$$\lambda_s = \exp(\mu_s/kT) \tag{2.1.8}$$

and $$z_s = \Lambda_s^{-3}\lambda_s \tag{2.1.9}$$

where T is the temperature of the two phases,

and Λ_s is the de Broglie thermal wavelength associated with one kinetic degree of freedom of a molecule of the s th component.

An explicit expression for Λ_s is

$$\Lambda_s = h/(2\pi m_s kT)^{\frac{1}{2}} \tag{2.1.10}$$

where k is the Boltzmann constant,

and h is the Planck constant.

The sets of chemical potentials, activities, absolute activities and thermal wavelengths for the σ-component system can now be defined by

$$\begin{aligned} \underset{\sim}{\mu} &= (\mu_1,\mu_2,\ldots,\mu_\sigma) \\ \underset{\sim}{z} &= (z_1,z_2,\ldots,z_\sigma) \\ \underset{\sim}{\lambda} &= (\lambda_1,\lambda_2,\ldots,\lambda_\sigma) \\ \text{and} \quad \underset{\sim}{\Lambda} &= (\Lambda_1,\Lambda_2,\ldots,\Lambda_\sigma) \end{aligned} \tag{2.1.11}$$

From the foregoing it should be apparent that in the set notation some, but certainly not all, of the operations defined for the sets $\underset{\sim}{n}$, $\underset{\sim}{N}$, $\underset{\sim}{m}$, $\underset{\sim}{\mu}$, etc., are like those with vectors in σ dimensions. For example, $\underset{\sim}{N}$, $\underset{\sim}{B}$, $\underset{\sim}{n}$, $\underset{\sim}{m}$, $\underset{\sim}{\mu}$ and $\underset{\sim}{\Lambda}$ do represent σ-tuples of ordered components, while (2.1.3), (2.1.5) and (2.1.7) parallel additions of vectors. On the other hand, addition, outer product and scalar contraction of arbitrarily chosen σ-tuples, such as

$\underset{\sim}{N} + \underset{\sim}{\mu}$, $\underset{\sim}{m} \wedge \underset{\sim}{\mu}$ and $\underset{\sim}{m} . \underset{\sim}{B}$, have not been defined.

The followings are examples of useful abbreviations for multicomponent systems:

Products of factorials

$$\begin{aligned} \underset{\sim}{n}! &= n_1!n_2!\ldots n_\sigma! \\ \underset{\sim}{N}! &= N_1!N_2!\ldots N_\sigma! \end{aligned} \qquad (2.1.12)$$

Products of exponentials

$$\begin{aligned} \underset{\sim}{\mu}^{\underset{\sim}{n}} &= \mu_1^{n_1}\mu_2^{n_2}\ldots\mu_\sigma^{n_\sigma} \\ \underset{\sim}{\lambda}^{\underset{\sim}{N}} &= \lambda_1^{N_1}\lambda_2^{N_2}\ldots\lambda_\sigma^{N_\sigma} \\ \underset{\sim}{\Lambda}^{\underset{\sim}{n}} &= \Lambda_1^{n_1}\Lambda_2^{n_2}\ldots\Lambda_\sigma^{n_\sigma} \end{aligned} \qquad (2.1.13)$$

Scalar products

$$\underset{\sim}{n}.\underset{\sim}{\mu} = \underset{\sim}{\mu}.\underset{\sim}{n} = n_1\mu_1+n_2\mu_2+\ldots+n_\sigma\mu_\sigma \qquad (2.1.14)$$

Out of these relations only (2.1.14) has any real vectorial significance.

2.2 CANONICAL PARTITION FUNCTION $Z(\underset{\sim}{n},T)$

Consider a subsystem of n distinguishable σ-component molecules of composition set $\underset{\sim}{n}$ and mass set $\underset{\sim}{m}$ in the j th cavity of space volume Δ_j. The classical Hamiltonian for this subsystem with the n molecules having momentum set $[\underset{\sim}{n}]$ at space positions $\{\underset{\sim}{n}\}$ is

$$H([\underset{\sim}{n}],\{\underset{\sim}{n}\}) = \sum_{s=1}^{\sigma} \frac{1}{2m_s} \sum_{i=1}^{n_s} (p_{xis}^2+p_{yis}^2+p_{zis}^2) + U(\{\underset{\sim}{n}\}) \tag{2.2.1}$$

where $(p_{xis},p_{yis},p_{zis})$ represents the set of scalar components of the momentum vector $\underset{\sim}{p}_{is}$ in a Cartesian frame of reference (x,y,z), and $U(\{\underset{\sim}{n}\})$ is the total potential energy of the n molecules interacting in n(n-1)/2 pairs between themselves and each interacting with the common environment consisting of the cavity wall and all other molecules and atoms outside this cavity.

The canonical partition function $Z^*(\underset{\sim}{n},j,T)$ for the j th subsystem at temperature T is given by

$$Z^*(\underset{\sim}{n},j,T) = h^{-3n}\int_{\Delta_j} d\{\underset{\sim}{n}\}\int d[\underset{\sim}{n}] \exp(-H([\underset{\sim}{n}],\{\underset{\sim}{n}\})/kT) \tag{2.2.2}$$

where

$$d[\underset{\sim}{n}] = \prod_{s=1}^{\sigma} d[n_s]$$

$$d[n_s] = \prod_{i=1}^{n_s} d\underset{\sim}{p}_{is} = \prod_{i=1}^{n_s} dp_{xis}dp_{yis}dp_{zis}$$

$$d\{\underset{\sim}{n}\} = \prod_{s=1} d\{n_s\}$$

and
$$d\{n_s\} = \prod_{i=1}^{n_s} d\underset{\sim}{r}_{is} = \prod_{i=1}^{n_s} dx_{is}dy_{is}dz_{is} \qquad (2.2.3)$$

The integration with respect to each of the momentum components is performed over all possible values of this ranging from $-\infty$ to ∞. The integration with respect to the space coordinates of each molecule is restricted to the space volume Δ_j of the cavity. The dividing factor h^{3n} takes account of the fact that the 6n-dimensional volume:

$$\prod_{s=1}^{\sigma} \prod_{i=1}^{n_s} \Delta p_{xis}\Delta p_{yis}\Delta p_{zis}\Delta x_{is}\Delta y_{is}\Delta z_{is}$$

in the classical phase space $([\underset{\sim}{n}],\{\underset{\sim}{n}\})$ associated with a single quantum-mechanical state of the subsystem is h^{3n}. Certainly this factor can also be regarded as a consequence of the quantization of phase space, for essentially it represents the uncertainty principle limit of accuracy in assigning the position coordinates and momenta of the n molecules in the neighbourhood of a specified point of the 6n-dimensional phase space.

According to classical mechanics the Hamiltonian $H([\underset{\sim}{n}],\{\underset{\sim}{n}\})$ can be separated into the kinetic part

$$\sum_{s=1}^{\sigma} \frac{1}{2m_s} \sum_{i=1}^{n_s} (p_{xis}^2+p_{yis}^2+p_{zis}^2)$$

and the configurational part $U(\{\underset{\sim}{n}\})$. Therefore, in classical statistical mechanics the momentum integration in (2.2.2) can be performed directly, giving

$$Z^{*}(\underset{\sim}{n},j,T) = \underset{\sim}{\Lambda}^{-3\underset{\sim}{n}} Q(n,j,T) \tag{2.2.4}$$

where $Q(\underset{\sim}{n},j,T)$ is the configuration integral of the subsystem which is defined by

$$Q(\underset{\sim}{n},j,T) = \int_{\Delta_j} d\{\underset{\sim}{n}\} \exp[-U(\{\underset{\sim}{n}\})/kT] \tag{2.2.5}$$

Since the zeolite cavities are of identical structure and the subsystem is quasi-independent, the internal energy $U(\{\underset{\sim}{n}\})$ does not depend directly on the label j. So the configuration integral and the canonical partition function for the subsystem of composition set $\underset{\sim}{n}$ in any chosen cavity with identical space volume Δ are given respectively by

$$\begin{aligned} Q(\underset{\sim}{n},T) &= Q(\underset{\sim}{n},j,T) = \int_{\Delta} d\{\underset{\sim}{n}\} \exp[-U(\{\underset{\sim}{n}\})/kT] \\ \text{and} \quad Z^{*}(\underset{\sim}{n},T) &= Z^{*}(\underset{\sim}{n},j,T) = \underset{\sim}{\Lambda}^{-3\underset{\sim}{n}} Q(\underset{\sim}{n},T) \end{aligned} \tag{2.2.6}$$

for all $j = 1,2,\ldots,B$.

In the physical subsystem of composition set $\underset{\sim}{n}$ of subsequent interest, the n_s molecules of each component ($s = 1,2,\ldots,\sigma$) are actually indistinguishable. This is a result of the invariance of the quantum-mechanical wave function describing the subsystem with respect to any permutation of the n_s molecules. So its canonical partition function is now given by

$$Z(\underset{\sim}{n},T) = Z^{*}(\underset{\sim}{n},T)/\underset{\sim}{n}! = \underset{\sim}{\Lambda}^{-3\underset{\sim}{n}} Q(\underset{\sim}{n},T)/\underset{\sim}{n}! \qquad (2.2.7)$$

It is important to note carefully the various assumptions inherent in the above derivation of $Z(\underset{\sim}{n},T)$. So far the essential argument has been based on classical statistics. Nevertheless the presence of the dividing factor $\underset{\sim}{n}!h^{3n}$ is basically a quantum-mechanical result. But apart from this fact the use of classical Boltzmann statistics is well justified, for in this case the number of accessible quantum-mechanical states characterizing the subsystem is necessarily so large compared with the number of molecules in it that both Bose-Einstein and Fermi-Dirac statistics should approach their common limiting form of Boltzmann statistics, and thus the choice of the dividing factor $\underset{\sim}{n}!$ to take account of the indistinguishability of the non-localized sorbate molecules in any single subsystem should indeed be appropriate. (Mayer 1958) In sorption studies, quantum phenomena are generally of interest only as regards the sorption of light molecules at very low temperatures. Therefore, in this thesis quantum effects associated with the sorption in zeolites will not be considered any further.

2.3 A LOCALIZED ASSEMBLY OF ISOTHERMAL CLOSED SUBSYSTEMS

First, consider a theoretical system of N distinguishable σ-component molecules of composition set $\underset{\sim}{N}$ in an ordered assembly of B distinguishable cavities such that in each of the $B_{\underset{\sim}{n}}$ labelled cavities n molecules of composition set $\underset{\sim}{n}$ are sorbed. The n molecules in any single cavity will then be regarded as an isothermal closed subsystem which cannot exchange any molecules with outside. All the localized subsystems are in thermal equilibrium at temperature T with each other and with their common environment.

Let the j th cavity with space volume Δ_j contain $n_{(j)}$ molecules of composition set $\underset{\sim}{n}_{(j)}$. The canonical partition function for this subsystem is

$$
\begin{aligned}
Z^{*}(\underset{\sim}{n}_{(j)},T) &= \underset{\sim}{\Lambda}^{-3\underset{\sim}{n}(j)} \int d\{\underset{\sim}{n}_{(j)}\} \exp[-U(\{\underset{\sim}{n}_{(j)}\})/kT] \\
&= \underset{\sim}{\Lambda}^{-3\underset{\sim}{n}(j)} \; Q(\underset{\sim}{n}_{(j)},T) \qquad (2.3.1)
\end{aligned}
$$

Since each subsystem is quasi-independent, closed, and localized within the assembly, the canonical partition function for the system of N sorbate molecules is evidently a direct product of those of the subsystems, and is thus given by

$$
Z^{*}_{\text{closed}}(\underset{\sim}{N},B,T) = \prod_{j=1}^{B} Z^{*}(\underset{\sim}{n}_{(j)},T) \qquad (2.3.2)
$$

In this case every subsystem is completely distinguishable in the sense that a subsystem of n molecules sorbed in a chosen cavity is to be labelled both by the label of the cavity and by the n labels of the individual molecules of this subsystem, which are necessarily different from the labels of other subsystems in the assembly.

Now, consider a more realistic system of N molecules sorbed in an ordered assembly of B distinguishable closed cavities in almost the same manner as the above system except that the n_s molecules of each component $(s = 1,2,\ldots,\sigma)$ in a particular cavity are in the present case indistinguishable. Two molscules of different components in a single cavity, or of the same component but in two distinct cavities, nevertheless remain distinguishable. The canonical partition function for this system is

$$Z_{\text{closed}}(\underset{\sim}{N},B,T) = \prod_{j=1}^{B} Z(\underset{\sim}{n}_{(j)},T) \tag{2.3.3}$$

Such a system can indeed be physically realized. Examples are the clathrates of σ-component guest molecules in closed cavities of the host lattice structures, with varying number and composition set of molecules from one cavity to another but with a definite number and composition set in each. In these instances a molecule is localized in the sense that it is confined to a single cavity after clathration.

The molecular statistical model just described may also be of some interest in connection with the present study of sorption in zeolites. Mention should be made of the specific case of sorption of comparatively large molecules at low temperatures, especially when the sizes of the sorbate molecules are approximately the same as the free diameters of openings and channels connecting the sorption cavities. Once the sorbate molecules have been trapped within the cavities, any molecular exchange between them may be quite negligible. However, in such a situation there may arise certain difficulties associated with the metastable equilibrium of the sorption system. This will be considered in Section 9.2.

It is clear that in the theoretical models considered above there is in effect no coupling between the subsystems other than thermal exchange. Any extensive statistical thermodynamic quantity of the total system is accordingly a direct sum of the distinct contributions from individual subsystems. For a macroscopic assembly of isothermal closed subsystems with a large total number of sorbed molecules, it can be expected that fluctuations in the internal energy of the assembly, as averaged over an appropriate ensemble of statistical mechanics, are very much reduced by thermal exchange. Therefore, in the macroscopic limit this internal energy can correctly be identified with the corresponding thermodynamic quantity measured for the system, even though the internal energy of any individual subsystem may not itself be a thermodynamically measurable quantity.

When the fixed distribution of molecules among the closed cavities is known, the internal energy of the assembly can be evaluated, since this is simply a sum of the statistical mechanical values of the corresponding quantities for individual subsystems. With regard to the entropy of an assembly, however, some complication may arise in connection with the 'residual entropy' that persists down to absolute zero temperature. (Wilson 1957b) If the assembly with a fixed arrangement of distinct subsystems were indeed in complete and infinitely stable thermodynamic equilibrium, and if these subsystems were also closed at all temperatures, the entropy would again be just the sum of the contributions from individual subsystems, for then in principle all the relevant information concerning the partitioning of molecules among the ordered arrangement of cavities is completely known.

But, physically, it is more likely that the equilibrium is in fact only metastable; and hence there is in reality a finite residual entropy associated with the arrangement of the subsystems in the assembly. For the present this point will not be discussed any further; nevertheless it should be mentioned that the preceding consideration does have an important theoretical implication when the 'communal entropy' of an assembly of open subsystems is considered in Section 4.4.

2.4 COMBINATORIAL COEFFICIENTS

The combinatorial coefficients which have subsequent applications in this thesis are presented here. Further details of the results quoted can be found in any standard work on Combinatorial Mathematics. (For examples, MacMahon 1915, 1916, Riordan 1958, Beckenbach 1964)

The coefficient $(N_s;n_{s(1)},n_{s(2)},\ldots,n_{s(B)})$ is defined as the number of ways of putting

$$N_s = n_{s(1)}+n_{s(2)}+\ldots+n_{s(B)}$$

distinguishable molecules of the s th component into B distinguishable cavities, with exactly $n_{s(j)}$ (ranging from 0 to N_s) of these molecules in the j th cavity together with any unrestricted number of molecules of the other components, where $j = 1,2,\ldots,B$, and $s = 1,2,\ldots,\sigma$. This is given by

$$(N_s;n_{s(1)},n_{s(2)},\ldots,n_{s(B)}) = \frac{N_s!}{n_{s(1)}!n_{s(2)}!\ldots n_{s(B)}!} \qquad (2.4.1)$$

which is immediately recognized as the multinomial coefficient of the term

$$x_1^{n_{s(1)}}x_2^{n_{s(2)}}\ldots x_B^{n_{s(B)}}$$

in the expansion:

$$(x_1+x_2+\ldots+x_B)^{N_s} = \sum \frac{N_s!}{n_{s(1)}!n_{s(2)}!\ldots n_{s(B)}!} \cdot x_1^{n_{s(1)}}\ldots x_B^{n_{s(B)}} \qquad (2.4.2)$$

The summation in (2.4.2) is over all possible partitions of the N_s molecules into the sets of $n_{s(j)}$ $(j = 1,2,\ldots,B)$. Clearly

$$\sum_{\substack{n_{s(1)}+n_{s(2)}+\ldots+n_{s(B)} \\ = N_s}} (N_s;n_{s(1)},n_{s(2)},\ldots,n_{s(B)}) = B^{N_s} \tag{2.4.3}$$

By using the set notation these results can be generalized to the case of a σ-component system:

$$(\underset{\sim}{N};\underset{\sim}{n}_{(1)},\underset{\sim}{n}_{(2)},\ldots,\underset{\sim}{n}_{(B)}) = \frac{\underset{\sim}{N}!}{\underset{\sim}{n}_{(1)}!\underset{\sim}{n}_{(2)}!\ldots\underset{\sim}{n}_{(B)}!}$$
$$= \prod_{s=1}^{\sigma}(N_s;n_{s(1)},n_{s(2)},\ldots,n_{s(B)}) \tag{2.4.4}$$

and

$$\sum_{(\text{all partitions of } \underset{\sim}{N})} (\underset{\sim}{N};\underset{\sim}{n}_{(1)},\underset{\sim}{n}_{(2)},\ldots,\underset{\sim}{n}_{(B)}) = B^N \tag{2.4.5}$$

By definition the coefficient $\{N_s;B_{0s},B_{1s},\ldots,B_{N_s s}\}$ is the number of ways of partitioning the set of

$$N_s = B_{1s}+2B_{2s}+\ldots+N_sB_{N_s s}$$

distinguishable molecules of the s th component into the B distinguishable cavities, B_{is} of which each contains exactly i of these molecules together with any unrestricted number of molecules of the other components, where $i = 0,1,\ldots,N_s$. This is given by

$$\left\{N_s;B_{0s},B_{1s},\ldots,B_{N_s s}\right\} = \frac{B!\ N_s!}{(0!)^{B_{0s}}B_{0s}!(1!)^{B_{1s}}B_{1s}!\ldots(N_s!)^{B_{N_s s}}B_{N_s s}!}$$

$$= \frac{N_s!(B;B_{0s},B_{1s},\ldots,B_{N_s s})}{(0!)^{B_{0s}}(1!)^{B_{1s}}\ldots(N_s!)^{B_{N_s s}}} \qquad (2.4.6)$$

A generalization of this gives

$$\left\{\underset{\sim}{N};\underset{\sim}{B}_0,\underset{\sim}{B}_1,\ldots,\underset{\sim}{B}_{\underset{\sim}{N}}\right\} = \prod_{s=1}^{\sigma}\frac{N_s!\ B!}{(0!)^{B_{0s}}B_{0s}!\ \ldots\ (N_s!)^{B_{N_s s}}B_{N_s s}!}$$

$$= \prod_{s=1}^{\sigma}\left\{N_s;B_{0s},B_{1s},\ldots,B_{N_s s}\right\} \qquad (2.4.7)$$

By considering all the possible permutations of the N distinguishable molecules of composition set $\underset{\sim}{N}$ in all the B distinguishable cavities, it follows that

$$\sum\left\{\underset{\sim}{N};\underset{\sim}{B}_0,\underset{\sim}{B}_1,\ldots,\underset{\sim}{B}_{\underset{\sim}{N}}\right\} = B^N \qquad (2.4.8)$$

where the summation is restricted by the 2σ simultaneous conditions:

$$B_{0s}+B_{1s}+\ldots+B_{N_s s} = B$$

and

$$B_{1s}+2B_{2s}+\ldots+N_s B_{N_s s} = N_s$$

for all $s = 1,2,\ldots,\sigma$.

2.5 A LOCALIZED CLOSED ASSEMBLY OF ISOTHERMAL SUBSYSTEMS

It is now appropriate to study the statistical mechanics of a molecular model that truly describes the macroscopic sorption system of interest with respect to a specific thermodynamic environment. Consider a closed system of N distinguishable σ-component molecules of composition set $\underset{\sim}{N}$ sorbed in an ordered assembly of B distinguishable cavities such that these molecules can distribute themselves in any possible manner among the cavities, and each of them is accordingly free to move to any part of the entire closed system. As in the cases previously considered in Section 2.3, all the sorbate molecules are regarded here as a closed thermodynamic system in thermal equilibrium with a large heat bath that forms its environment. However, in contrast, as regards the present case the individual subsystems are themselves open and isothermal.

At a given instant any subsystem can contain only a relatively small number of the sorbed molecules; and this can vary from one cavity to another. Thus, a free exchange of molecules between the cavities does not necessarily imply that a complete material equilibrium is actually established between the subsystems in the sense that the chemical potential of each molecular species as defined by statistical mechanics is uniform at the molecular level throughout the assembly. In fact, for a single subsystem the meaning of a chemical potential that is thermodynamically measurable cannot properly be attached to the corresponding theoretical value. The Helmholtz free energy $A(\underset{\sim}{n},T)$ appropriately averaged over the canonical ensemble at temperature T can be defined for each composition set $\underset{\sim}{n}$ of the subsystem; but this is not a continuous function of n_s $(s = 1,2,\ldots,\sigma)$ which is itself a small integer. In consequence $A(\underset{\sim}{n},T)$ cannot be directly differentiated with respect to n_s in the same manner as for a macroscopic system. Clearly, difference equations can be used in place of the ordinary differentiations to obtain statistical mechanical estimates of the chemical potentials. However, the resulting quantities are not experimentally measurable; and indeed they must always be characterized by both the initial and the final composition sets.

On the other hand, the system of all the sorbate molecules in an ordered assembly of B cavities is macroscopic and can correctly be regarded as a thermodynamic system for which the chemical potentials may in practice be measured. Nevertheless it should be noted that each of these chemical potentials is defined only in the macroscopic sense and must not be identified with the corresponding statistical thermodynamic quantities of individual subsystems.

As each of the N distinguishable molecules can at a particular instant be in any one of the B cavities of space volumes $\Delta_1,\Delta_2,\ldots,\Delta_B$, the canonical partition function for this closed system is

$$Z^{*}(\underset{\sim}{N},B,T) = \underset{\sim}{\Lambda}^{-3\underset{\sim}{N}} \int_{\Delta_1+\Delta_2+\ldots+\Delta_B} d\{\underset{\sim}{N}\} \exp[-U(\{\underset{\sim}{N}\})/kT] \tag{2.5.1}$$

where the integration with respect to each of the N molecules is carried out over the whole sorption space of the B cavities.

By partitioning the N molecules into the B cavities, the 3N-dimensional configuration integral can be rewritten in terms of the integrals each restricted to a single cavity, so that

$$\begin{aligned} Z^{*}(\underset{\sim}{N},B,T) &= \underset{\sim}{\Lambda}^{-3\underset{\sim}{N}} \sum (\underset{\sim}{N};\underset{\sim}{n}_{(1)},\underset{\sim}{n}_{(2)},\ldots,\underset{\sim}{n}_{(B)}) \cdot \\ &\qquad \prod_{j=1}^{B} \int_{\Delta_j} d\{\underset{\sim}{n}_{(j)}\} \exp[-U(\{\underset{\sim}{n}_{(j)}\})/kT] \\ &= \sum (\underset{\sim}{N};\underset{\sim}{n}_{(1)},\ldots,\underset{\sim}{n}_{(B)}) \prod_{j=1}^{B} Z^{*}(\underset{\sim}{n}_{(j)},j,T) \end{aligned} \tag{2.5.2}$$

where the summations concerned are over all the partitions:

$$\underset{\sim}{n}_{(1)} + \underset{\sim}{n}_{(2)} + \ldots + \underset{\sim}{n}_{(B)} = \underset{\sim}{N}$$

and $Z^{*}(\underset{\sim}{n}_{(j)},j,T)$ is the canonical partition function at temperature T for the $n_{(j)}$ molecules of composition set $\underset{\sim}{n}_{(j)}$ in the j th cavity.

The quasi-independence of each subsystem implies that $Z^{*}(\underset{\sim}{n}_{(j)},j,T)$ is independent of the label j ; i.e.,

$$Z^{*}(\underset{\sim}{n}_{(j)},j,T) \quad = \quad Z^{*}(\underset{\sim}{n}_{(j)},T) \qquad (2.5.3)$$

for all $j = 1,2,\ldots,B$. Hence (2.5.2) can be rewritten as:

$$Z^{*}(\underset{\sim}{N},B,T) \quad = \sum (\underset{\sim}{N};\underset{\sim}{n}_{(1)},\ldots,\underset{\sim}{n}_{(B)}) \prod_{j=1}^{B} Z^{*}(\underset{\sim}{n}_{(j)},T) \qquad (2.5.4)$$

where the summation has the same specification as for (2.5.2).

Since $Z^{*}(\underset{\sim}{n}_{(j)},T)$ depends only on the magnitudes of the components $n_{s(j)}$ $(s = 1,2,\ldots,\sigma)$ and is not otherwise a function of j, the product in (2.5.4) can now be written in terms of the products of powers of $Z^{*}(\underset{\sim}{n},T)$:

$$Z^{*}(\underset{\sim}{N},B,T) \quad = \sum \{\underset{\sim}{N};\underset{\sim}{B}_{0},\underset{\sim}{B}_{1},\ldots,\underset{\sim}{B}_{\underset{\sim}{N}}\} \prod_{\underset{\sim}{n}\leqslant\underset{\sim}{N}} \left[Z^{*}(\underset{\sim}{n},T)\right]^{B_{\underset{\sim}{n}}} \qquad (2.5.5)$$

where the products are of the distinct contributions from all the possible sets of the $B_{\underset{\sim}{n}}$ subsystems each with a composition set $\underset{\sim}{n}$. The summation is over all possible partitions of the N molecules among the B cavities, with the restriction that

$$\sum_{i=1}^{N_s} B_{is} = B \qquad \text{and} \qquad \sum_{n_s \geqslant 0} n_s B_{n_s s} = N_s$$

for all $s = 1,2,\ldots,\sigma$. These form 2σ simultaneous conditions. The right hand side of (2.5.5) may also be regarded as a homogeneous polynomial of degree B in the parameter set $Z^{*}(\mathbf{n},T)$ (with variable $\mathbf{n}$), in which the coefficient of a typical monomial term is $\{\mathbf{N};\mathbf{B}_0,\mathbf{B}_1,\ldots,\mathbf{B}_{\mathbf{N}}\}$.

Now, in the physical system of N σ-component molecules of composition set $\mathbf{N}$ sorbed in B open zeolite cavities, although the subsystems of the ordered assembly are in fact localized, the molecules of each component in any specific subsystem are themselves non-localized, and are thus indistinguishable. As each subsystem is here assumed to be quasi-independent, the canonical partition function for the system of N molecules is therefore given by

$$\begin{aligned} Z(\mathbf{N},B,T) &= \sum \{\mathbf{N};\mathbf{B}_0,\mathbf{B}_1,\ldots,\mathbf{B}_{\mathbf{N}}\} \prod_{\mathbf{n}\leq\mathbf{N}} \left[Z(\mathbf{n},T)\right]^{B_{\mathbf{n}}} \\ &= \mathbf{N}! \sum (\mathbf{B};\mathbf{B}_0,\mathbf{B}_1,\ldots,\mathbf{B}_N) \prod_{\mathbf{n}\leq\mathbf{N}} \left[\frac{Z(\mathbf{n},T)}{\mathbf{n}!}\right]^{B_{\mathbf{n}}} \end{aligned} \qquad (2.5.6)$$

where the products and sums have the same specifications as in (2.5.5), and

$$(\mathbf{B};\mathbf{B}_0,\mathbf{B}_1,\ldots,\mathbf{B}_N) = \frac{(B!)^{\sigma}}{\mathbf{B}_0!\,\mathbf{B}_1!\ldots\,\mathbf{B}_N!} \qquad (2.5.7)$$

In the last paragraph $Z(\mathbf{N},B,T)$ was obtained from $Z^{*}(\mathbf{N},B,T)$ by replacing each contribution of $Z^{*}(\mathbf{n},T)$ in (2.5.5) by $Z(\mathbf{n},T)$. This means that, whereas the n_s identical molecules of the s th component are indistinguishable within an individual subsystem, the molecules of the same component in different subsystems nevertheless remain distinct, and they can be simultaneously identified by the labels of the distinguishable cavities containing the localized subsystems at any particular instant. Undoubtedly this is a consequence of the quasi-independence of individual subsystems. For, if the subsystems were themselves non-localized, $Z(\underset{\sim}{N},B,T)$ would then be equal to $Z^{*}(\underset{\sim}{N},B,T)/\underset{\sim}{N}!$. But this is not the case, since the arrangement of zeolite cavities is known to be fixed and ordered. If, on the other hand, the subsystems were completely independent with regard to material exchange, yet remain thermally equilibrated, so that in working out the canonical partition function of the assembly each subsystem could be regarded as independent, closed, and isothermal, then the system would in fact be identical with that considered in Section 2.3, at least in the mathematical sense.

It should be emphasized that in the evaluations of $Z^{*}(\underset{\sim}{N},B,T)$ and $Z(\underset{\sim}{N},B,T)$ every region of the 6N-dimensional phase space has indeed been taken into account. In this respect, (2.4.5) and (2.4.8) could provide very valuable means of checking the correctness of the summations over the molecular partitions in (2.5.2), (2.5.4), (2.5.5) and (2.5.6). As regards the physical implication of the foregoing results, however, these should become more apparent in the subsequent applications.

2.6 THE CONTOUR INTEGRAL FORM OF $Z(\underset{\sim}{N},B,T)$

Because of the restrictive conditions of series summations in the analytical expression (2.5.6) for the canonical partition function Z(N,B,T), it is not convenient to apply this directly in calculating statistical thermodynamic quantities characterizing the macroscopic sorption system. It is interesting to express $Z(\underset{\sim}{N},B,T)$ in the form of a generalized contour integral in σ complex variables, as this may lead eventually to a more effective method for relating the canonical partition functions $Z(\underset{\sim}{n},T)$ of individual quasi-independent subsystems to some thermodynamic relations and quantities that truly describe the sorbate in the total assembly. By inspection of the form of $Z(\underset{\sim}{N},B,T)$ in (2.5.6) it appears that the use of certain generating functions should be appropriate to this type of combinatorial problem. More specifically, the use of an exponential generating function for the sequence of $Z(\underset{\sim}{N},B,T)$ is suggested.

By definition the exponential generating function of a sequence $a_0,a_1,\ldots,a_n,\ldots$ is the sum:

$$E(t) = a_0+a_1t+a_2t^2/2!+\ldots+a_nt^n/n! +\ldots \qquad (2.6.1)$$

whereas the ordinary generating function of the same sequence is given by

$$A(t) = a_0+a_1t+ a_2t^2+\ldots+a_nt^n +\ldots \qquad (2.6.2)$$

The sequence $a_0, a_1, \ldots, a_n, \ldots$ is ordered and may be finite or infinite. Its elements can be regarded collectively as a multiple entity in their separated forms; and these may, but need not, be distinct. The parameter t is taken as an abstract mark or indeterminate, the function of which is to keep distinct through its powers the elements of the sequence united in the sum defining the generating function. (Riordan 1958a, Beckenbach 1964a)

The definitions of these two generating functions can readily be generalized to the case of many parameters. The σ-parameter generating functions for the sequence of $a_{\underset{\sim}{n}}$ are defined by

$$E(\underset{\sim}{t}) = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} a_{\underset{\sim}{n}} \underset{\sim}{t}^{\underset{\sim}{n}} / \underset{\sim}{n}! \qquad (2.6.3)$$

and

$$A(\underset{\sim}{t}) = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} a_{\underset{\sim}{n}} \underset{\sim}{t}^{\underset{\sim}{n}} \qquad (2.6.4)$$

where $\underset{\sim}{t} = (t_1, t_2, \ldots, t_\sigma)$

and $\underset{\sim}{n} = (n_1, n_2, \ldots, n_\sigma)$

In particular, the 2-parameter generating functions are given by

$$E(r,t) = a_{00}+a_{10}r+a_{01}t+a_{20}r^2/2!+a_{11}rt+a_{02}t^2/2!+\ldots \qquad (2.6.5)$$

and

$$A(r,t) = a_{00}+a_{10}r+a_{01}t+a_{20}r^2+a_{11}rt+a_{02}t^2+\ldots \qquad (2.6.6)$$

Formal operations such as addition, multiplication, differentiation and integration with respect to any number of the parameters t_s $(s = 1,2,\ldots,\sigma)$, can be defined for each set of the sequences $E(\underset{\sim}{t})$ and $A(\underset{\sim}{t})$. These are known as Blissard or umbral calculus for those involving the sequences $E(\underset{\sim}{t})$, and as Cauchy calculus for those involving the sequences $A(\underset{\sim}{t})$ alone. (Bell 1940)

Now consider the exponential generating function $E(\underset{\sim}{t})$ for the sequence of the canonical partition functions $Z(\underset{\sim}{n},T)$ of a subsystem, viz.,

$$E(\underset{\sim}{t},T) = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} Z(\underset{\sim}{n},T)\, \underset{\sim}{t}^{\underset{\sim}{n}} / \underset{\sim}{n}! \qquad (2.6.7)$$

In order to find the multinomial expression for $E^B(\underset{\sim}{t},T)$ the technique of Blissard calculus is applied. Thus, a sequence of $Z(\underset{\sim}{n},T)$ is replaced by that of

$$\underset{\sim}{Z}^{\underset{\sim}{n}} = Z_1^{n_1} Z_2^{n_2} \ldots Z_\sigma^{n_\sigma}$$

with the exponents treated as powers during all formal operations, and only restored as indices when the operations have been completed. The exponential generating function $E(\underset{\sim}{t},T)$ accordingly behaves like an exponential function in the sense of Blissard calculus:

$$E(\underset{\sim}{t},T) = \exp(\underset{\sim}{Z}\cdot\underset{\sim}{t}) \quad : \quad \underset{\sim}{Z}^{\underset{\sim}{n}} \equiv Z(\underset{\sim}{n},T) \qquad (2.6.8)$$

where $\underset{\sim}{Z}$ and $\underset{\sim}{t}$ in the formal relation may be regarded as σ-component vectors.

On applying this technique to the generalized multinomial expansion of $E^{B}(\underset{\sim}{t},T)$, it follows that

$$E^{B}(\underset{\sim}{t},T) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} \frac{\underset{\sim}{t}^{\underset{\sim}{N}}}{\underset{\sim}{N}!} \sum{}' \left\{\underset{\sim}{N};\underset{\sim}{B}_0,\underset{\sim}{B}_1,\ldots,\underset{\sim}{B}_{N}\right\} \prod_{\underset{\sim}{n} \leqslant \underset{\sim}{N}} \left[Z(\underset{\sim}{n},T)\right]^{B_{\underset{\sim}{n}}}$$

$$= \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} \underset{\sim}{t}^{\underset{\sim}{N}} \sum{}' \left(\underset{\sim}{B};\underset{\sim}{B}_0,\underset{\sim}{B}_1,\ldots\underset{\sim}{B}_{N}\right) \prod_{\underset{\sim}{n} \leqslant \underset{\sim}{N}} \left[\frac{Z(\underset{\sim}{n},T)}{\underset{\sim}{n}!}\right]^{B_{\underset{\sim}{n}}} \tag{2.6.9}$$

where B is any positive integer, and the summations $\sum{}'$ are carried out for all partitions of the composition set $\underset{\sim}{N}$, with the restriction that

$$\sum_{i=1}^{N_s} B_{is} = B \qquad \text{and} \qquad \sum_{n_s \geqslant 0} n_s B_{n_s s} = N_s$$

for all $s = 1,2,\ldots,\sigma$.

By comparing (2.6.9) with (2.5.6) it becomes apparent that the canonical partition function $Z(\underset{\sim}{N},B,T)$ of the assembly is just the coefficient of $\underset{\sim}{t}^{\underset{\sim}{N}}/\underset{\sim}{N}!$ in the exponential generating function $E(B,T,\underset{\sim}{t})$ defined by

$$E(B,T,\underset{\sim}{t}) \equiv E^{B}(\underset{\sim}{t},T) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} Z(\underset{\sim}{N},B,T)\, \underset{\sim}{t}^{\underset{\sim}{N}}/\underset{\sim}{N}! \tag{2.6.10}$$

Up to this point the σ parameters $\underset{\sim}{t}$ are still indeterminate. In the followings the parameter set $\underset{\sim}{t}$ will be replaced by a set of complex variables $\underset{\sim}{\zeta} = (\zeta_1, \zeta_2, .. \zeta_\sigma)$. Then (2.6.7) and (2.6.10) give

$$E(\underset{\sim}{\zeta}, T) = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} Z(\underset{\sim}{n}, T) \underset{\sim}{\zeta}^{\underset{\sim}{n}} / \underset{\sim}{n}! \tag{2.6.11}$$

and $$E(B, T, \underset{\sim}{\zeta}) = E^B(\underset{\sim}{\zeta}, T) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} Z(\underset{\sim}{N}, B, T) \underset{\sim}{\zeta}^{\underset{\sim}{N}} / \underset{\sim}{N}! \tag{2.6.12}$$

Evidently the functions $E(\underset{\sim}{\zeta}, T)$ and $E(B, T, \underset{\sim}{\zeta})$ are holomorphic, since these are polynomials with bounded sequences of real positive coefficients of powers of the σ complex variables $\underset{\sim}{\zeta}$. Without going into the mathematical detail of considering the holomorphy of these functions of many complex variables, it is quite sufficient to use only a relatively simple geometrical concept as regards the 'continuity' of the functions concerned within the closed domains of physical interest. In view of this the preceding statement can be regarded as merely implying that $E(\underset{\sim}{\zeta}, T)$ and $E(B, T, \underset{\sim}{\zeta})$ are single-valued, non-singular, as well as continuously differentiable, within their radii of convergence, with respect to each variable ζ_s ($s = 1, 2, .., \sigma$) separately (with other variables fixed).

According to the generalized Laurent's theorem (Vladimirov 1966a) and Cauchy's theorem of residues of multivariable complex calculus (Vladimirov 1966b), $Z(\underset{\sim}{N}, B, T)$ can be expressed as a contour integral on the appropriate complex planes with respect to the σ separable complex variables $\underset{\sim}{\zeta}$:

$$Z(\underset{\sim}{N},B,T) = \frac{\underset{\sim}{N}!}{(2\pi i)^{\sigma}} \oint d\underset{\sim}{\zeta}\ \frac{E(B,T,\underset{\sim}{\zeta})}{\underset{\sim}{\zeta}^{\underset{\sim}{N}+\underset{\sim}{1}}} \qquad (2.6.13)$$

where the point $\underset{\sim}{\zeta} = \underset{\sim}{0}$ is within the inner region of the integration contour on the complex plane of each variable, and each integration is carried out in the positive (counterclockwise) direction. The point $\underset{\sim}{\zeta} = \underset{\sim}{0}$ can, of course, be regarded as the common intersection of the σ complex planes. Geometrically the integration contour can then be visualized as a continuous path encircling the origin on the Riemannian surface that describes the holomorphic continuation of the functions concerned with respect to the σ complex variables. (Cartan 1963) Moreover, for physical reasons it is clear the resulting surface which represents the holomorphic domain of interest is single-sheeted (schlicht).

Because of the restriction on the number of relevant terms in the summations of (2.6.9) when applied to the physical system of sorption in zeolites, it is mathematically desirable to study the convergence problem concerning the termination of the series in (2.6.12) in more detail. For simplicity, only the case of a single-component system will be analyzed. In this case a useful result can easily be obtained by considering the absolute activity λ of the sorbate as a value specified by some point on the real positive axis of the complex plane of the single variable ζ.

From the specialized forms of (2.6.10) and (2.6.13), it follows after bringing the summation under the integral sign that

$$E(B,T,\lambda) = \frac{1}{2\pi i}\oint \frac{E^B(\zeta)}{\zeta} \sum_{n=0}^{Bn^*} \left(\frac{\lambda}{\zeta}\right)^n d\zeta$$

$$= \frac{1}{2\pi i}\oint \frac{E^B(\zeta)}{\zeta-\lambda}\, d\zeta - \frac{1}{2\pi i}\oint \frac{E^B(\zeta)}{\zeta-\lambda}\cdot\left(\frac{\lambda}{\zeta}\right)^{Bn^*+1} d\zeta \tag{2.6.14}$$

where n^* is any positive integer greater than the maximum number of molecules in any cavity at temperature T. Here the series $E(B,T,\lambda)$ is terminated after Bn^* terms.

By applying Cauchy's theorem of residues to the first contour integral in (2.6.14), the integrand of which is certainly analytic on the whole complex plane (i.e., its radius of convergence is infinite) except at the point of singularity $\zeta=\lambda$, it follows immediately that this integral is just equal to $E^B(\lambda)$. (Phillips 1957) The contour of the second integral encloses the singularities at $\zeta = 0$ and $\zeta=\lambda$, but may take any arbitrary shape on the complex plane. It is thus possible to choose this contour to be outside the circle of radius λ about the origin such that $|\lambda/\zeta| < 1$. (Fowler 1936, Eyring et al. 1964) Consequently, for a macroscopic thermodynamic system of the sorbate in an assembly of B zeolite cavities with $B \sim 10^{20}$, the second integral is always negligible in comparison with the first.

It has thus been shown that, as regards the special case of a single-component system, the use of the truncated series in (2.6.12) and (2.6.13) is well justified, both mathematically and on an obvious physical basis. A slightly more elaborate analysis should lead to a similar conclusion for the cases of multicomponent sorbates in zeolites. The summations concerned are now restricted to the 2σ simultaneous conditions:

$$\underset{\sim}{0} \leq \underset{\sim}{N} \leq B\,\underset{\sim}{n}^{*}$$

where $\underset{\sim}{n}^{*} = (n_1^{*}, n_2^{*}, \ldots, n_\sigma^{*})$ represents any σ-tuple of positive integers each greater than the maximum number of molecules of the appropriate component in any single cavity at temperature T. At this stage the real physical implication of the foregoing analysis should at least be intuitively clear.

2.7 AN OPEN ASSEMBLY OF ISOTHERMAL SUBSYSTEMS

This section deals with a macroscopic system consisting of a variable number N of chemically inert molecules of component set $\underset{\sim}{N}$ sorbed in a large ordered assembly of B distinguishable zeolite cavities with identical structure. Both the assembly and the individual subsystems are open, so that any chosen molecule can be in any one of the cavities, or, alternatively, in the gas phase that is in thermal and material equilibrium with the sorbed phase. It is recalled that this molecular model of the sorbate in zeolite was briefly mentioned in Section 1.3.

Again, it should be pointed out that the molecular exchange among the cavities does not necessarily indicate that the chemical potential of each component is uniform and definite at the subsystem level throughout the assembly. In fact, although a chemical potential that is thermodynamically measurable cannot be defined for a single subsystem, it can nevertheless be defined for the macroscopic sorbate system as a whole. It is the chemical potential of the total assembly in this case that is actually equated to that of the gas phase. Certainly this chemical potential depends not only upon the statistical thermodynamic Helmholtz free energies of the individual subsystems but also upon how the molecules are physically distributed among the cavities. Here fluctuations in the number of molecules in each cavity should give a significant contribution to the randomness, and hence to the entropy, of the macroscopic system.

The grand partition function $\Xi(B,T,\underset{\sim}{\lambda})$ for the system that is in thermal and material equilibrium with the gas phase at temperature T and absolute activity set $\underset{\sim}{\lambda}$ is given by

$$\Xi(B,T,\underset{\sim}{\lambda}) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} Z(\underset{\sim}{N},B,T)\,\underset{\sim}{\lambda}^{\underset{\sim}{N}} \tag{2.7.1}$$

Its inverse formula then gives the canonical partition function as a contour integral of $\Xi(B,T,\underset{\sim}{\lambda})$:

$$Z(\underset{\sim}{N},B,T) = \frac{1}{(2\pi i)^{\sigma}} \oint \frac{\Xi(B,T,\underset{\sim}{\lambda})}{\underset{\sim}{\lambda}^{\underset{\sim}{N}+\underset{\sim}{1}}}\, d\underset{\sim}{\lambda} \tag{2.7.2}$$

where the contour integration with respect to each complex variable λ_s $(s = 1,2,\ldots,\sigma)$ is in the positive direction and encloses the origin at $\underset{\sim}{\lambda} = \underset{\sim}{0}$.

The grand partition function $\Xi(B,T,\underset{\sim}{\lambda})$ as given by (2.7.1) is a polynomial in the parameter set $\underset{\sim}{\lambda}$ with real positive coefficients each representing a canonical partition function of an individual subsystem. Physically, it is known that the power series for $\Xi(B,T,\underset{\sim}{\lambda})$ is absolutely convergent in all the applications of interest, for certainly any thermodynamic function characterizing a finite macroscopic system of the sorbate in zeolite is experimentally well-defined. However, as the relevant summations cannot be carried out explicitly, it is not yet convenient to use $\Xi(B,T,\underset{\sim}{\lambda})$ directly in this form to evaluate the required statistical thermodynamic quantities. The results in Chapter 4 will show that this difficulty can best be avoided by using $E(B,T,\underset{\sim}{\lambda})$ instead to relate theoretical results to thermodynamics of the sorption.

It may have been noticed that $\Xi(B,T,\underset{\sim}{\lambda})$ is in effect the ordinary generating function for the sequence of $Z(\underset{\sim}{N},B,T)$, whereas the corresponding exponential generating function is given by $E(B,T,\underset{\sim}{\lambda})$ in (2.6.12). According to a well-known result in combinatorial analysis, the ordinary generating function $A(\underset{\sim}{t})$ as given by (2.6.4) and the exponential generating function $E(\underset{\sim}{t})$ as given by (2.6.3) for the same sequence of $a_{\underset{\sim}{n}}$ are related formally by

$$A(\underset{\sim}{t}) = \int_0^\infty (\exp -\underset{\sim}{s})\, E(\underset{\sim}{t}\underset{\sim}{s})\, d\underset{\sim}{s} \qquad (2.7.3)$$

where t and s are regarded as sets of real variables:

$$\underset{\sim}{t} = (t_1, t_2, \ldots, t_\sigma)$$

and $$\underset{\sim}{s} = (s_1, s_2, \ldots, s_\sigma)$$

Also, by definition,

$$\underset{\sim}{t}\underset{\sim}{s} = (t_1 s_1, t_2 s_2, \ldots, t_\sigma s_\sigma)$$

and $\quad d\underset{\sim}{s} = ds_1 ds_2 \ldots ds_\sigma$. (Riordan 1958a)

This is just the generalized relation for Borel's summation of series. (Whittaker & Watson 1927) Hence, by substituting $E(B,T,\underset{\sim}{\lambda}\underset{\sim}{s})$ for $E(\underset{\sim}{t}\underset{\sim}{s})$ and $\Xi(B,T,\underset{\sim}{\lambda})$ for $A(\underset{\sim}{t})$ in (2.7.3), it follows that the grand partition function is analytically given by

$$\Xi(B,T,\underset{\sim}{\lambda}) = \int_0^\infty (\exp - \underset{\sim}{s})\, E(B,T,\underset{\sim}{\lambda}\underset{\sim}{s})\, d\underset{\sim}{s} \qquad (2.7.4)$$

This relation suggests that $E(B,T,\underset{\sim}{\lambda})$ may have an interesting physical interpretation. Subsequent studies will show that this is in fact the case. For the present it suffices to point out that mathematically $E(B,T,\underset{\sim}{\lambda})$ is well-defined and is necessarily convergent whenever $\Xi(B,T,\underset{\sim}{\lambda})$ has the physical significance of defining a proper thermodynamic system.

2.8 STATISTICAL THERMODYNAMICS OF THE SORPTION

The multicomponent sorbate in the localized assembly of subsystems is macroscopic. Thus, in principle thermodynamic association of its statistical mechanical results can be achieved by means of any one of the partition functions which characterize some specific ensembles. In this case it is clear that fluctuations of extensive thermodynamic quantities within any particular ensemble are quite negligible in magnitude in comparison with the mean values.

A sorption system that is closed and isothermal has already been discussed in Section 2.5. Of immediate interest is the fact that its internal energy can be expected to be non-fluctuating. It follows from this that the thermodynamic significance of such a theoretical model should not alter when the constraint of constant internal energy is additionally imposed on it. In other words, for the purpose of effecting thermodynamic association the equilibrium properties of an adiabatic sorption system can also be correctly averaged over the appropriate microcanonical ensemble. This case will now be considered as another illustrative example of the representative ensembles for the present formal studies.

The microcanonical partition function $\Omega(U)$ is the state density of distinguishable statistical mechanical systems within the microcanonical ensemble, each system having a fixed internal energy U. This is formally related to the canonical partition function $Z(\underset{\sim}{N},B,T)$ by

$$Z(\underset{\sim}{N},B,T) = \int_{U_0}^{\infty} \Omega(U) \exp(-U/kT)\, dU \qquad (2.8.1)$$

where U_0 is the zero point energy of the system. In addition $\Omega(U)$ has to satisfy the conditions:

$$\Omega(U) \geq 0 \,, \quad \lim_{U\to\infty} \Omega(U) \exp(-\alpha U) = 0 \qquad (2.8.2)$$

for all $\alpha > 0$.

According to (2.8.1), when $\beta = 1/kT$ is regarded as a complex variable, $Z(\underset{\sim}{N},B,T)$ is the one-dimensional Laplace transform of the function $\Omega(U)$ of one real variable U. Its inverse relation then gives

$$\Omega(U) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} Z(\beta) \exp(\beta U)\, d\beta \,, \quad (\beta' > 0)$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} Z(\beta'+i\beta'') \exp\left[(\beta'+i\beta'')U\right] d\beta'' \qquad (2.8.3)$$

where β' and β'' are real, and $Z(\beta) = Z(\underset{\sim}{N},B,T)$ as given by (2.5.6), or, equivalently, by (2.6.13). The contour of the complex integration is along the infinite line parallel to the imaginary axis of the complex plane of β and cutting the real positive axis at β'. (Kubo 1965)

Statistical thermodynamic quantities specifying the sorption system can be related to the partition functions already referred to by means of standard results of equilibrium statistical mechanics. (Hill 1956a) The relations of interest are presented here, and their physical interpretation will be considered in Chapter 4. The general sets of extensive and intensive quantities specifying a sorption system are represented by $\underset{\sim}{x}$ and $\underset{\sim}{X}$, respectively, where x_i and X_i are conjugate components. Certainly, the variable B can also be included in the set $\underset{\sim}{x}$. The bar over any fluctuating quantity represents an averaging over the appropriate ensemble.

(a) Microcanonical Ensemble

$\Omega(U,N,\underset{\sim}{x})$ is a function of the parameters U, $\underset{\sim}{N}$ and $\underset{\sim}{x}$. The relevant fundamental thermodynamic relation is given by

$$TS = kT \ln\Omega \tag{2.8.4}$$

So

$$1 = kT \left(\frac{\partial \ln\Omega}{\partial U}\right)_{\underset{\sim}{x},\underset{\sim}{N}} \tag{2.8.5}$$

$$\bar{X}_i = kT \left(\frac{\partial \ln\Omega}{\partial x_i}\right)_{U,\underset{\sim}{N},x_j(j\neq i)} \tag{2.8.6}$$

and

$$\bar{\mu}_s = -kT \left(\frac{\partial \ln\Omega}{\partial N_s}\right)_{U,\underset{\sim}{x},N_t(t\neq s)} \tag{2.8.7}$$

(b) Canonical Ensemble

$Z(\underset{\sim}{N},B,T)$ is a function of the environmental variables $\underset{\sim}{N}$, $\underset{\sim}{x}$ and T. Thermodynamic association is made through

$$A = U - TS = -kT \ln Z \qquad (2.8.8)$$

For an open system,

$$dA = -SdT - \underset{\sim}{\overline{X}}.d\underset{\sim}{x} + \underset{\sim}{\overline{\mu}}.d\underset{\sim}{N} = -d(kT \ln Z) \qquad (2.8.9)$$

It follows that

$$\overline{\mu}_s = -kT \left(\frac{\partial \ln Z}{\partial N_s}\right)_{T,\underset{\sim}{x},N_t(t\neq s)} \qquad (2.8.10)$$

$$S = k \ln Z + kT \left(\frac{\partial \ln Z}{\partial T}\right)_{\underset{\sim}{x},\underset{\sim}{N}} \qquad (2.8.11)$$

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_{\underset{\sim}{x},\underset{\sim}{N}} \qquad (2.8.12)$$

and $$\overline{X}_i = kT \left(\frac{\partial \ln Z}{\partial x_i}\right)_{T,\underset{\sim}{N},x_j(j\neq i)} \qquad (2.8.13)$$

(c) Grand Canonical Ensemble

$\Xi(B,T,\underset{\sim}{\lambda})$ is a function of $T,\underset{\sim}{\mu}$ and $\underset{\sim}{x}$. The fundamental thermodynamic equation concerned is

$$\underset{\sim}{x}.\underset{\sim}{\overline{X}} = TS + \underset{\sim}{N}.\underset{\sim}{\overline{\mu}} - U = kT \ln \Xi \qquad (2.8.14)$$

This can also be written in the differential form:

$$d(\underset{\sim}{x}.\underset{\sim}{X}) = \underset{\sim}{X}.d\underset{\sim}{x} + SdT + \underset{\sim}{N}.d\bar{\underset{\sim}{\mu}} = d(kT \ln \Xi) \qquad (2.8.15)$$

As a consequence,

$$\bar{X}_i = kT \left(\frac{\partial \ln \Xi}{\partial x_i}\right)_{T,\underset{\sim}{\mu},x_j(j\neq i)} \qquad (2.8.16)$$

$$S = kT \ln \Xi + kT\left(\frac{\partial \ln \Xi}{\partial T}\right)_{\underset{\sim}{x},\underset{\sim}{\mu}} \qquad (2.8.17)$$

$$U = kT^2\left(\frac{\partial \ln \Xi}{\partial T}\right)_{\underset{\sim}{x},\underset{\sim}{\mu}} \qquad (2.8.18)$$

and

$$N_s = kT \left(\frac{\partial \ln \Xi}{\partial \mu_s}\right)_{T,\underset{\sim}{x},\mu_t(t\neq s)} \qquad (2.8.19)$$

Certainly, apart from the three cases just considered there exist other ensembles of statistical mechanics that could equivalently be used to effect the required thermodynamic association. However, these will not be further discussed here, since for the purpose of giving a molecular interpretation to the sorption in zeolites these ensembles appear to be only of formal interest. For example, the generalized ensemble (Hill 1956a) represents a physical system that is in complete thermal, mechanical and material equilibrium with its environment; and, therefore, its thermodynamic meaning in the case of sorption in zeolites is not likely to be straightforward. Owing to the presence of sorbent surface that gives a potential field significantly affecting every sorbate molecule, the condition of complete mechanical equilibrium is in reality not attained. The same conclusion should apply to the use of any other ensemble that implies a complete mechanical equilibrium in this sense.

On the other hand, it will be shown in Chapter 4 how a certain ensemble that is intermediate between the grand canonical and the generalized ensemble, which thus does not imply a complete mechanical equilibrium, can be directly related to the generating function $E(B,T,\underset{\sim}{\lambda})$. As a matter of fact this turns out to be mathematically the most convenient ensemble to use in making the required thermodynamic association. The constituent systems in this case can be interpreted as being in complete thermal and material but only in partial mechanical equilibrium with the environment.

Admittedly, some of the foregoing remarks call for further clarification. So this will be the primary object of the theoretical studies in the next two chapters.

CHAPTER 3

THE SUBSYSTEMS

3.1 INTRODUCTION

A notable feature of the thermodynamics of a small subsystem is the breakdown of the principle of equivalence of environments that applies in general to macroscopic thermodynamics. In order to characterize the subsystem a distinct set of thermodynamic quantities is required for a particular environment, so that in this case it may be convenient to consider each environment separately. For subsequent physical interpretation it is certainly very important to choose only the appropriate environments; and these could be open or closed, isothermal or adiabatic, isobaric or undeformable, etc.. Admittedly it is also possible to consider the most general case and thereupon to derive some thermodynamic equations that are applicable to all environments. But for most purposes this does not appear to be the most convenient approach. (Hill 1963, 1964)

In analyzing the subsystems certain operational restrictions should be noted. Thermodynamic properties that can be continuously varied at will for any macroscopic system may not under actual circumstances be so varied in the case of a single subsystem. This is well illustrated by a variation in the number of molecules in the subsystem, which are themselves relatively small integral quantities. Extensive thermodynamic functions of the subsystem evidently cannot be differentiated directly in the usual manner with respect to any of such quantities; but, instead, difference equations must be used.

In the following statistical thermodynamic analyses it is very important to observe that the sorbate and sorbent are treated theoretically on quite different bases. The subsystems consist of the sorbate molecules alone interacting with the potential fields provided by the sorbent. The physical implication of this will be discussed in Sections 4.8 and 9.2.

3.2 STATISTICAL THERMODYNAMICS OF THE SUBSYSTEMS

In interpreting the sorption it is desirable to consider the relatively small number of multicomponent sorbate molecules in a particular zeolite cavity as a closed isothermal subsystem and to identify certain thermodynamic quantities that characterize this with their corresponding ensemble-averaged values. The subsystem is in thermal equilibrium at temperature T with its surroundings and is specified by a set of extensive variables $\underset{\sim}{x}$ which are conjugate to the set of intensive variables $\underset{\sim}{X}$. In the following an ensemble-averaged quantity will be indicated by a bar over it.

The internal energy $u(T;\underset{\sim}{n},\underset{\sim}{x})$ of the closed subsystem is a function of the equilibrium temperature T, the extensive parameters $\underset{\sim}{x}$, and the fixed composition set $\underset{\sim}{n}$. The ensemble-averaged internal energy $\bar{u}(T;\underset{\sim}{n},\underset{\sim}{x})$ can now be appropriately identified with the corresponding time-averaged quantity $u(T;\underset{\sim}{n},\underset{\sim}{x})$:

$$u(T;\underset{\sim}{n},\underset{\sim}{x}) \longleftrightarrow \bar{u}(T;\underset{\sim}{n},\underset{\sim}{x}) \qquad (3.2.1)$$

where
$$\bar{u}(T;\underset{\sim}{n},\underset{\sim}{x}) = \int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\, p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})\; H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \qquad (3.2.2)$$

In (3.2.2) $H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})$ is the classical Hamiltonian of the subsystem in the state $([\underset{\sim}{n}],\{\underset{\sim}{n}\})$, and this state is constrained by the set of extensive variables $\underset{\sim}{x}$. The probability density of the state $([\underset{\sim}{n}],\{\underset{\sim}{n}\})$ at temperature T is given by

$$p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) = \frac{\exp[-H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})/kT]}{Z(\underset{\sim}{n},T;\underset{\sim}{x})\ \underset{\sim}{n}!h^{3n}} \qquad (3.2.3)$$

where $Z(\underset{\sim}{n},T;\underset{\sim}{x})$ is the canonical partition function of the subsystem:

$$Z(\underset{\sim}{n},T;\underset{\sim}{x}) = \frac{1}{\underset{\sim}{n}!h^{3n}}\int d[\underset{\sim}{n}]\ d\{\underset{\sim}{n}\}\exp[-H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})/kT] \qquad (3.2.4)$$

The presence of the dividing factor $\underset{\sim}{n}!h^{3n}$ in the above expressions indicates that in each case an integration has to be carried out with respect to the 6n continuous dynamical variables $([\underset{\sim}{n}],\{\underset{\sim}{n}\})$ instead of a summation over the quantum states.

Further associations of the type (3.2.1) can be obtained when (3.2.2) is written in the differential form:

$$\begin{aligned} d\bar{u}(T;\underset{\sim}{n},\underset{\sim}{x}) = &\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})\ dH([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \\ &+\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})\ dp(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \end{aligned} \qquad (3.2.5)$$

It is then postulated that, for the set of intensive variables $\underset{\sim}{X}$, the following association could be made:

$$X_j \longleftrightarrow \bar{X}_j \qquad (3.2.6)$$

where $$\bar{X}_j = -\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})\ \frac{\partial}{\partial x_j}\ H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \qquad (3.2.7)$$

x_j and X_j being a conjugate pair. Since the extensive quantities $\underset{\sim}{x}$ are here regarded as continuous variables and each dx_j is an exact differential, it follows that

$$d\bar{u}(T;\underset{\sim}{n},\underset{\sim}{x}) = -\bar{\underset{\sim}{X}}.d\underset{\sim}{x} - kT\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}[\ln p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})$$

$$+ \ln Z(\underset{\sim}{n},T;\underset{\sim}{x})]dp(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})$$

$$= -\bar{\underset{\sim}{X}}.d\underset{\sim}{x} - kT\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\ p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})$$

$$.\ln p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \qquad (3.2.8)$$

The fundamental thermodynamic equation appropriate for this closed subsystem is

$$du = T\,ds - \underset{\sim}{X}.d\underset{\sim}{x} \qquad (3.2.9)$$

Therefore the statistical thermodynamic entropy s of the subsystem can now be defined by

$$s(T;n,x) = -k\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})\ \ln p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \qquad (3.2.10)$$

Equations (3.2.4), (3.2.9) and (3.2.10) then lead to

$$kT \ln Z(\underset{\sim}{n},T;\underset{\sim}{x}) = Ts - \bar{u} = -A(\underset{\sim}{n},T;\underset{\sim}{x})\ , \qquad (3.2.11)$$

where $A(\underset{\sim}{n},T;\underset{\sim}{x})$ is the Helmholtz free energy of the subsystem of composition set $\underset{\sim}{n}$ at temperature T and at specified extensive parameter set $\underset{\sim}{x}$. Also,

$$s(\underset{\sim}{n},T;\underset{\sim}{x}) = k \ln Z(\underset{\sim}{n},T;\underset{\sim}{x}) + kT\left(\frac{\partial}{\partial T} \ln Z(\underset{\sim}{n},T;\underset{\sim}{x})\right)_{\underset{\sim}{x},\underset{\sim}{n}} \qquad (3.2.12)$$

and

$$\bar{X}_i(\underset{\sim}{n},T) = kT\left(\frac{\partial}{\partial x_i} \ln Z(\underset{\sim}{n},T;\underset{\sim}{x})\right)_{T,\underset{\sim}{n},x_j(j\neq i)} \qquad (3.2.13)$$

It is important to observe that the chemical potentials of the σ molecular species of the subsystem have not hitherto been defined. The fundamental thermodynamic equation for an open macroscopic system is

$$dU = T\,dS - \underset{\sim}{X}.d\underset{\sim}{x} + \underset{\sim}{\mu}.d\underset{\sim}{N} \qquad (3.2.14)$$

If this were indeed also applicable to the small subsystem, it would then follow from (3.2.11) in its differential form that

$$\begin{aligned} d\left[kT \ln Z(\underset{\sim}{n},T;\underset{\sim}{x})\right] &= s dT + \overline{\underset{\sim}{X}}.d\underset{\sim}{x} - \underset{\sim}{\mu}.d\underset{\sim}{n} \\ &= dA(\underset{\sim}{n},T;\underset{\sim}{x}) \end{aligned} \qquad (3.2.15)$$

The chemical potential of the s th component would accordingly be given by

$$\mu_s(T,\underset{\sim}{x}) = \left(\frac{\partial}{\partial n_s} A(\underset{\sim}{n},T;\underset{\sim}{x})\right)_{T,\underset{\sim}{x},n_t(t\neq s)} = -kT\left(\frac{\partial}{\partial n_s} \ln Z(\underset{\sim}{n},T;\underset{\sim}{x})\right)_{T,\underset{\sim}{x},n_t} \qquad (3.2.16)$$

where $s = 1,2,\ldots,\sigma$. On the other hand it has previously been pointed out that the canonical partition function $Z(\underset{\sim}{n},T;\underset{\sim}{x})$ for a small subsystem is in reality properly defined only for the discrete values of n_s; and thus it follows that the Helmholtz free energy $A(\underset{\sim}{n},T;\underset{\sim}{x})$ is in this case not a continuous function of n_s. In other words, although $A(\underset{\sim}{n},T;\underset{\sim}{x})$ is itself well-defined, it cannot be differentiated in the way represented in (3.2.16). However, it is still quite conceivable that by some suitable means this difficulty could be avoided. So this problem will again be considered in Section 3.4.

3.3 FLUCTUATIONS IN THE SUBSYSTEMS

Consider the canonical ensemble of isothermal closed subsystems. From (3.2.2) and (3.2.3) it follows that

$$\bar{u}(T;\underset{\sim}{n},\underset{\sim}{x})\ Z(\underset{\sim}{n},T;\underset{\sim}{x}) = \frac{1}{\underset{\sim}{n}!h^{3n}}\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\ H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \cdot\exp\left[-H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})/kT\right] \tag{3.3.1}$$

Differentiation of this with respect to T gives

$$\left(\frac{\partial\bar{u}}{\partial T}\right)_{\underset{\sim}{n},\underset{\sim}{x}} Z + \frac{\bar{u}}{kT}\cdot\frac{1}{\underset{\sim}{n}!h^{3n}}\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\ H\exp(-H/kT) = \frac{1}{kT^{2}}\cdot\frac{1}{\underset{\sim}{n}!h^{3n}}\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\ H^{2}\exp(-H/kT) \tag{3.3.2}$$

where $H = H([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})$ and $\bar{u} = \bar{u}(T;\underset{\sim}{n},\underset{\sim}{x})$ as defined by (3.2.2). It is now appropriate to define $\overline{u^2}$ by

$$\overline{u^{2}} = \int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\, p(T,[\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x})\ H^{2}([\underset{\sim}{n}],\{\underset{\sim}{n}\};\underset{\sim}{x}) \tag{3.3.3}$$

so that (3.3.2) may be rewritten simply as

$$\overline{u^{2}} - (\bar{u})^{2} = \overline{(u-\bar{u})^{2}} = kT^{2}\left(\frac{\partial\bar{u}}{\partial T}\right)_{\underset{\sim}{n},\underset{\sim}{x}} \tag{3.3.4}$$

In the foregoing results an averaging over the canonical ensemble is indicated by a bar over the quantity concerned. Thermodynamic association can be achieved by postulating that the time-averaged internal energy of the subsystem could be identified with $\bar{u}$. That is,

$$u(T;n,x) \longleftrightarrow \bar{u}(T;n,x) \qquad (3.3.5)$$

So it follows that the heat capacity of the subsystem at constant extensive variables $\underset{\sim}{x}$ and at fixed composition set $\underset{\sim}{n}$ is given by

$$C(T;\underset{\sim}{n},\underset{\sim}{x}) = \left(\frac{\partial \bar{u}}{\partial T}\right)_{\underset{\sim}{n},\underset{\sim}{x}} \qquad (3.3.6)$$

Consequently,

$$\frac{\overline{u - \bar{u}^{\,2}}}{(\bar{u})^2} = \frac{kT^2 C(T;\underset{\sim}{n},\underset{\sim}{x})}{u^2} \qquad . \qquad (3.3.7)$$

As $C(T;\underset{\sim}{n},\underset{\sim}{x})$ can be expected to be $O(nk)$ and u to be $O(nkT)$, it becomes apparent that fluctuations of u as given by

$$\frac{\overline{u - \bar{u}^{\,2}}}{(\bar{u})^2} = O(1/n) \qquad (3.3.8)$$

can be comparatively large for the small number of molecules n (up to about 16) in any one subsystem. Thermodynamically, therefore, $\bar{u}$ must not be thought of as a directly measurable quantity for an individual subsystem.

Fluctuations in an intensive variable X_i can be obtained by differentiating the expression:

$$\bar{X}_i(T;\underset{\sim}{n},\underset{\sim}{x})\; Z(\underset{\sim}{n},T;\underset{\sim}{x}) = \frac{1}{\underset{\sim}{n}!\,h^{3n}} \int d[\underset{\sim}{n}] \int d\{\underset{\sim}{n}\} \left(\frac{\partial H}{\partial x_i}\right) \exp(-H/kT) \qquad (3.3.9)$$

with respect to the conjugate variable x_i. This leads to

$$Z(\underset{\sim}{n},T;\underset{\sim}{x})\left(\frac{\partial \overline{X}_i}{\partial x_i}\right) - \frac{\overline{X}_i}{kT}\cdot\frac{1}{\underset{\sim}{n}!h^{3n}}\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\left(\frac{\partial H}{\partial x_i}\right)\exp(-H/kT)$$

$$= \frac{1}{\underset{\sim}{n}!h^{3n}kT}\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\left(\frac{\partial H}{\partial x_i}\right)^2\exp(-H/kT) - \frac{1}{\underset{\sim}{n}!h^{3n}kT}\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\left(\frac{\partial^2 H}{\partial x_i^2}\right).\exp(-H/kT) \qquad (3.3.10)$$

As a result

$$\overline{X_i^{\,2}}-(\overline{X}_i)^2 = kT\left[\frac{\partial \overline{X}_i}{\partial x_i} + \overline{\frac{\partial^2 u}{\partial x_i^2}}\right] = kT\left[\frac{\partial \overline{X}_i}{\partial x_i} - \overline{\frac{\partial X_i}{\partial x_i}}\right] \qquad (3.3.11)$$

in which the statistical thermodynamic meaning of the ensemble-averaged quantities should need no further explanation. Thermodynamic association: $X_i \leftrightarrow \overline{X}_i$, then gives

$$\frac{\overline{(X_i-\overline{X}_i)^2}}{(\overline{X}_i)^2} = \frac{kT}{X_i^{\,2}}\left[\frac{\partial X_i}{\partial x_i} - \overline{\frac{\partial X_i}{\partial x_i}}\right] \qquad (3.3.12)$$

To obtain any quantitative information concerning the terms: $\frac{\partial X_i}{\partial x_i}$, $\overline{\frac{\partial X_i}{\partial x_i}}$ and $\overline{\frac{\partial^2 u}{\partial x_i^2}}$, the equation of state of the subsystem together with the detailed laws of sorbate-sorbate and sorbate-sorbent interactions are required. Qualitatively, however, it is clear that fluctuations in X_i are not always negligible for the small subsystem. And for this reason it is relatively difficult to find any useful concept for the interpretation of those mechanical variables which characterize the sorption in zeolites at the level of individual subsystems.

3.4 AN ASSEMBLY OF SUBSYSTEMS CHARACTERIZED BY $\underset{\sim}{\mu}, \underset{\sim}{x}$, T

In order to demonstrate further the influence of the sorbent on statistical thermodynamic properties of the sorbate and also to motivate the thermodynamic consideration in Chapter 4, it is appropriate to study in some detail the effects of a specific set of environmental variables on an assembly of the small subsystems. For the present it is required to find out how certain thermodynamic parameters characterizing the assembly are interrelated and subsequently to show how some thermodynamic functions that are average properties of the assembly can properly be defined.

Consider an assembly of B equivalent, distinguishable and quasi-independent subsystems, each with a fixed position in space and all characterized by the environmental variables $\underset{\sim}{\mu}$, $\underset{\sim}{x}$ and T. In this case B is not included in the set of extensive properties $\underset{\sim}{x}$. Also the partial characterization of a subsystem by $\underset{\sim}{\mu}$ should be carefully noted. Let the number of molecules of each component be macroscopically large. The entire assembly with a very large fixed value of B is a thermodynamic system. Thus, the fundamental thermodynamic equation appropriate for this is

$$dU = T\,dS - B\underset{\sim}{X}.d\underset{\sim}{x} + \underset{\sim}{\mu}.d\underset{\sim}{N} \qquad (3.4.1)$$

Now, for a similar assembly but with variable B, it is apparent that U is a function of S, $\underset{\sim}{x}$, $\underset{\sim}{N}$ and B, so that

$$dU = T\,dS - B\underset{\sim}{X}.d\underset{\sim}{x} + \underset{\sim}{\mu}.d\underset{\sim}{N} + I.dB \qquad (3.4.2)$$

where by definition the intensive variable I is given by

$$I = \left(\frac{\partial U}{\partial B}\right)_{S,\underset{\sim}{x},\underset{\sim}{N}} \qquad (3.4.3)$$

It is useful to define a set of intensive functions $\underset{\sim}{\hat{X}}$ by

$$I = -\underset{\sim}{\hat{X}}.\underset{\sim}{x} \qquad (3.4.4)$$

When $\underset{\sim}{\mu}$, $\underset{\sim}{x}$ and T are fixed, U is a linear homogeneous function of S, $\underset{\sim}{N}$ and B. Consequently, by Euler's theorem on homogeneous differential functions, (3.4.2) on integration gives

$$U = TS + \underset{\sim}{\mu}.\underset{\sim}{N} - B\underset{\sim}{\hat{X}}.\underset{\sim}{x} \qquad (3.4.5)$$

In the macroscopic limit of each subsystem when x_i tends to infinity individually, $\hat{X}_i$ can be identified with X_i, for then (3.4.1) implies that

$$U = TS + \underset{\sim}{\mu}.\underset{\sim}{N} - B\underset{\sim}{X}.\underset{\sim}{x} \qquad (3.4.6)$$

Clearly (3.4.6) is not true in general, and in particular it does not apply to the case of an assembly of small subsystems. It is the difference between $\hat{X}_i$ and X_i that characterizes such an assembly.

The next reasonable step is to define $\bar{u}$, $\underset{\sim}{\bar{n}}$ and $\bar{s}$ for an assembly with fixed B by

$$U = B\,\bar{u}$$

$$\underset{\sim}{N} = B\,\underset{\sim}{\bar{n}} \qquad (3.4.7)$$

and $$S = B\,\bar{s}$$

By using this notation (3.4.5) can be rewritten as

$$\bar{u} = T\bar{s} + \underset{\sim}{\mu}.\underset{\sim}{\bar{n}} - \underset{\sim}{\hat{X}}.\underset{\sim}{x} \qquad (3.4.8)$$

Hence $$I = \underset{\sim}{\hat{X}}.\underset{\sim}{x} = \bar{u} - T\bar{s} - \underset{\sim}{\mu}.\underset{\sim}{\bar{n}} \qquad (3.4.9)$$

Likewise (3.4.1) and (3.4.8) can be rewritten as

$$d\bar{u} = T\,d\bar{s} - \underset{\sim}{X}.d\underset{\sim}{x} + \underset{\sim}{\mu}.d\underset{\sim}{\bar{n}} \tag{3.4.10}$$

and
$$\bar{u} = T\bar{s} - \underset{\sim}{X}.\underset{\sim}{x} + \underset{\sim}{\mu}.\underset{\sim}{\bar{n}} + (\underset{\sim}{X}-\underset{\sim}{\hat{X}}).\underset{\sim}{x} \tag{3.4.11}$$

If $\bar{u}$ were a linear homogeneous function of $\bar{s}$, $\underset{\sim}{x}$ and $\underset{\sim}{\bar{n}}$, the last term of (3.4.11) would be identically zero, as would then follow from the integration of (3.4.10). Thus, as regards the sorption in zeolites it seems appropriate to consider the term $(\underset{\sim}{X}-\underset{\sim}{\hat{X}}).\underset{\sim}{x}$ as arising from the 'surface effect' of the sorbent on the thermodynamics of individual small subsystems.

It follows from the foregoing results that the exact differential of I can be related to the exact differentials of the environmental variables T, $\underset{\sim}{x}$ and $\underset{\sim}{\mu}$ by

$$dI = \bar{s}\,dT + \underset{\sim}{X}.d\underset{\sim}{x} + \underset{\sim}{\bar{n}}.d\underset{\sim}{\mu} \tag{3.4.12}$$

Thus
$$\bar{s} = \left(\frac{\partial I}{\partial T}\right)_{\underset{\sim}{\mu},\underset{\sim}{x}} \tag{3.4.13}$$

$$X_i = \left(\frac{\partial I}{\partial x_i}\right)_{T,\underset{\sim}{\mu},x_j(j\neq i)} \tag{3.4.14}$$

and
$$\bar{n}_s = \left(\frac{\partial I}{\partial \mu_s}\right)_{T,\underset{\sim}{x},\mu_t(t\neq s)} \tag{3.4.15}$$

At this point other fundamental thermodynamic equations for the assembly of small subsystems can be presented; for example,

$$d((\underset{\sim}{X}-\underset{\sim}{\hat{X}}).\underset{\sim}{x}) = -\bar{s}\,dT + \underset{\sim}{x}.d\underset{\sim}{X} - \underset{\sim}{\bar{n}}.d\underset{\sim}{\mu} \tag{3.4.16}$$

and

$$d((\underset{\sim}{X}-\underset{\sim}{\hat{X}}).\underset{\sim}{x}/T) = -\bar{u}\,d(1/T) - \underset{\sim}{x}.d(\underset{\sim}{X}/T) + \underset{\sim}{\bar{n}}.d(\underset{\sim}{\mu}/T) \tag{3.4.17}$$

For a macroscopic system the left hand side of each of these equations certainly vanishes, in which case these equations would be just some identities connecting the interdependent variables T, $\underset{\sim}{X}$ and $\underset{\sim}{\mu}$. Thus it is clear that the assembly of subsystems has one more degree of freedom than an ordinary macroscopic system.

The results thus far may seem to be merely of formal interest; but in reality these are very important to the full understanding of the sorption system under study. They help to clarify the relationships between the time-averaged behaviour of a closed subsystem, the statistical mechanical functions averaged over various ensembles, and the thermodynamic properties of the macroscopic sorption system which can be experimentally measured. In the next chapter they will be used to support the argument for setting up the fundamental thermodynamic equation that can be most conveniently related to the statistical mechanical results of sorption in zeolites.

It may be tempting to regard the functions $\bar{u}$, $\underset{\sim}{\bar{n}}$ and $\bar{s}$ as defined by (3.4.10) as the physical properties of a specific subsystem. So it is here emphasized that, strictly speaking, this is incorrect. Indeed each of these quantities is meaningful only in a very specific sense as an average property of the macroscopic localized assembly. Certainly the chemical potential of any individual subsystem is not properly defined. Nevertheless the above results do indicate that it is still meaningful to think of the average chemical potential of a subsystem in the assembly, provided of course that the very specific manner of the averaging implied by this is fully recognized.

CHAPTER 4

THERMODYNAMICS OF SORPTION IN ZEOLITES

4.1 THERMODYNAMIC ASSOCIATION

This chapter is concerned with the physical interpretation of certain statistical thermodynamic results previously obtained for a macroscopic system of the multicomponent sorbate in a localized assembly of open small subsystems. It was shown in Section 2.8 how the sorption system could be characterized by the microcanonical, canonical and grand partition functions. In principle these partition functions can be calculated directly from the relevant atomic and molecular parameters for the chosen theoretical model; and any statistical thermodynamic quantity of interest can hence be deduced. Nevertheless, in practice, because of the presence of complicated summations and integrations in the analytical expressions for these partition functions, it is not mathematically convenient to use any of them for the purpose of obtaining numerical results.

The following discussion will show how the exponential generating function $E(B,T,\underset{\sim}{\lambda})$ could alternatively be used to effect the desired thermodynamic association. This function is simply related to the canonical partition functions of individual subsystems, and seems to have emerged quite naturally from the combinatorial analysis in Chapter 2.

4.2 THERMODYNAMIC SIGNIFICANCE OF $E(B,T,\underset{\sim}{\lambda})$

The sorbate is a dense phase that is in thermal and material equilibrium with the multicomponent gas. For the present interest it is proposed to study certain properties of the exponential generating function $E(B,T,\underset{\sim}{\lambda})$ in relation to the statistical mechanics of this equilibrium. In the thermodynamic method of dealing with a polyphase assembly, various expressions for thermodynamic functions of the separate phases are first derived by means of statistical mechanical analysis. The equilibrium compositions of the assembly, more specifically the relative amounts of the various phases, can then be determined by the method of equating the chemical potentials of each component. (Rushbrooke 1949a) It is essentially this approach that has been used to obtain the grand partition function $\Xi(B,T,\underset{\sim}{\lambda})$ in Section 2.7.

In the case of sorption in zeolites, the canonical and the grand partition functions are complicated functions of both B and $\underset{\sim}{N}$. However, in the thermodynamic limit only the asymptotic forms of this dependence is of real interest. Physically the intensive thermodynamic properties for a macroscopic amount of the sorbate are explicit functions of $\underset{\sim}{\bar{n}} = \underset{\sim}{N}/B$ but not of $\underset{\sim}{N}$ and B separately. On the other hand extensive properties are also linearly dependent on B, or equivalently on each component of $\underset{\sim}{N}$. Therefore, in the macroscopic limit it can be expected that

$$Z(\underset{\sim}{N},B,T) = f^{B}(\underset{\sim}{\bar{n}},T) \qquad (4.2.1)$$

and

$$\Xi(B,T,\underset{\sim}{\lambda}) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} T(\underset{\sim}{N}) \qquad (4.2.2)$$

where $$T(\underset{\sim}{N}) = f^{B}(\underset{\sim}{\bar{n}},T)\,\underset{\sim}{\lambda}^{B\underset{\sim}{\bar{n}}} \qquad (4.2.3)$$

and $f(\underset{\sim}{\bar{n}},T)$ is independent of B. Because of the restrictive condition that fixes B, it is clear that the summation over all $\underset{\sim}{N}$ in (4.2.2) cannot be performed directly. However, in view of subsequent thermodynamic applications it is still reasonable to assume that only the greatest term in the grand partition function (4.2.2) actually makes any significant contribution to the sum; so that, to a very good approximation,

$$\Xi(B,T,\underset{\sim}{\lambda}) = \left[f(\underset{\sim}{\bar{n}},T)\,\underset{\sim}{\lambda}^{\underset{\sim}{\bar{n}}}\right]^{B} \qquad (4.2.4)$$

where $B\underset{\sim}{\bar{n}}$ is the equilibrium composition set of the sorbate.

Neither $Z(\underset{\sim}{N},B,T)$ as given by (2.5.6) and (2.6.13) nor $\Xi(B,T,\underset{\sim}{\lambda})$ as given by (2.7.4) appears to be expressible as the B th power of some function that is independent of B. Yet, physically, it is known that (4.2.1) and (4.2.4) are both valid when B tends to infinity. On the other hand the discussion in Section 2.6 has shown that

$$E(B,T,\underset{\sim}{\lambda}) = E^{B}(T,\underset{\sim}{\lambda}) \qquad (4.2.5)$$

is an exact mathematical result whenever $Z(\underset{\sim}{N},B,T)$ and $\Xi(B,T,\underset{\sim}{\lambda})$ have the real thermodynamic significance.

Thus for a macroscopic assembly $E(B,T,\underset{\sim}{\lambda})$ and $E(T,\underset{\sim}{\lambda})$ are simply related to the asymptotic forms of $\Xi(B,T,\underset{\sim}{\lambda})$ and $Z(\underset{\sim}{N},B,T)$ by

$$\Xi(B,T,\underset{\sim}{\lambda}) = E(B,T,\underset{\sim}{\lambda})\,K^{B}(\underset{\sim}{\bar{n}},T) \qquad (4.2.6)$$

and $$Z(\underset{\sim}{N},B,T)\,\underset{\sim}{\lambda}^{\underset{\sim}{N}} = E(B,T,\underset{\sim}{\lambda})\,K^{B}(\underset{\sim}{\bar{n}},T) \qquad (4.2.7)$$

so that $$f(\underset{\sim}{\bar{n}},T)\,\underset{\sim}{\lambda}^{\underset{\sim}{\bar{n}}} = \Xi(T,\underset{\sim}{\lambda})\,K(\underset{\sim}{\bar{n}},T) \qquad (4.2.8)$$

where K is a parameter not directly dependent on the extensive variable B. If K and $E(B,T,\underset{\sim}{\lambda})$ could be given a thermodynamic interpretation, the latter would accordingly be a very convenient function to use in effecting the desired thermodynamic association of previously derived statistical mechanical results for the sorption assembly, since mathematically $E(T,\underset{\sim}{\lambda})$ is very simply related to the canonical partition functions of individual subsystems by (2.6.11).

The physical significance of $E(B,T,\underset{\sim}{\lambda})$ is suggested by the following phenomenological considerations. First, it is observed that ln $E(B,T,\underset{\sim}{\lambda})$ as given by (4.2.6) is a linear homogeneous function of B, whereas $E(T,\underset{\sim}{\lambda})$ as defined by (2.6.7) is independent of the parameter B which specifies the dimension of the assembly. Also $E(T,\underset{\sim}{\lambda})$ is completely determined by the environmental variables T and $\underset{\sim}{\mu}$ as well as by the intrinsic nature of the sorbate-sorbent and sorbate-sorbate interactions within individual subsystems. Thus it is quite conceivable that the exponential generating function $E(B,T,\underset{\sim}{\lambda})$ should describe the growth in extent of the macroscopic sorption system that is thermodynamically linear in B.

Now, as regards an assembly of small subsystems the discussion in Section 3.4 has indicated the rather special circumstances under which the fundamental thermodynamic equations are integrable with respect to the variable B. It is recalled that, owing to the effect of sorbent surface on each subsystem, the dependence of any thermodynamic function characterizing the sorption system upon an appropriate set of environmental variables is not in general quite straightforward. In particular the necessary condition for U to be a linear homogeneous function of S, $\underset{\sim}{N}$ and B is that $\underset{\sim}{\mu}$, $\underset{\sim}{x}$ and T be simultaneously fixed. Here the intrinsic nature of the sorbent is assumed to be independent of B. Physically it is clear that the increase in magnitude of a measurable extensive thermodynamic function of the assembly is directly proportional to the increase in B or $\underset{\sim}{N}$ only when the growth in extent of the assembly takes place at constant temperature T and at constant sorbate concentration $\underset{\sim}{\bar{n}}$. However, for the purpose of effecting the thermodynamic association of statistical mechanical results it is mathematically inconvenient to describe such growth of the assembly by varying B in the analytical expressions for $Z(\underset{\sim}{N},B,T)$ and $\Xi(B,T,\underset{\sim}{\lambda})$ while keeping T and $\underset{\sim}{\bar{n}}$ or $\underset{\sim}{\mu}$ fixed.

In order to obtain a better insight into the nature of dependence of the statistical mechanical description of the sorption system on B and $\underset{\sim}{N}$ it is appropriate to approach the present problem from a different angle by simultaneously taking into account the sorbate and the gas phase which exist in equilibrium. Consider a compound system of N+xN molecules of composition set $\underset{\sim}{N}+x\underset{\sim}{N}$, consisting of N molecules of composition set $\underset{\sim}{N}$ in an assembly of B zeolite cavities and another xN molecules in the equilibrating gas phase which surrounds this assembly, where x is an unspecified number. Let v be the gross volume of each subsystem, and V be the volume of the gas phase. The volume of the compound system is Bv+V.

Imagine the growth in extent of this compound system at constant $\underset{\sim}{\bar{n}}$, $\underset{\sim}{\mu}$ and T, while keeping the ratio of the numbers of molecules of each component in the two phases 1:x. Thermodynamically these phases have to remain in thermal and material equilibrium throughout. When ΔB subsystems are added to the assembly the volume of the gas phase has to be increased by $(V\Delta B)/B$, so that the volume of the compound system now becomes $(Bv+V)+(v+V/B)\Delta B$. With these restrictions the compound system can grow linearly to any desired extent from $B=0$ onward. For the gas phase, when all second-order effects such as those caused by the presence of surfaces and gravitational fields are neglected, the only mechanical work term is PV, where P is the static gas pressure. The mechanical work of the sorbate, on the other hand, is given by $\hat{\underset{\sim}{X}}.\underset{\sim}{x}$ as defined by (3.4.4). As regards the compound assembly it is clear that the linear growth just described is actually accompanied by a volume increase of $(v+V/B)\Delta B$ instead of just $(V\Delta B)/B$ for the expansion of the gas phase alone. Thus the work done by the compound assembly on its environment also has a contribution of $Pv\Delta B$ from the growth of the sorption assembly.

This suggests that, when the sorption assembly alone is considered as a thermodynamic system, its linear growth at constant T and $\underset{\sim}{\mu}$ will cause the work of $Pv\Delta B$ to be performed on the surroundings. Accordingly the statistical mechanical function which describes the assembly in such environment would be truly linear homogeneous in B only when the mechanical work enters the resulting statistical thermodynamic fundamental relations as $B(\hat{\underset{\sim}{X}}.\underset{\sim}{x}-Pv)$ instead of the more familiar $\underset{\sim}{X}.\underset{\sim}{x}$ terms, for example in the grand partition function case in (2.8.14). The next step is thus to find an explicit function with this property.

Consider a statistical mechanical compound system consisting of the sorbed phase in thermal and material equilibrium with the gas phase surrounding it. Let $\Gamma(B,V,T,\underset{\sim}{\lambda})$ represent the partition function appropriate to the statistical mechanical ensemble which characterizes this compound system subject to the restriction that the ratio of the numbers of molecules in the two phases be 1:1, i.e. $x=1$. The number of molecules in any representative system itself is not specified. On the other hand the environmental variables B, V, T and $\underset{\sim}{\mu}$ are all fixed.

At equilibrium the volume V is certainly a characteristic of the sorbent concerned, for it specifies the sorption capacity of this sorbent under the environment T and $\underset{\sim}{\mu}$. When there are 2N molecules in the compound system, the canonical partition function for the sorbate assembly is $Z(\underset{\sim}{N},B,T)$, whereas that of the ideally non-localized gas phase is given by $\underset{\sim}{\Omega}^{\underset{\sim}{N}}(V,T)/\underset{\sim}{N}!$ where $\Omega_s(V,T)$ is the microcanonical partition function at temperature T of each gas molecule of the s th component within the volume V. Since the compound system of interest is macroscopic, its canonical partition function $Z(2\underset{\sim}{N},B,V,T)$ is simply the product of the canonical partition functions of the two separate phases. Thus

$$Z(2\underset{\sim}{N},B,V,T) = Z(\underset{\sim}{N},B,T)\,\underset{\sim}{\Omega}^{\underset{\sim}{N}}(V,T)/\underset{\sim}{N}! \qquad (4.2.9)$$

By definition $\Gamma(B,V,T,\underset{\sim}{\lambda})$ can be written as

$$\Gamma(B,V,T,\underset{\sim}{\lambda}) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} Z(2\underset{\sim}{N},B,V,T)\,\underset{\sim}{\lambda}^{2\underset{\sim}{N}} \qquad (4.2.10)$$

It is clear that this summation takes into account all the restrictions imposed on the compound system.

For mathematical simplicity consider a single-component compound system. The generalization of the following results to the case of multicomponent systems should be fairly straightforward. Choose the contour integral in (2.6.13) as the explicit expression for $Z(\underset{\sim}{N},B,T)$ in (4.2.9). With this choice, substitution of (4.2.9) in (4.2.10) gives

$$\Gamma(B,V,T,\lambda) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} \frac{1}{2\pi i} \oint d\zeta \, \frac{E(B,T,\zeta)}{\zeta} \left[\frac{\Omega(V,T)\,\lambda^2}{\zeta} \right]^N \tag{4.2.11}$$

After reversing the orders of summation and integration and carrying out the summation of the resulting geometrical series, (4.2.11) gives

$$\begin{aligned} \Gamma(B,V,T,\lambda) &= \frac{1}{2\pi i} \oint \frac{E(B,T,\zeta)}{\zeta - \Omega(V,T)\lambda^2} \, d\zeta \\ &\quad - \lim_{N\to\infty} \frac{1}{2\pi i} \oint \frac{E(B,T,\zeta)}{\zeta - \Omega(V,T)\lambda^2} \left[\frac{\Omega(V,T)\lambda^2}{\zeta} \right]^N d\zeta \end{aligned} \tag{4.2.12}$$

In order to evaluate the two integrals in (4.2.12) Cauchy's theorem of residues is applied, as in the analysis of Section 2.6. The integrand of the first contour integral is analytic on the whole complex plane of ζ except at the isolated point singularity $\zeta = \Omega(V,T)\lambda^2$. Thus the value of this integral is given by the residue of $E(B,T,\zeta)$ at this point which is a pole of order one, that is $E(B,T,\Omega(V,T)\lambda^2)$. The contour of the second integral on the other hand encloses the two isolated singularities at $\zeta = 0$ and $\zeta = \Omega(V,T)\lambda^2$. Nevertheless this may take any arbitrary shape on the complex plane of ζ . It is thus possible to choose this contour to be outside the circle of radius $\Omega(V,T)\lambda^2$ about the origin, such that $|\Omega(V,T)\lambda^2/\zeta| < 1$. As a consequence this integral vanishes when N tends to infinity in the macroscopic system. The final result for a general case is

$$\Gamma(B,V,T,\underset{\sim}{\lambda}) = E(B,T,\underset{\sim}{\Omega}(V,T)\,\underset{\sim}{\lambda}^2) \qquad (4.2.13)$$

This result is of fundamental importance. It indicates that $E(B,T,\underset{\sim}{\Omega}(V,T)\underset{\sim}{\lambda}^2)$ should have some statistical thermodynamic significance of describing the growth in extent of the compound system that is truly linear in B. However, at this stage there appears to be no direct physical interpretation of the restriction imposed on the summation in (4.2.10).

In order to obtain a further insight into the meaning of $\Gamma(B,V,T,\underset{\sim}{\lambda})$, it is proposed to study the following idealized situation. Consider a compound system with a similar specification as that described by the partition function $\Gamma(B,V,T,\underset{\sim}{\lambda})$ above, but in the present case it is assumed that there is no sorbent surface present. In other words, at equilibrium this is simply a system consisting of the gas molecules in volume 2V divided into two halves by a hypothetical partition. In this case the relations equivalent to (4.2.9) and (4.2.10) are given by

$$Z(2\underset{\sim}{N},V,V,T) = \underset{\sim}{\Omega}^{2\underset{\sim}{N}}(V,T)\,/(\underset{\sim}{N}!)^2 \qquad (4.2.14)$$

and $$\Gamma(V,V,T,\underset{\sim}{\lambda}) = \sum_{\underset{\sim}{N}\geqslant\underset{\sim}{0}} Z(2\underset{\sim}{N},V,V,T)\,\underset{\sim}{\lambda}^{2\underset{\sim}{N}} \qquad (4.2.15)$$

For this compound system $\Gamma(V,V,T,\underset{\sim}{\lambda})$ can indeed be given a physical interpretation. The following discussion will show that in the macroscopic limit

$$kT \ln \Gamma(V,V,T,\underset{\sim}{\lambda}) = 2PV \qquad (4.2.16)$$

where P is the equilibrium gas pressure. First, for a single-component system (4.2.15) can be rewritten as

$$\Gamma(V,V,T,\lambda) = \sum_{N \geqslant 0} T(N) \qquad (4.2.17)$$

where $$T(N) = \Omega^{2N}(V,T)\,\lambda^{2N}/(N!)^2 \qquad (4.2.18)$$

and T(0) = 1. Then it is assumed that in the macroscopic limit only the maximum term in (4.2.17) need be taken into account in making a thermodynamic association. Differentiation of ln T(N) with respect to N and use of Stirling's approximation give

$$\frac{\partial}{\partial N} \ln T(N) = 2 \ln\Omega(V,T) + 2 \ln\lambda - 2 \ln N \qquad (4.2.19)$$

T(N) is maximum when both sides of this equation vanish. Thus

$$N = \Omega(V,T)\lambda \qquad (4.2.20)$$

and $$\Gamma(V,V,T,\lambda) \simeq N^{2N}/(N!)^2 \qquad (4.2.21)$$

Use of Stirling's approximation leads to

$$kT \ln \Gamma(V,V,T,\lambda) \simeq 2NkT \qquad (4.2.22)$$

so that if the gas is perfect (4.2.16) immediately follows.

Thus it appears that as far as the thermodynamic association is concerned $\Gamma(V,V,T,\underset{\sim}{\lambda})$ behaves as if it were the grand partition function of the compound system. However, it may be observed that the derivation in the previous paragraph is rather cursory, as the essential step in the argument involves the picking out of the greatest term in (4.2.17) and the use of Stirling's approximation. Before any conclusion similar to (4.2.16) will be made concerning $\Gamma(B,V,T,\underset{\sim}{\lambda})$, therefore, it is important to examine the mathematical significance of the above derivation in more detail. For the macroscopic compound system without a restriction on the ratio of the numbers of molecules in its two separate parts, the appropriate grand partition function is given by

$$\Xi(V,V,T,\underset{\sim}{\lambda}) = \Xi(V,T,\underset{\sim}{\lambda})\ \Xi(V,T,\underset{\sim}{\lambda}) \qquad (4.2.23)$$

where

$$\Xi(V,T,\underset{\sim}{\lambda}) = \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} Z(\underset{\sim}{N},V,T)\,\underset{\sim}{\lambda}^{\underset{\sim}{N}}$$

$$= \sum_{\underset{\sim}{N} \geqslant \underset{\sim}{0}} \underset{\sim}{\Omega}^{\underset{\sim}{N}}(V,T)\,\underset{\sim}{\lambda}^{\underset{\sim}{N}}/\underset{\sim}{N}! \qquad (4.2.24)$$

It is clear that mathematically $\Xi(V,V,T,\underset{\sim}{\lambda})$ differs from $\Gamma(V,V,T,\underset{\sim}{\lambda})$ only in that the former includes additional terms in the summation concerned. The fact that they lead to *thermodynamically* equivalent results means that the neglect of certain terms in this case does not produce any appreciable effect. In other words only the contribution from the greatest terms need be taken into account in both cases.

It is thus reasonable to think that when only *thermodynamic* applications are of interest the use of

$\Gamma(B,V,T,\underset{\sim}{\lambda})$ as defined by (4.2.13) instead of $\Xi(B,V,T,\underset{\sim}{\lambda})$ to describe the compound assembly should at least give a good approximation of the subsequent thermodynamic results. However, it is quite possible that the neglect of small terms in $\Gamma(B,V,T,\underset{\sim}{\lambda})$ as a result of the restriction already described could produce some finite effect in this case. So it is proposed to examine (4.2.13) in more detail.

For a single-component system this can be rewritten as

$$\Gamma(B,V,T,\lambda) = \left[\sum_{n\geqslant 0} Z(n,T)\ \Omega^{n}(V,T)\,\lambda^{2n}/n!\right]^{B}$$

$$= \left[\sum_{n\geqslant 0} Z(n,T)\ Z(n,V,T)\,\lambda^{2n}\right]^{B} \qquad (4.2.25)$$

where Z(n,T) is given by (2.2.7) and Z(n,V,T) is the canonical partition function for n gas molecules in the volume V. On the other hand the grand partition function of this compound system is given by

$$\Xi(B,V,T,\lambda) = \Xi(B,T,\lambda)\ \Xi(V,T,\lambda)$$

$$= \sum_{M,N} Z(N,B,T)\ Z(M,V,T)\,\lambda^{M+N} \qquad (4.2.26)$$

where the summation concerned is over all M and N each ranging from 0 to infinity. It is quite clear that $\Xi(B,V,T,\lambda)$ includes additional terms not already present in (4.2.25). However, if it could be assumed that only the greatest terms are really significant in both cases, the two partition functions $\Gamma(B,V,T,\lambda)$ and $\Xi(B,V,T,\lambda)$ would accordingly be *thermodynamically* equivalent.

When the *exact* mathematical forms of $\Gamma(B,V,T,\underset{\sim}{\lambda})$ and $\Xi(B,V,T,\underset{\sim}{\lambda})$ are also of interest, there is indeed a marked difference between these two functions. The function $\ln \Gamma(B,V,T,\underset{\sim}{\lambda})$ is truly linear homogeneous in B, whereas, in the strict sense, $\Xi(B,V,T,\underset{\sim}{\lambda})$ is not. On the other hand the foregoing phenomenological consideration has indicated that the non-linearity should be attributed to the presence of the BPv work term, the magnitude of which is certainly very small compared with the total mechanical work associated with any sorbate system of physical interest. Thus it is reasonable to postulate that the magnitudes of $kT \ln \Xi(B,V,T,\underset{\sim}{\lambda})$ and $kT \ln \Gamma(B,V,T,\underset{\sim}{\lambda})$ differ only by the BPv term which results from the neglect of certain small terms of $\Xi(B,V,T,\underset{\sim}{\lambda})$ in $\Gamma(B,V,T,\underset{\sim}{\lambda})$. In other words

$$kT \ln \Xi(B,V,T,\underset{\sim}{\lambda}) - kT \ln \Gamma(B,V,T,\underset{\sim}{\lambda}) = BPv \qquad (4.2.27)$$

In (4.2.27) $\Xi(B,V,T,\underset{\sim}{\lambda})$ is given in terms of the grand partition functions of the two phases by (4.2.26), whereas $\Gamma(B,V,T,\underset{\sim}{\lambda})$ is given in the unseparated form by (4.2.13).

Now, if the sorbate assembly alone is considered, it should also be expected that the non-linearity is again a result of the small BPv term as in (4.2.26). Since it is known that the function $\ln E(B,T,\underset{\sim}{\lambda})$ is truly linear homogeneous in B, whereas the actual grand partition will not behave thus in the strict sense, it is reasonable to conjecture that

$$kT \ln \Xi(B,T,\underset{\sim}{\lambda}) - kT \ln E(B,T,\underset{\sim}{\lambda}) = BPv \qquad (4.2.28)$$

In view of (2.8.14) and (3.4.5) this leads to

$$kT \ln E(B,T,\underset{\sim}{\lambda}) = B(\hat{\underset{\sim}{X}}.\underset{\sim}{x} - Pv) \qquad (4.2.29)$$

and
$$kT \ln E(T,\underset{\sim}{\lambda}) = \hat{\underset{\sim}{X}}.\underset{\sim}{x} - Pv \qquad (4.2.30)$$

As a consequence the parameter K in (4.2.6)-(4.2.8) can be given the following physical meaning:

$$K(\underset{\sim}{\overline{n}},T) = \exp(Pv/kT) \qquad (4.2.31)$$

Then, with the assumption that the thermodynamics of the sorption assembly is completely specified by T, B, $\underset{\sim}{\mu}$ and the intrinsic nature of the sorbent (which is independent of B), (3.4.11) and (3.4.16) take the specialized forms:

$$kT \ln E(B,T,\underset{\sim}{\lambda}) = B(\hat{\underset{\sim}{X}}.\underset{\sim}{x}-Pv) = TS - BPv + \underset{\sim}{\mu}.\underset{\sim}{N} - U \qquad (4.2.32)$$

and
$$d\left[kT \ln E(B,T,\underset{\sim}{\lambda})\right] = d\left[B(\hat{\underset{\sim}{X}}.\underset{\sim}{x}-Pv)\right]$$
$$= S\,dT + Bv\,dP - \underset{\sim}{N}.d\underset{\sim}{\mu} \qquad (4.2.33)$$

Accordingly the required thermodynamic association for the sorption system can now be achieved with the help of $E(B,T,\underset{\sim}{\lambda})$ or of $E(T,\underset{\sim}{\lambda})$. This will be studied in the next section.

At this point it is appropriate to define the Gibbs free energy and the enthalpy of the sorbate by

$$G = A + BPv = U - TS + BPv \qquad (4.2.34)$$

and
$$H = U + BPv \qquad (4.2.35)$$

Thus (4.2.32) and (4.2.33) may be rewritten as

$$kT \ln E(T,\underset{\sim}{\lambda}) = \hat{\underset{\sim}{X}}.\underset{\sim}{x} - Pv = T\overline{s} + \underset{\sim}{\overline{n}}.\underset{\sim}{\mu} - H/B \qquad (4.2.36)$$

and $$d\left[kT \ln E(T,\underset{\sim}{\lambda})\right] = d(\underset{\sim}{\hat{X}}.\underset{\sim}{x} - Pv)$$

$$= \bar{s}\, dT + v\, dP - \underset{\sim}{\bar{n}}.d\underset{\sim}{\mu} \qquad (4.2.37)$$

for a sorption system with fixed B.

Now the grand partition of the multicomponent gas at temperature T and total pressure P that would occupy the volume Bv in the absence of the sorbent is given by

$$\Xi(Bv,T,\underset{\sim}{\lambda}) = \exp(BPv/kT) \qquad (4.2.38)$$

It follows from (4.2.6), (4.2.32) and (4.2.38) that

$$E(B,T,\underset{\sim}{\lambda}) = \Xi(B,T,\underset{\sim}{\lambda})/\Xi(Bv,T,\underset{\sim}{\lambda}) \qquad (4.2.39)$$

This indicates that $E(B,T,\underset{\sim}{\lambda})$ is closely connected to the 'surface excess' thermodynamic properties of the sorption system. (Steele 1966)

Here it should be pointed out that the postulates given in (4.2.27) and (4.2.28) are based upon the phenomenological consideration of this section and does not appear to have any obvious statistical mechanical interpretation. The essential arguments are physically very plausible, but on the other hand it has not been possible to prove the uniqueness of the descriptions of linear homogeneous growths by the functions $E(B,V,T,\underset{\sim}{\lambda})$ and $E(B,T,\underset{\sim}{\lambda})$. In many respects, however, the function $E(B,T,\underset{\sim}{\lambda})$ behaves very similarly to the grand partition function $\Xi(B,T,\underset{\sim}{\lambda})$ of the sorbate. It will thus be referred to as the 'quasi-grand' partition function of the sorption assembly.

In fact $E(B,T,\underset{\sim}{\lambda})$ is intermediate between the actual grand partition function $\Xi(B,T,\underset{\sim}{\lambda})$ and the generalized partition function that describes a system in complete thermal, material and mechanical equilibrium with its environment. In the absence of the sorbent the only work term of the system would be just BPv, and in view of (4.2.28) $E(B,T,\underset{\sim}{\lambda})$ would then be the generalized partition function of this system so that $kT \ln E(B,T,\underset{\sim}{\lambda}) = 0$. Because of the presence of the sorbent surface which significantly affects each subsystem, however, a complete mechanical equilibrium is not attainable, and accordingly the expression $-kT \ln E(B,T,\underset{\sim}{\lambda})$ describes the finite surface excess free energy of the sorbate. Following this it is appropriate to regard the quasi-grand partition function as describing a thermodynamic system that is in complete thermal and material, but only in partial mechanical equilibrium with its surroundings. As for the real justification in using $E(B,T,\underset{\sim}{\lambda})$ to effect the desired thermodynamic association, strictly speaking, this should finally rest upon the reasonableness of the subsequent physical applications.

In the present connection it should be pointed out that the non-linearity associated with the coupling together of two different phases is not only peculiar to the present situation. Even in the very simple case of an equilibrium between a perfect crystal and a perfect gas of the same molecular species, it has been noted by Rushbrocke (1949b) that a rather uncritical derivation of the grand partition function of the solid by assuming a linear growth of this phase can give a result which is slightly different from the exact result. In this case it is possible to find a simple explanation for this difference. Strictly speaking, the use of the Einstein model to describe the condensed phase is physically appropriate only when it is also taken into account the fact that each energy state and its degeneracy depend not on the total volume V of the assembly but on the specific volume V/N, where N is the number of independent subsystems in the assembly. Accordingly the linear description of the assembly can only be correct when the canonical partition function of each independent subsystem is a function of T and V/N, but not of V and N separately. In this case it is also easy to show that the small difference is thermodynamically associated with a PV term, where P is the equilibrium gas pressure and V is the volume of the solid.

Rushbrooke has used the term 'quasi-grand' partition function to describe the function the logarithm of which is linear homogeneous with respect to the size of the assembly. The analogy of this situation with the case of an assembly of quasi-independent subsystems of interest should be obvious. The function $E(T,\underset{\sim}{\lambda})$ which describes the quasi-independent subsystems is truly independent of B except through $\underset{\sim}{\bar{n}}$ and $\underset{\sim}{\mu}$, and thus the quasi-grand partition function $E(B,T,\underset{\sim}{\lambda})$ is a linear homogeneous description of the extent of the assembly.

Finally it is pertinent to remark that (4.2.4) does not imply that $f(\underset{\sim}{\bar{n}},T)\,\underset{\sim}{\lambda}^{\underset{\sim}{\bar{n}}}$ is the grand partition function of a single open subsystem in the strict sense. The subsystems are not in reality completely independent. In this case it is certainly incorrect to think of the grand partition function of the assembly simply as the B th power of the 'grand' partition function of a representative subsystem.

4.3 INTEGRAL THERMODYNAMIC FUNCTIONS

It has been shown that the function $E(B,T,\underset{\sim}{\lambda})$ can be identified with the quasi-grand partition function of the sorbate. Thus any thermodynamic function of interest may now be conveniently deduced from the theoretical results of Sections 2.8 and 4.2. From (2.6.11) and (2.6.12),

$$E(B,T,\underset{\sim}{\lambda}) = E^{B}(T,\underset{\sim}{\lambda}) \qquad (4.3.1)$$

and

$$E(T,\underset{\sim}{\lambda}) = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} Z(\underset{\sim}{n},T)\,\underset{\sim}{\lambda}^{\underset{\sim}{n}}/\underset{\sim}{n}! \qquad (4.3.2)$$

It is from hence assumed that the volume of the subsystem is constant and that the sorbent acts as an inert solid furnishing the potential field of interaction with the sorbate. In other words the sorbent structure does not vary with the sorbate concentration. Under this condition any thermodynamic function characterizing the sorption system can be regarded as a property of the sorbate alone. A detailed consideration of this will be given in Section 4.8. Also here B is kept fixed.

Then, from (4.2.39) it follows that the integral thermodynamic functions of the sorbate are given by

$$X_i = kT\left(\frac{\partial}{\partial x_i}\ln E(T,\underset{\sim}{\lambda})\right)_{T,\underset{\sim}{\mu},x_j(j\neq i)} \qquad (4.3.3)$$

$$\bar{s} = S/B = k \ln E(T,\underset{\sim}{\lambda}) + kT\left(\frac{\partial}{\partial T} \ln E(T,\underset{\sim}{\lambda})\right)_{\underset{\sim}{x},\underset{\sim}{\mu}} \qquad (4.3.4)$$

$$\bar{n}_s = N_s/B = kT\left(\frac{\partial}{\partial \mu_s} \ln E(T,\underset{\sim}{\lambda})\right)_{T,\underset{\sim}{x},\mu_t (t \neq s)} \qquad (4.3.5)$$

$$H/B = kT^2\left(\frac{\partial}{\partial T} \ln E(T,\underset{\sim}{\lambda})\right)_{\underset{\sim}{x},\underset{\sim}{\mu}} \qquad (4.3.6)$$

and $$(\hat{\underset{\sim}{X}}\cdot\underset{\sim}{x} - Pv) = kT \ln E(T,\underset{\sim}{\lambda}) \qquad (4.3.7)$$

In (4.3.5) N_s is the number of sorbate molecules of the s th component in the sorption system less N_s^o, the number of molecules of the same component in the equilibrating gas phase that would occupy the same volume as the bulk sorbent. Similarly, in (4.3.4) S is the entropy of the sorbate less the entropy of the N^o molecules of the gas phase. The thermodynamic meaning of the remaining quantities should be quite obvious.

At this point, following Bakaev (1966), it is appropriate to introduce a new function:

$$g(\underset{\sim}{n},T) = \frac{Z(\underset{\sim}{n},T)\underset{\sim}{\lambda}^{\underset{\sim}{n}}/\underset{\sim}{n}!}{E(T,\underset{\sim}{\lambda})} \qquad (4.3.8)$$

which can be interpreted as the probability of finding the composition $\underset{\sim}{n}$ in a chosen cavity at temperature T. Or alternatively it can be regarded as the fraction of all the subsystems in the macroscopic assembly that have the same composition set $\underset{\sim}{n}$ at any chosen instant.

From this it follows immediately that

$$\sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} g(\underset{\sim}{n},T) = 1 \qquad (4.3.9)$$

$$\sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} n_s \, g(\underset{\sim}{n},T) = \bar{n}_s = N_s/B \qquad (4.3.10)$$

and
$$\sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} u(\underset{\sim}{n},T) \, g(\underset{\sim}{n},T) = H/B \qquad (4.3.11)$$

where the internal energy of the subsystem of composition set $\underset{\sim}{n}$ is given by

$$u(\underset{\sim}{n},T) = kT^2 \left(\frac{\partial}{\partial T} \ln Z(\underset{\sim}{n},T) \right)_{\underset{\sim}{x},\underset{\sim}{n}} \qquad (4.3.12)$$

The entropy of the sorbate as given by (4.3.4) can now be related to $g(\underset{\sim}{n},T)$. By (3.2.12) the entropy of the subsystem of composition set $\underset{\sim}{n}$ is

$$s(\underset{\sim}{n},T) = T^{-1} \, u(\underset{\sim}{n},T) + k \ln Z(\underset{\sim}{n},T) \qquad (4.3.13)$$

Thus,
$$S(\underset{\sim}{N},T) = S_1 + S_2 \qquad (4.3.14)$$

where
$$S_1/B = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} g(\underset{\sim}{n},T) \, s(\underset{\sim}{n},T) \qquad (4.3.15)$$

and
$$S_2/B = -k \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} g(\underset{\sim}{n},T) \ln g(\underset{\sim}{n},T) \qquad (4.3.16)$$

4.4 MOLECULAR INTERPRETATION

The physical significance of (4.3.10) should be clear, for (4.3.9) indicates that the distribution probability $g(\underset{\sim}{n},T)$ has been normalized to unity. On the other hand the interpretation of (4.3.11) is not quite straightforward and in fact needs rather careful consideration. Intuitively the presence of H instead of U in this can be explained by the fact that in a hypothetical assembly with variable B the introduction of an additional subsystem into the assembly will displace the same volume of the gas phase, and this has to be taken into account by a Pv work term. The real physical implication of this should become clearer after the subsequent discussion on the role of the sorbent and on the nature of the mechanical variables characterizing the sorption system.

It should, however, be emphasized that the results of the last section have been based implicitly upon an assumption that the sorbent could be considered as an inert solid of rigid structure furnishing an interaction potential between each sorbate molecule and the sorbent, such that there were no dimensional change in its structure following any change in the sorbate concentration. Otherwise, (4.2.39) would not have led directly to the statistical thermodynamic relations presented in the previous section.

An interpretation of the two distinct contributions to the entropy in (4.3.14) is as follows. The principal term S_1 represents the direct sum of the entropies of all individual subsystems which have a distribution probability $g(\underset{\sim}{n},T)$ in the localized assembly. The other term S_2 can be associated with the indefiniteness of the number of molecules in any particular subsystem of the assembly at any moment. As $g(\underset{\sim}{n},T)$ is normalized to unity, S_2 is certainly non-negative. Alternatively it can be considered as the 'communal entropy' of the sorbate molecules which are free to move to any part of the entire sorption system. This entropy should be regarded as a property that is associated with the assembly as a whole, and not with the individual subsystems.

An interesting question now arises concerning the behaviour of S_2 at very low temperatures. If in a theoretical model of the sorption the redistribution of molecules among the cavities were permitted even down to a temperature approaching absolute zero, S_2 would always be positive, and in consequence there would be a definite residual entropy. This is in striking contrast to the case of an assembly of closed subsystems discussed in Section 2.3. The redistribution necessarily implies an incomplete knowledge of the molecular dynamics of the sorption system; and this lack of information is reflected in the positive entropy contribution. Physically, however, the model could not be expected to be really applicable at very low temperatures, for presumably some complication due to the system being in a state of metastable equilibrium now becomes significant. Thus the foregoing remark can probably be only of formal interest.

The form of (4.3.8) does indicate that $g(\underset{\sim}{n},T)$ changes continuously when the parameters $\underset{\sim}{\lambda}$ or $\underset{\sim}{\mu}$ are varied. Nonetheless it will be observed that with any particular set of values of $\underset{\sim}{\lambda}$ the probability $g(\underset{\sim}{n},T)$ need not be highly peaked at a single composition set $\underset{\sim}{n}$. This reflects the important fact that in any single subsystem fluctuations in its composition can indeed be quite significant. Explicit results in Chapter 8 will confirm this conclusion.

As it now appears that the function $\Xi(B,T,\underset{\sim}{\lambda})$ is of fundamental importance in the statistical thermodynamics of sorption in zeolites, it is interesting to look at its form as given by (4.3.1) and (4.3.2) more critically. In a sense the presence of the factorial factor in this is rather a surprise. For if it were assumed that each zeolite cavity constitutes a thermodynamic subsystem for which the chemical potential of any component is defined, at first sight the grand partition function for the subsystem would be expected to be given by

$$\xi(T,\underset{\sim}{\lambda}) = \sum_{(\text{all }\underset{\sim}{n})} z(\underset{\sim}{n},T)\,\underset{\sim}{\lambda}^{\underset{\sim}{n}} \qquad (4.4.1)$$

where $\underset{\sim}{\mu}$ is the chemical potential set of the subsystem. In this case the grand partition function for a localized assembly of B equivalent subsystems would be just

$$\Xi(B,T,\underset{\sim}{\lambda}) = \xi^{B}(T,\underset{\sim}{\lambda}) \qquad (4.4.2)$$

As already pointed out in Section 3.2, the main objection to this type of deduction is that in (4.4.1) and

(4.4.2) it is tacitly assumed that the chemical potentials are thermodynamically well-defined and are uniform throughout the assembly even down to the level of individual subsystems. It has been argued that in the case of sorption in zeolites such an assumption would not be valid. The chemical potential of any component of the subsystem is not just an inherent property of the sorbate molecules, but is in addition strongly dependent on the nature of the sorbent. Evidently this fact cannot be properly taken into account when the grand partition function is defined for the representative subsystem, since in the theory of the grand canonical ensemble the nature of the boundary of any subsystem is not at all explicitly defined. The only assumption concerning this appears to be that it is permeable to all the molecules put into the ensembles but is 'thick' enough so that the interactions among the molecules in different subsystems are negligible. Certainly such a boundary cannot meet all the physical requirements of the actual sorption system, as in the case under study. It is therefore not surprising that the use of (4.4.1) and (4.4.2) would not give a satisfactory basis for investigating the surface properties of the real system. (Mayer 1958, Friedman 1962b)

A result rather similar to (4.4.2) has in fact been presented by Bakaev (1966) in an analysis of the sorption in zeolites. His argument is only slightly different from that given immediately above (4.4.1), being based essentially upon an assumption analogous to the generalized cell theory of liquids. However, it is clear that such an approach would also be open to the same objections as given above.

4.5 DIFFERENTIAL MOLAR QUANTITIES

Experimentally it may be convenient to measure the change of enthalpy of the sorbate system caused by an additional sorption of a small number of molecules of a particular component. Thus it is useful to derive certain statistical thermodynamic expressions for the differential molar parameters.

Partial differentiation of (4.3.8) with respect to the absolute activity of the s th component gives

$$\lambda_s \frac{\partial}{\partial \lambda_s} g(\underset{\sim}{n},T) = g(\underset{\sim}{n},T)(n_s-\bar{n}_s) \qquad (4.5.1)$$

where

$$\bar{n}_s = N_s/B \qquad (4.5.2)$$

Now by (4.3.10)

$$\sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} g(\underset{\sim}{n},T)(n_s-\bar{n}_s) = 0 \qquad (4.5.3)$$

It follows from these equations and (4.3.11) that

$$\left(\frac{\partial H}{\partial N_s}\right)_{T,\underset{\sim}{x},N_t(t\neq s)} = \frac{1}{D(\bar{n}_s,T)} \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} u(\underset{\sim}{n},T)(n_s-\bar{n}_s)g(\underset{\sim}{n},T) \qquad (4.5.4)$$

where

$$D(\bar{n}_s,T) = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} g(\underset{\sim}{n},T)(n_s-\bar{n}_s)^2 \qquad (4.5.5)$$

Clearly $D(\bar{n}_s,T)$ as defined by (4.5.5) is the variance of the distribution $g(\underset{\sim}{n},T)$ with respect to n_s.

The differential molar entropies can then be obtained by differentiating (4.3.15) and (4.3.16) with respect to N_s. That is,

$$\left(\frac{\partial S_1}{\partial N_s}\right)_{T,\underset{\sim}{x},N_t(t\neq s)} = \frac{1}{D(\overline{n}_s,T)} \sum_{\underset{\sim}{n}\geqslant\underset{\sim}{0}} s(\underset{\sim}{n},T)(n_s-\overline{n}_s)g(\underset{\sim}{n},T) \tag{4.5.6}$$

and

$$\left(\frac{\partial S_2}{\partial N_s}\right)_{T,\underset{\sim}{x},N_t(t\neq s)} = \frac{-k}{D(\overline{n}_s,T)} \sum_{\underset{\sim}{n}\geqslant\underset{\sim}{0}} (n_s-\overline{n}_s)g(\underset{\sim}{n},T)\ \ln g(\underset{\sim}{n},T) \tag{4.5.7}$$

where $s(\underset{\sim}{n},T)$ is given by (4.3.13).

It is observed that the forms of (4.5.4), (4.5.6) and (4.5.7) have certain similarity. Their physical meaning is in fact quite straightforward. The common factor, $(n_s-\overline{n}_s)g(\underset{\sim}{n},T)/D(\overline{n}_s,T)$, can be associated with the partitioning among the B cavities of the molecules of the s th component infinitesimally added at constant temperature to the assembly in which the distribution of the σ-component sorbate molecules is initially described by the function $g(\underset{\sim}{n},T)$. Alternatively it can be considered as a measure of the redistribution of all the sorbate molecules when an infinitesimal amount of the s th component is added to the assembly. The variance $D(\overline{n}_s,T)$ indicates how far the number occupancy $\underset{\sim}{n}$ of any cavity does vary with respect to the s th component from the mean value $\overline{n}_s$. Of course, in the case of an assembly of small subsystems the fact that $\overline{n}_s$ is not necessarily an integer is really quite significant.

4.6 HEAT CAPACITIES

Theoretically the most interesting and important of second derivatives of the isothermal data with respect to temperature is the heat capacity of the sorbate at constant sorbate concentration. This is defined as

$$C(\underset{\sim}{\bar{n}},T) = \left(\frac{\partial U}{\partial T}\right)_{\underset{\sim}{\bar{n}},B} = T\left(\frac{\partial S}{\partial T}\right)_{\underset{\sim}{\bar{n}},B} \tag{4.6.1}$$

When the nature of the sorbent can be assumed to be completely independent of the temperature and sorbate concentration, the entropy of a specific subsystem, $s(\underset{\sim}{n},T)$, is not a function of $\underset{\sim}{\bar{n}}$ and B. As a consequence,

$$\frac{C(\underset{\sim}{\bar{n}},T)}{T} = \left(\frac{\partial S_1}{\partial T}\right)_{\underset{\sim}{\bar{n}},B} + \left(\frac{\partial S_2}{\partial T}\right)_{\underset{\sim}{\bar{n}},B} \tag{4.6.2}$$

where

$$\frac{1}{B}\left(\frac{\partial S_1}{\partial T}\right)_{\underset{\sim}{\bar{n}},B} = \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} g(\underset{\sim}{n},T)\frac{\partial}{\partial T}s(\underset{\sim}{n},T) + \sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}} s(\underset{\sim}{n},T)\left(\frac{\partial}{\partial T}g(\underset{\sim}{n},T)\right)_{\underset{\sim}{\bar{n}}} \tag{4.6.3}$$

and

$$\frac{1}{B}\left(\frac{\partial S_2}{\partial T}\right)_{\underset{\sim}{\bar{n}},B} = -k\sum_{\underset{\sim}{n} \geqslant \underset{\sim}{0}}\left[1 + \ln g(\underset{\sim}{n},T)\right]\left(\frac{\partial}{\partial T}g(\underset{\sim}{n},T)\right)_{\underset{\sim}{\bar{n}}} \tag{4.6.4}$$

Again the physical implication of the foregoing results can readily be explained in terms of the probability densities $g(\underset{\sim}{n},T)$. The principal contribution to $C(\underset{\sim}{\overline{n}},T)$ is certainly the first sum in (4.6.3), for it is recognized that $T\frac{\partial}{\partial T}s(\underset{\sim}{n},T)$ is the heat capacity at temperature T of the quasi-independent subsystem with composition set $\underset{\sim}{n}$. The second sum in (4.6.3) arises from the redistribution of the N sorbate molecules of composition set $\underset{\sim}{N} = B\underset{\sim}{\overline{n}}$ among the B cavities of the assembly following an infinitesimal change of temperature. For the assembly of small subsystems, as in the case of sorption in zeolites, this contribution can be quite significant, since the results in Section 8.1 will show that there is in general an appreciable change in the distribution densities $g(\underset{\sim}{n},T)$ at a particular value of $\underset{\sim}{\overline{n}}$ when the temperature is varied.

The sum in (4.6.4) is associated with the variation with respect to temperature of the degree of randomness in the distribution of sorbate molecules among the cavities. Following the interpretation of S_2 in Section 4.4, it can also be regarded as a measure of the change in the 'communal entropy' of the sorbate which accompanies an infinitesimal increase of temperature.

4.7 MECHANICAL VARIABLES AND EXCESS FREE ENERGIES

From a practical standpoint the fundamental thermodynamic equation which should be the most useful for a quantitative study is that given by (4.2.21). The mechanical work directly related to $E(B,T,\underset{\sim}{\lambda})$ is $B(\underset{\sim}{x}.\underset{\sim}{\hat{X}}-Pv)$, which can truly be interpreted as a measure of the effect of sorbent surface on the thermodynamics of the sorbate. If the only mechanical work term characterizing the sorbate were BPv, $E(B,T,\underset{\sim}{\lambda})$ would be identical with the generalized partition function $\Upsilon(P,T,\underset{\sim}{\lambda})$. That this is not so, because of an additional degree of freedom of the sorption system, has already been pointed out in Section 3.4, and thus requires no further discussion. In fact, in general

$$kT \ln E(T,\underset{\sim}{\lambda}) \quad = \quad (\underset{\sim}{\hat{X}}-\underset{\sim}{X}).\underset{\sim}{x} \qquad (4.7.1)$$

where $\underset{\sim}{X}.\underset{\sim}{x}$ now signifies the set of mechanical work terms associated with the gas phase, which can of course be just one Pv term.

In the case of sorption in zeolites the physical significance of the work term $\underset{\sim}{x}.\underset{\sim}{\hat{X}}$ in (4.7.1) is certainly difficult to visualize. It seems to be a normal practice in studying sorption to postulate that

$$\begin{aligned} \underset{\sim}{X}.\underset{\sim}{x} \quad &= \quad Pv \\ \text{and} \qquad \mathcal{B}(\underset{\sim}{\hat{X}}-\underset{\sim}{X}).\underset{\sim}{x} \quad &= \quad \phi\, A \end{aligned} \qquad (4.7.2)$$

in which A is then interpreted as the 'surface area' of the 'adsorbate' and ϕ as the 'surface pressure'. Also it is implicitly assumed that the sorbent concerned can only act as an inert solid, the dimensions of which do not change when the sorbate concentration is varied.

Certainly the use of (4.7.2) does not give a very reasonable physical picture when the sorbent surface is actually divided up into a large number of approximately spherical closed surfaces, each having a radius of curvature of the same order of magnitude as the molecular diameters, as indeed is the case of sorption in zeolites. It is also expected that at a moderate concentration of the sorbate the sorbate-sorbate interaction should not be ignored. The physical state of the sorbate molecules is thus necessarily rather complicated.

On the other hand, the theoretical results hitherto appear to indicate that it should be more satisfactory not to give any further physical interpretation to $(\hat{\underset{\sim}{X}}-\underset{\sim}{X}).\underset{\sim}{x}$ than to regard it as just an excess free energy of the sorption. Indeed, $\underset{\sim}{x}.\hat{\underset{\sim}{X}}$ and $\underset{\sim}{x}.\underset{\sim}{X}$ can in this case be sums of any number of terms of the types $x_i\hat{X}_i$ and x_jX_j, respectively, which need not even be explicitly specified.

4.8 ROLE OF THE SORBENT

From the foregoing theoretical results it appears that the sorbent has not been treated thermodynamically on an equivalent basis as the sorbate; but, instead, any observable change in a thermodynamic property of the sorption system has been attributed to that of the sorbate alone. For this reason it is desirable to examine more closely how the sorbent does in fact determine the physical behaviour of the sorbate.

In general, the sorption may lead to a change in certain intrinsic properties of the sorbent, such as its various polarizations and its shear strain energies. In order to provide for all the conceivable ways that the energy of the sorption system may change reversibly, the general form of the fundamental thermodynamic equation may be written as

$$dU = T\,dS + \underset{\sim}{A}.d\underset{\sim}{a} \qquad (4.8.1)$$

In this relation the requirement that TdS be present and dS be an exact differential is a direct consequence of pure thermodynamics. In contrast, the actual assignment of any observable parameters to the set of extensive variables $\underset{\sim}{a}$ and to the set of intensive variables $\underset{\sim}{A}$ is essentially based upon some phenomenological consideration and physical plausibility.

For the system of sorption in zeolites the expression $\underset{\sim}{A}.d\underset{\sim}{a}$ is a sum of:

(1) The work terms or their thermodynamic equivalents representing the work done by the system on its environment as it grows in extent from suitable sources with respect to the intrinsic extensive variables, while the physical nature or state of the system remaining invariant;

(2) The terms associated with the translational and rotational displacements of the system as a whole with respect to the permeating scalar potential fields;

and (3) Any other energy or work terms not obviously belonging to the two categories already specified.

In the present consideration the thermodynamic system consists of only the sorbate, whereas the sorbent is included in its environment. Now consider the growth in extent of this system. First it is noted that for any sorption system the internal energy is not necessarily a homogeneous function of first degree in the intrinsic extensive variables. More specifically, in the case of sorption in an assembly with a fixed number of zeolite cavities it does not appear reasonable to assume that a change in the internal energy of the system caused by an infinitesimal increase in sorbent concentration at constant temperature is directly proportional to the number of sorbate molecules added to the system. However, it is physically much more reasonable to assume that the nature of the sorbent does not change appreciably with sorbate concentration. The growth in extent of the system at constant sorbate concentration $\underset{\sim}{\bar{n}}$ by increasing B and $\underset{\sim}{N}$ proportionately is then associated with the change for which the physical nature of the system remains invariant. Accordingly in the present consideration the volume change of the sorbate is to be understood as an appropriate change in B and not as that caused by expanding and compressing the individual subsystems while B is being kept fixed. With this assumption a useful fundamental thermodynamic equation can conveniently be set up after eliminating all the other contributions to the change in internal energy of the system by keeping the corresponding differential parameters fixed. Thus, thermodynamic association of the theoretical results can be effected. Following this consideration the implicit, yet very significant, role of the sorbent should now become clearer. It is certainly of theoretical convenience to regard the sorbate as a thermodynamic system in the non-uniform potential fields provided by the sorbent.

CHAPTER 5

THE MONTE CARLO METHODS

5.1 INTRODUCTION

In an explicit calculation of statistical thermodynamic functions for the multicomponent sorbate in zeolites, it follows from the theoretical results of Chapters 2-4 that configuration integrals and Boltzmann averages have to be evaluated from the relevant physical parameters. The configuration integrals are multidimensional, and in general involve complex integrands that are non-separable with respect to their many variables. The Boltzmann averages of statistical mechanical quantities characterizing a subsystem are given by ratios of multidimensional integrals, which may individually be too complicated to be directly computed by means of conventional numerical methods. To obtain quantitative results for these problems, standard techniques of mathematical analysis and integrations by summation of quadratures are not very effective. In practice it is far more efficient to use the Monte Carlo methods to estimate the quantities of interest on a digital computer.

The general principles of Monte Carlo methods of statistical trials have been discussed in standard works, and thus need not be considered here. (Hammersley & Handscomb 1964, Shreider 1966) In the following only certain special features of the methods used in Chapter 7 will be discussed.

5.2 COMPUTATION OF MULTIDIMENSIONAL INTEGRALS

The multidimensional integrals to be evaluated are of the general form:

$$J = \int_G f(P)\, dP \tag{5.2.1}$$

where G is an arbitrary region of the integration in a d-dimensional space, P is the representative point $(x_1, x_2, \ldots, x_d)$ within G, dP is the volume element given by

$$dP = dx_1 dx_2 \ldots dx_d \quad , \tag{5.2.2}$$

and f(P) is the integrand which is an explicit function of P.

As regards the configuration integral $Q(\underset{\sim}{n},T)$, it follows from (2.2.6) that the dimensionality of integration $d = 3n$,

$$dP = d\{\underset{\sim}{n}\}$$

and

$$f(P) = \exp\left[-U(\{\underset{\sim}{n}\})/kT\right] \tag{5.2.3}$$

The restriction of the integration to a 3n-dimensional region G represents the physical confinement of the individual n molecules to a 3-dimensional space volume Δ of the single sorption cavity under consideration.

Now, for the integrals that represent differential coefficients of the configuration integrals with respect to some thermodynamic variables, and for integrals that are present in the expressions for Boltzmann averages and statistical fluctuations, the integrations concerned still have similar specifications as above, but the momentum integrations may have to be included. In each case the integrand has to be replaced by an appropriate function of the sets of variables $[\underset{\sim}{n}]$ and $\{\underset{\sim}{n}\}$. However, if the integrand of interest is indeed of the form:

$$f(P) \quad = \quad F(\{\underset{\sim}{n}\}) \exp\left[-H([\underset{\sim}{n}],\{\underset{\sim}{n}\})/kT\right] \qquad (5.2.4)$$

and $F(\{\underset{\sim}{n}\})$ is thus not an explicit function of the momentum set $[\underset{\sim}{n}]$, the momentum integrations and the configuration integrations can be performed separately. The total integral is then given by

$$J \quad = \quad \underset{\sim}{\Lambda}^{-3\underset{\sim}{n}} \int d\{\underset{\sim}{n}\}\, F(\{\underset{\sim}{n}\}) \exp\left[-U(\{\underset{\sim}{n}\})/kT\right] \quad (5.2.5)$$

5.3 THE SIMPLE MONTE CARLO METHODS

In the simple Monte Carlo calculation a sequence of independent random points $P(\underset{\sim}{\xi})$ has to be generated within the 3n-dimensional region G such that, for a sufficiently long sequence, the random points are uniformly distributed with a constant point density throughout the region. If $\underset{\sim}{\xi}$ denotes the set of 3n random variables $(\xi_1, \xi_2, \ldots\ldots, \xi_{3n})$ which locate the random point $P(\underset{\sim}{\xi})$ representing a definite configuration set $\{\underset{\sim}{n}\}$ of the n molecules within a cavity of space volume Δ, then the probability distribution function of the random point is defined by

$$p_{\underset{\sim}{\xi}}(\{\underset{\sim}{n}\}) = \begin{cases} \Delta^{-n} & \text{if } P(\underset{\sim}{\xi}) \text{ lies within } G, \\ 0 & \text{otherwise}, \end{cases} \qquad (5.3.1)$$

where Δ^n is the 3n-dimensional volume of the region G. The mathematical expectation of the function $f(\underset{\sim}{\xi})$ is

$$\begin{aligned} M\, f(\underset{\sim}{\xi}) &= \int_G f(P)\, p_{\underset{\sim}{\xi}}(\{\underset{\sim}{n}\})\, dP \\ &= J\, \Delta^{-n} \qquad . \qquad (5.3.2) \end{aligned}$$

For a long sequence of N independent random trials, each with a set of configurations $\underset{\sim}{\xi}_i = (\xi_{i,1}, \xi_{i,2}, \ldots, \xi_{i,3n})$, where $i = 1,2,\ldots,N$, the mathematical expectation of $f(\underset{\sim}{\xi})$ is given by

$$M\, f(\underset{\sim}{\xi}) \simeq N^{-1} \sum_{i=1}^{N} f(\underset{\sim}{\xi}_i) \qquad (5.3.3)$$

As a consequence, a simple Monte Carlo estimate of the integral J can be conveniently calculated from

$$(J)_{MC} \simeq \Delta^n N^{-1} \sum_{i=1}^{N} f(\underset{\sim}{\xi}_i) \qquad (5.3.4)$$

In practice, $f(\underset{\sim}{\xi}_i)$ is evaluated from a sequence of $\underset{\sim}{\xi}_i$, the sum $\sum_{i=1}^{N} f(\underset{\sim}{\xi}_i)$ is accumulated within the computer, and $(J)_{MC}$ is computed after all the N trials have been made.

It is clear that in a simple Monte Carlo calculation methods are required to generate the sequences of random variables $\underset{\sim}{\xi}_i$ with rectangularly uniform distribution of point density in the 3n-dimensional configuration space. How these can be realized on a digital computer will now be considered.

A sequence of pseudorandom numbers with rectangularly uniform distribution in one dimension in the range 0 to 1 is generated on the computer by a multiplicative congruential process. (S hreider 1966b) The sequence is determinate, and begins with a fixed standard initial value which is set at the beginning of each Program Execution. From this the required sequence of $\underset{\sim}{\xi}_i$ can be generated by:

(a) <u>Method of Independent Random Trials</u>

A sequence of ordered triples of random numbers (ξ_1,ξ_2,ξ_3) each ranging from -a' to a' is first obtained from the series of pseudorandom numbers, such that the modulus $|(\xi_1,\xi_2,\xi_3)|$ of each triple, defined by

$$|(\xi_1,\xi_2,\xi_3)| = |(\xi_1{}^2+\xi_2{}^2+\xi_3{}^2)^{\frac{1}{2}}|, \qquad (5.3.5)$$

satisfies the restrictive condition:

$$|(\xi_1,\xi_2,\xi_3)| \leq a' \qquad (5.3.6)$$

where a' ($a' \leq a$, the cavity radius) is physically the maximum distance allowed for any molecule from the centre of the sorption cavity. In this way a sequence of random points $P(\underset{\sim}{\xi}_i) = P(\xi_{i,1},\xi_{i,2},\dots,\xi_{i,3n})$ can be generated, each from n of the triples. These points are distributed with a rectangularly uniform density in the 3n-dimensional configuration space and satisfy the boundary conditions restricting each molecule to the spherical space of radius a'.

(b) Method of Stochastic Sequence

At the beginning of the stochastic sequence a random point $P(\underset{\sim}{\xi})$ specified by the ordered 3n-tuple of quasirandom numbers $(\xi_1,\xi_2,\dots\dots,\xi_{3n})$ that satisfy the condition:

$$\left|(\xi_{3j+1}^{2}+\xi_{3j+2}^{2}+\xi_{3j+3}^{3})^{\frac{1}{2}}\right| \leq a' \qquad (5.3.7)$$

simultaneously for all $j = 0,1,2,\dots,n-1$, is generated. The next point in the sequence is obtained by displacing each i th element of the 3n-tuple by $\delta\xi_i$ for all $i = 1,2,\dots\dots,3n$, where $\delta\xi_i$ is a quasirandom number between $-a$ and a (a being a numerical constant which is small in comparison with a'), such that the conditions:

$$\left|\left[\sum_{k=1}^{3}(\xi_{3j+k}+\delta\xi_{3j+k})^2\right]^{\frac{1}{2}}\right| \leq a' \qquad (5.3.8)$$

are satisfied simultaneously for all $j = 0,1,\dots,n-1$.

By repeating this procedure a stochastic sequence of points, each of which represents a chosen configuration set, is obtained. In the asymptotic limit when the number of such points tends to infinity and the magnitude of the maximum displacement δa is sufficiently small, the distribution of these points in the 3n-dimensional Euclidean space can be shown to have the required distribution properties. It is clear that since topologically the bounded Euclidean space is simply-connected the sequence is ergodic. Thus the arithmetic mean of the magnitudes of the integrand calculated for each configuration set of the sequence gives the correct mathematical expectation value of the integral concerned.

In actual computation, the stochastic sequence is large but finitely generated ($N \sim 10^5$), whereas the displacement is $\sim 0.01a$. So the correctness of this method in generating the required distribution density has to be justified a posteriori. Of course, when the displacement is finite the distribution of points near the boundary of the configuration space will be modified by the geometry of the boundary surface. This is because the condition that each point of a sequence can be anywhere within the 3n-dimensional cubic neighbourhood(of sides δa) of the points immediately preceding it is no longer satisfied when the sequence moves to a position nearer to the boundary than $|\delta a|$.

5.4 METHODS OF REDUCING VARIANCE

In general the rate of convergence of the estimates of simple Monte Carlo methods depends on the magnitude of $N^{-\frac{1}{2}}$. So for any practical computation on a digital computer, within a reasonable number of random trials ($N \sim 10^5$), some techniques for reducing the variance of the quantities estimated are required in order to improve their accuracy. As a rule, if analytic integrations can be performed effectively with respect to some of the variables concerned, the variance can be much reduced by carrying our these integrations explicitly before applying any specific Monte Carlo method. In subsequent calculations in Chapter 7, analytical results will therefore be used wherever practicable. Accuracy can be further improved by applying the methods of extracting regular and singular parts of the integrands, and by applying the methods of importance sampling and group sampling. (Shreider 1966a)

As regards certain integrals of the statistical thermodynamic quantities that characterize a canonical subsystem, effective methods of variance reduction can normally be suggested by considering the physical behaviour of the molecules sorbed in it. The interaction potentials appropriate for the case of sorption in zeolites have highly repulsive cores, causing their effective values to increase rapidly at short separations. An integrand having a factor $\exp[-U(\{\underset{\sim}{n}\})/kT]$ will thus become negligible, particularly at low temperatures, for the configurations with short intermolecular distances. The contributions from these configurations can accordingly be excluded from an approximate estimate of the integral concerned. Hence, by assuming a hard-core potential at a suitably chosen distance, the sampling domain of the 3n-dimensional configuration space can be much reduced; and the efficiency of the Monte Carlo calculation is thereby increased.

If Δ is the volume of a zeolite cavity with only one molecule sorbed in it, and if Δ' is its portion that is accessible to the molecule when this is assumed to interact with the cavity wall by a hard-core cut-off potential, then the value of $\int f(\underset{\sim}{r})\, d\underset{\sim}{r}$ is given by

$$\frac{\Delta}{N}\sum_{i=1}^{N} f(\underset{\sim}{\xi}_i) \simeq \frac{\Delta'}{M}\sum_{i=1}^{M} f(\underset{\sim}{\zeta}_i) \qquad (5.4.1)$$

where the configurations $\underset{\sim}{\xi}_i$ and $\underset{\sim}{\zeta}_i$ are randomly distributed with uniform point densities in the space volumes Δ and Δ', respectively. The 3-dimensional restricted volume is in fact the effective configuration integral for a hard sphere with no attractive potential in the cavity.

For n identical molecules sorbed in a single zeolite cavity of space volume Δ, the estimate of $\int f(\{n\})\, d\{n\}$ is likewise given by

$$\frac{\Delta^n}{N}\sum_{i=1}^{N} f(\underset{\sim}{\xi}_i) \simeq \frac{Q_n^0}{M}\sum_{i=1}^{M} f(\underset{\sim}{\zeta}_i) \qquad (5.4.2)$$

where Q_n^o is the configuration integral for n hard spheres with no attractive potential in the cavity, which thus remains to be evaluated. Methods for estimating Q_n^o will be considered in Section 7.2.

Now it is clear that when the hard-core cut-off potentials have been introduced new methods are required for the purpose of generating the sequence of random points $P(\underset{\sim}{\zeta})$ that satisfy the subsequent restrictions. This can be achieved by modifying the method of independent random trials mentioned in the previous section, by requiring that that the 3n-tuples satisfy, in addition to (5.3.6), the condition:

$$\left|\left[\sum_{k=1}^{3}(\zeta_{3j+k}-\zeta_{3m+k})^{2}\right]^{\frac{1}{2}}\right| \geqslant \sigma' \qquad (5.4.3)$$

for all $j \neq m$ $(j,m = 0,1,\ldots,n-1)$, where σ' is the minimum distance allowed between any two approaching molecules.

Alternatively, an efficient calculation can be obtained by using the stochastic sequence with (5.4.3) added to the restriction (5.3.8). This method gives the required estimates in the asymptotic limit of $\sigma' \ll a'$ and $\delta a \rightarrow 0$; but in the actual computation some complication may arise. The 3n-dimensional configuration space is no longer simply-connected, since the presence of hard molecules in the subsystem causes certain regions of this space to be physically inaccessible. A correct interpretation of the Monte Carlo results in this case thus depends more on their physical plausibility than on any mathematically rigorous basis.

5.5 MONTE CARLO METHODS FOR ESTIMATING BOLTZMANN AVERAGES

According to classical statistical mechanics the Boltzmann average of a function $F([\underset{\sim}{n}],\{\underset{\sim}{n}\})$ characterizing the subsystem of n interacting molecules of composition set $\underset{\sim}{n}$ in a single zeolite cavity is given by

$$\langle F([\underset{\sim}{n}],\{\underset{\sim}{n}\})\rangle = \frac{\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}F([\underset{\sim}{n}],\{\underset{\sim}{n}\})\exp\left[-H([\underset{\sim}{n}],\{\underset{\sim}{n}\})/kT\right]}{\int d[\underset{\sim}{n}]\int d\{\underset{\sim}{n}\}\ \exp\left[-H(\{\underset{\sim}{n}\},[\underset{\sim}{n}])/kT\right]} \tag{5.5.1}$$

A classical Hamiltonian can in general be separated into the kinetic part involving the set $[\underset{\sim}{n}]$ only, and the configurational part involving the set $\{\underset{\sim}{n}\}$ only. So, if F is in fact not an explicit function of $[\underset{\sim}{n}]$, the integration with respect to all the momentum coordinates can be performed directly, giving

$$\langle F(\{\underset{\sim}{n}\})\rangle = \frac{\int d\{\underset{\sim}{n}\}F(\{\underset{\sim}{n}\})\ \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]}{\int d\{\underset{\sim}{n}\}\ \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]} \tag{5.5.2}$$

Certainly the Boltzmann average $\langle F(\{\underset{\sim}{n}\})\rangle$ can be estimated by evaluating the integrals of the numerator and of the denominator separately, by using some simple Monte Carlo methods with variance reduction. However, more accurate results can alternatively be obtained by applying a specific Monte Carlo technique in the following way without having to evaluate the two integrals individually.

Consider a sorption subsystem of composition set $\underset{\sim}{n}$. The n molecules are assumed to be in a known configuration set $\{\underset{\sim}{n}\}$ at the sequential time t. It is important to note that this sequential time is <u>not</u> the same as the actual time of physical development of the molecular subsystem being considered. Instead, it is to be understood in the sense of a Markov process as the label of a term in an ordered sequence of random trials. By using a certain transition probability $p(\{\underset{\sim}{n}\}_t, \{\underset{\sim}{n}\}_{t+1})$ for the change from the configuration set $\{\underset{\sim}{n}\}_t$ to a set $\{\underset{\sim}{n}\}_{t+1}$ at time t+1, a random sequence of states $\{\underset{\sim}{n}\}_1$, $\{\underset{\sim}{n}\}_2, \ldots, \{\underset{\sim}{n}\}_t, \ldots$ can be generated. Further, the transition probability can be chosen in such a way that the distribution of states in this sequence is approximately a Boltzmann distribution. The estimate of the Boltzmann-averaged $F(\{\underset{\sim}{n}\})$ is then given simply as

$$\left\langle F(\{\underset{\sim}{n}\}) \right\rangle = \frac{1}{M} \sum_{t=1}^{M} F(\{\underset{\sim}{n}\}_t) \qquad (5.5.3)$$

Fosdick (1963) has investigated the mathematical theory of Monte Carlo estimations of Boltzmann averages. In the following two sections some specific choice of the transition probabilities that will efficiently generate the desired distribution of configuration states will be discussed.

5.6 METROPOLIS METHOD OF IMPORTANCE SAMPLING

A natural choice of the probability density $p(\{\underset{\sim}{n}\})$ for a canonical subsystem of composition set $\underset{\sim}{n}$ to be in the state described by the configuration set $\{\underset{\sim}{n}\}$ is

$$p(\{\underset{\sim}{n}\}) = \frac{\exp\left[-U(\{\underset{\sim}{n}\})/kT\right]}{\int d\{\underset{\sim}{n}\}\ \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]} . \qquad (5.6.1)$$

This is precisely the distribution in a canonical ensemble at temperature T of a very large number of statistical mechanical subsystems each characterized by the same composition set $\underset{\sim}{n}$ and the same configurational energy U. The probability density (5.6.1) has been used extensively in the computation of some equations of state of simple liquids and dense gases by Metropolis et al. (1953), by Rosenbluth & Rosenbluth (1954), by Wood & Parker (1957), by Wood & Jacobson (1957), and by Wood et al. (1958). In Chapter 7 it will be used to calculate certain statistical thermodynamic quantities characterizing the subsystem of molecules sorbed in a single zeolite cavity.

This specific choice of the method for realizing the required Boltzmann distribution is particularly advantageous as regards efficient calculation on a digital computer, because, by using a uniform Markov chain to generate the distribution of states that satisfies (5.6.1), it is not necessary to know the denominator of this expression explicitly. In the Markov chain of interest the transition probability from one configuration state to any neighbouring state is a constant which depends only upon the probability densities of these two states. It does not, otherwise, depend upon the history of the whole Markov chain of successive configuration states. In this case the conditional probability $p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}')$ for finding the subsystem in the state $\{\underset{\sim}{n}\}'$ at time t+1, given that the subsystem is in state $\{\underset{\sim}{n}\}$ at time t, is independent of t.

The existence problem and the uniqueness of the asymptotic behaviour of Markov chains will not be discussed here in detail. The nature of these is well understood and has been discussed in standard works on the theories of Markov and stochastic processes. (Doob 1953, Kenemy & Snell 1960, Dynkin 1965) For the present purpose it suffices to state the following. Under the assumption that no periodicity exists and that any state can be reached within a finite sequential time, it can be proved that any arbitrarily chosen sections from far separated parts of the Markov chain do not correlate. In other words, if all the states $\{\underset{\sim}{n}\}$ form one ergodic class and $p^{(s)}(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}')$ is defined as the probability that the subsystem which at time t was known to be in the state $\{\underset{\sim}{n}\}$ should at time t+s be in the state $\{\underset{\sim}{n}\}'$, then

$$\lim_{s\to\infty} p^{(s)}(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}')$$

is stationary and is independent of the initial state $\{\underset{\sim}{n}\}$.

Note that, from the definitions of the various probability functions, it follows that

$$\sum_{\{\underset{\sim}{n}\}'} p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = 1$$

$$p^{(2)}(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = \sum_{\{\underset{\sim}{n}\}''} p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}'')p(\{\underset{\sim}{n}\}'',\{\underset{\sim}{n}\}')$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \qquad (5.6.2)$$

$$p^{(s)}(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = \sum_{\{\underset{\sim}{n}\}''} p^{(s-1)}(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}'')p(\{\underset{\sim}{n}\}'',\{\underset{\sim}{n}\}')$$

The immediate problem is then to find an explicit specification of $p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}')$ such that

$$\lim_{s\to\infty} p^{(s)}(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = p(\{\underset{\sim}{n}\}') \text{ as given by (5.6.1),}$$

$$\text{and} \quad p(\{\underset{\sim}{n}\}') = \sum_{\{\underset{\sim}{n}\}} p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}')p(\{\underset{\sim}{n}\}) \qquad (5.6.3)$$

It is not difficult to see that a solution to this is given by

$$p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = \text{some number } A(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}'), \text{ if } U(\{\underset{\sim}{n}\}') \leqslant U(\{\underset{\sim}{n}\})$$

$$p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = A(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') \exp -\left[U(\{\underset{\sim}{n}\}')-U(\{\underset{\sim}{n}\})\right]/kT, \text{ if } U(\{\underset{\sim}{n}\}') > U(\{\underset{\sim}{n}\})$$

$$\text{and} \quad p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}) = 1 - \sum_{\text{all } \{\underset{\sim}{n}\}' \neq \{\underset{\sim}{n}\}} p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') \tag{5.6.4}$$

where $A(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}')$ is symmetric, i.e.,

$$A(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = A(\{\underset{\sim}{n}\}',\{\underset{\sim}{n}\})$$

A Markov chain defined by (5.6.4) can now be generated on a computer in the following way. The random initial configuration state $\{\underset{\sim}{n}\}_1$ of the subsystem at sequential time t = 1 is chosen in such a way that it is known to be outside the regions of singularity, and the configurational energy $U(\{\underset{\sim}{n}\}_1)$ is calculated. Next this state is displaced to

$$\{\underset{\sim}{n}\}' = (\underset{\sim}{r}_1+\delta\underset{\sim}{r}_1, \underset{\sim}{r}_2+\delta\underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_n+\delta\underset{\sim}{r}_n)$$

where $\delta\underset{\sim}{r}_i = (\delta x_i, \delta y_i, \delta z_i)$ is a triple of random numbers each ranging from $-\delta a$ to δa (the maximum displacement allowed $\delta a \ll$ the cavity radius a). The configurational energy $U(\{\underset{\sim}{n}\}')$ is again calculated. If it is found that $U(\{\underset{\sim}{n}\}') \leq U(\{\underset{\sim}{n}\})$, the new configuration set $\{\underset{\sim}{n}\}'$ is accepted as the state of the subsystem at sequential time t = 2; otherwise, $\exp-[U(\{\underset{\sim}{n}\}')-U(\{\underset{\sim}{n}\})]/kT$ has to be calculated. The latter, which is necessarily between 0 and 1, is then compared with a random number in the same range of values. If the random number is found to be less, the configuration state $\{\underset{\sim}{n}\}'$ is again accepted; if not, the state at sequential time t = 2 remains as $\{\underset{\sim}{n}\}$. This procedure is repeated so that successive configuration states are generated as the sequential time is increased monotonically.

It is clear that the process just described is stochastic. The transition probability $p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}')$ from any chosen state $\{\underset{\sim}{n}\}$ to any other state $\{\underset{\sim}{n}\}'$ is stationary and forms the representative element of a stochastic square matrix of degree equal to the total number of accessible states, which in general may not even be finite. By its definition this stochastic matrix satisfies the necessary and sufficient conditions :

$$\sum_{\{\underset{\sim}{n}\}'} p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = 1$$

$$(5.6.5)$$

and

$$p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') \geqslant 0$$

It may also be of interest to note that the microreversibility condition :

$$p(\{\underset{\sim}{n}\})\, p(\{\underset{\sim}{n}\},\{\underset{\sim}{n}\}') = p(\{\underset{\sim}{n}\}',\{\underset{\sim}{n}\})\, p(\{\underset{\sim}{n}\}') \qquad (5.6.6)$$

which is certainly more restrictive than (5.6.3), has not been assumed here. However, it is well known that (5.6.6) necessarily implies (5.6.3) but the converse is not true in general, provided of course that the normalization condition for $p(\{\underset{\sim}{n}\})$ is satisfied. (Verlet 1966)

When the Metropolis method of importance sampling is used, the variance of any Monte Carlo estimate of a Boltzmann-averaged function is given by (Fosdick 1963)

$$V_M = \frac{\frac{1}{M}\int d\{\underset{\sim}{n}\}\left[F(\{\underset{\sim}{n}\})/\langle F(\{\underset{\sim}{n}\})\rangle -1\right]^2 \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]}{\int d\{\underset{\sim}{n}\}\exp\left[-U(\{\underset{\sim}{n}\})/kT\right]} \qquad (5.6.7)$$

Since this is an explicit function of $\langle F(\{\underset{\sim}{n}\})\rangle$, which is in fact the quantity to be evaluated, the variance cannot be conveniently calculated. In such a situation the most practical way to test the reliability of a Monte Carlo calculation is to study directly the fluctuations in the estimates of $\langle F(\{\underset{\sim}{n}\})\rangle$ with respect to the number of random trials.

5.7 FOSDICK METHOD OF OPTIMUM SAMPLING

By considering a general probability function for the biassed selection scheme of random configuration states of a canonical subsystem, Fosdick (1963) has shown that the optimum convergence of the estimated Boltzmann average $\langle F(\{\underset{\sim}{n}\})\rangle_{MC}$ could be obtained in the general procedure of importance sampling when the probability density of the representative state $\{\underset{\sim}{n}\}$ is given by

$$p(\{\underset{\sim}{n}\}) = \frac{\left|F(\{\underset{\sim}{n}\})/\langle F(\{\underset{\sim}{n}\})\rangle -1\right| \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]}{\int d\{\underset{\sim}{n}\}\left|F(\{\underset{\sim}{n}\})/\langle F(\{\underset{\sim}{n}\})\rangle -1\right| \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]} \qquad (5.7.1)$$

The optimum criterion concerned is based on a minimization of the variance $\left|\langle F(\{\underset{\sim}{n}\})\rangle_{MC}/\langle F(\{\underset{\sim}{n}\})\rangle -1\right|^2$ of the reduced random variable $\langle F(\{\underset{\sim}{n}\})_{MC}\rangle/\langle F(\{\underset{\sim}{n}\})\rangle$, which is of course very near unity. However, it is clear that $p(\{\underset{\sim}{n}\})$ does depend explicitly on $\langle F(\{\underset{\sim}{n}\})\rangle$, which is in fact the quantity to be estimated. Accordingly, this optimum sampling scheme can be of practical use only in an iterative procedure for successive approximations of $\langle F(\{\underset{\sim}{n}\})\rangle$. The estimate of $\langle F(\{\underset{\sim}{n}\})\rangle$ to be used in the first step of the iteration has to be obtained initially be using the Metropolis method of importance sampling or by using some simple Monte Carlo methods with variance reduction.

As in the case of the Metropolis method, the denominator in (5.7.1) need not be known explicitly when only the asymptotic behaviour of a Markov chain is of actual interest in realizing the Boltzmann distribution of configuration states. In the infinite limit, the transition probability from the state $\{\underset{\sim}{n}\}$ at time t to a neighbouring state $\{\underset{\sim}{n}\}'$ at time t+1 is again independent of t. The distribution of states of a Markov chain satisfying the condition (5.7.1) can be obtained in a real computation by a method similar to that considered in the last section. However, in this case the quantity to be compared with the random number between 0 and 1 is

$$\frac{\left|F(\{\underset{\sim}{n}\}')/\langle F(\{\underset{\sim}{n}\})\rangle -1\right| \exp\left[-U(\{\underset{\sim}{n}\}')/kT\right]}{\left|F(\{\underset{\sim}{n}\})/\langle F(\{\underset{\sim}{n}\})\rangle -1\right| \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]}$$

instead of just the exponential factors by themselves.

Fosdick has also shown that the variance of an estimate obtained by the method of optimum sampling is given by

$$V_M^o = \frac{\frac{1}{M}\left\{\int d\{\underset{\sim}{n}\} \left|F(\{\underset{\sim}{n}\})/\langle F(\{\underset{\sim}{n}\})\rangle -1\right| \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]\right\}^2}{\left\{\int d\{\underset{\sim}{n}\} \exp\left[-U(\{\underset{\sim}{n}\})/kT\right]\right\}^2} \qquad (5.7.3)$$

From (5.6.7) and (5.7.3) it is clear that the difference $V_M - V_M^o$ represents the variance of $M^{-\frac{1}{2}}\left|F(\{\underset{\sim}{n}\})/\langle F(\{\underset{\sim}{n}\})\rangle -1\right|$ with respect to the Boltzmann distribution. This suggests that the optimum sampling procedure might be particularly advantageous for the calculation of statistical mechanical quantities characterizing a small canonical subsystem. In this regard it should be noted that fluctuations of the configurational energy of this subsystem can indeed be relatively large.

5.8 GENERAL REMARKS

Concerning their subsequent applications in Chapter 7 the Monte Carlo methods already described should be regarded merely as mathematical techniques. The statistical models used for the purpose of obtaining numerical results do not directly represent the physical system under study. But, rather, they are just some mathematical constructions to facilitate efficient calculations, on a digital computer, of certain expressions which involve multidimensional integrals. In particular, the time development of a Markov chain is a completely fictitious process. So this should not be confused with the time development of a real sorption subsystem of molecules in a single zeolite cavity, even though the two different processes may sometimes correlate very well by physical intuition.

In principle, only in the infinite limit of sequential time would the use of a stationary Markov chain give the desired distribution of selected states satisfying all the boundary conditions imposed on a specific subsystem. For practical computation, however, the number of random trials is necessarily finite. Therefore, the reliability in using a particular Markov chain to find the Monte Carlo estimate has to be justified a posteriori by some statistical evidence as regards fluctuations of the estimate concerned, as well as by the physical reasonableness and consistency of the calculated quantity.

For practical reasons it is important to choose the mathematical conditions in such a way that a Markov chain should give the best representation of all the points over the whole configuration space. When the molecules are densely packed in a subsystem, it is certainly difficult to visualize the detailed behaviour of any Markov chain in the corresponding configuration space, or to guess the optimum conditions and relevant parameters for the purpose of an efficient calculation. Apparently, as regards the interaction potentials of interest, the resulting configuration space, and hence also the phase space, has no finite inaccessible volume bounded by a surface of singularity. Nevertheless the configuration space can still be expected to be partitioned into many dense regions which make comparable contributions to the statistical mechanical quantity to be evaluated. In this case the probability of a transition from one region to another may be extremely small, despite the fact that the points in all these regions do belong to one and the same ergodic class of states. Some elementary aspects of this type of 'quasi-ergodic' problems have been discussed by Wood & Parker (1957) and by Fisher (1964).

So it appears that in practice the sizes of the displacements, the boundary conditions and the initial configurations of Markov chains could only be adjusted basically by trial and error. In this regard it should be pointed out that some subsequent studies of fluctuations in the quantities estimated with respect to the number of random trials, together with an observation of the effects of changing the initial state of a specific Markov chain, can normally give much useful information. Also for practical reasons the choice of an optimum value for the maximum displacement δa allowed is of special importance. Too small a value of this may result in the necessity of generating an extremely long chain, whereas too large a value may cause certain groups of states to be totally inaccessible.

CHAPTER 6

PHYSICAL PARAMETERS

6.1 SORBENT STRUCTURE

Synthetic Linde molecular sieve 5A, $\frac{1}{3}Na_2O.\frac{2}{3}CaO.Al_2O_3.xH_2O$, has been chosen for the subsequent detailed study of its sorption properties. This zeolite is a crystalline aluminosilicate with approximately spherical sorption cavities interconnected by channels and openings of known geometry and dimensions. Its crystal structure has been determined in the hydrated form, containing 25-35 wt % H_2O, by Broussard & Shoemaker (1960). Its structural unit is the 'sodalite' cubo-octahedron containing 24(Si,Al) cations interconnected with 36 O anions which form 6 octahedrally positioned 4-membered rings and two sets of 4 tetrahedrally positioned 6-membered rings.

The structure of Linde 5A, excluding the Na and Ca cations, has space group O_h^1-Pm3m with lattice constant 12.31±0.01 Å. In this structure the $(Si,Al)O_4$ tetrahedra are symmetrically arranged so as to place each 4-membered ring of O anions in a plane and to yield point symmetry O_h for each sodalite unit. Studies of superstructures as well as other evidence have further indicated that the SiO_4 and the AlO_4 tetrahedra alternate in accordance with the rule forbidding Al-O-Al bonds. (Barrer & Meier 1958, Meier

1967) The sodalite units are arranged in a simple cubic array, with 8 of them located at the corners of the cubic unit cell. Accordingly, each sodalite unit is joined to each of its 6 neighbours by 4 'bridge' O anions connecting the 4-membered rings of the $(Si,Al)O_4$ tetrahedra. (Figure 6.1)

The truncated octahedral cavity of each sodalite unit is called a 'β-cavity' or a 'sodalite cage'. The sorption space of interest, on the other hand, is the 'α-cavity' which is a relatively large truncated cubo-octahedron surrounded by 8 sodalite units placed at the corners of the cubic unit cell. Entry into this sorption cavity is by means of 6 channels each bounded by 4 sodalite units interconnecting 2 neighbouring cavities to form an opening of 8-membered ring of O anions at the centre of the cube face. Alternatively, the α-cavity can be considered as a building unit of Linde 5A framework, which is thus obtained by connecting the square faces of α-cavities with each other. (Figure 2) Access to a β-cavity is through the 6 openings of 6-membered rings of O anions. These openings are much smaller than those of the 8-membered rings which join all the α-cavities so as to form a series of large intersecting channels at right angles to each other. As a consequence, β-cavities are of little interest except in ion-exchange studies.

In general, any precise information concerning the cation positions in zeolites is still rather limited, as thermal and positional disorders, partially occupied sites, twinnings and crystal imperfections have made their complete determination very difficult. Nonetheless the cation positions of Linde 5A are actually known with the required accuracy. Furthermore, its cation distribution has cubic symmetry; and this is very simple to deal with mathematically. So it appears that Linde 5A should be a particularly appropriate choice for the purpose of a detailed theoretical study.

The positions of all the atoms in Linde 5A are given in Table 6.1, with the origin located at the centre of a β-cavity at m3m, and with all the Cartesian coordinates expressed in fractions of the lattice parameter. Table 6.2 lists the numbers of atoms and ions forming the wall of an α-cavity, together with their distances from the centre of this cavity.

TABLE 6.1 Atomic Coordinates of Linde 5A

(Broussard & Shoemaker 1960)

Atom	Number in unit cell	Coordinates (Origin at m3m) x	y	z
(Si,Al)	24	0.0000	0.1972	0.3727
0_1(bridge)	12	0.0000	0.2280	0.5000
0_2(single)	12	0.0000	0.2878	0.2878
0_3(4-ring)	24	0.1118	0.1118	0.3482
(Na,Ca)	8	0.1950	0.1950	0.1950

TABLE 6.2 Parameters for α-Cavity

Atom	Number	Distance from cavity centre
(Si,Al)	48	0.5983
0_1(bridge)	24	0.5692
0_2(single)	24	0.5832
0_3(4-ring)	24	0.5696
(Na,Ca)	8	0.5283

Lattice Constant 12.31 ± 0.01 Å

FIGURE 6.1 Arrangement of the Sodalite Cages in Linde 5A (From Meier 1967)

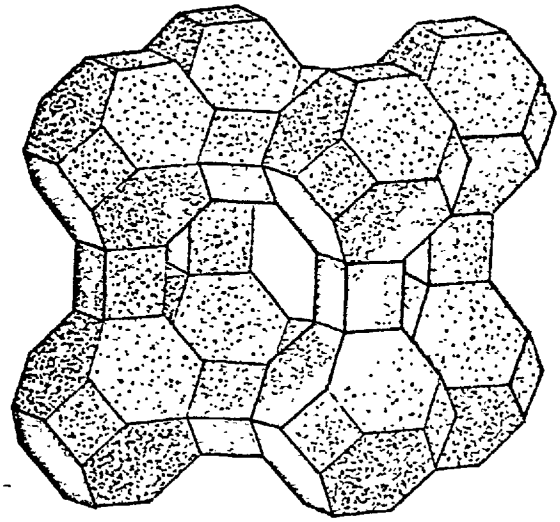
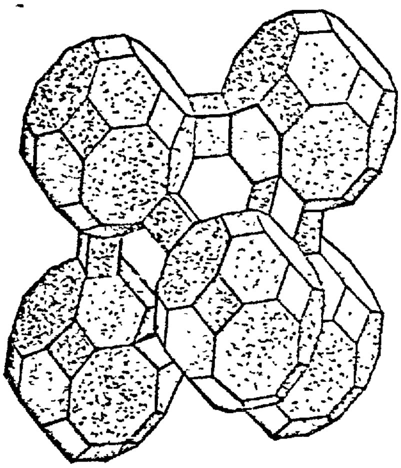


FIGURE 6.2 Arrangement of the Truncated Cubo-octahedral Structural Units in Linde 5A (From Meier 1967)



6.2 SORBATE-SORBENT INTERACTIONS

In evaluating the statistical thermodynamic functions that characterize a specific sorption system, it is necessary to know the relevant potential functions for the sorbate-sorbent interactions in detail. Krypton and methane have been chosen for study here, primarily because the forms of their interaction potentials with Linde 5A can be expected to be relatively simple. In fact, the potential functions concerned are known sufficiently accurately for a satisfactory quantitative investigation.

The molecules of krypton and methane possess no permanent dipole moment and are incapable of any specific molecular interactions with the sorbent. (Kiselev 1965, Kiselev & Lopatkin 1967) As a result the main contributions to the attractive potentials are from the non-polar dispersion forces and from the interactions of electrostatic fields of the sorbent with induced electric dipoles of the sorbate molecules. Incidentally, interactions involving electric multipoles of higher orders, as well as those involving magnetic multipoles, need not be explicitly taken into account in this case. As regards the present interest, any effect of this should not be really significant. Indeed most of the physical parameters required for their determination are at the present not known accurately.

(a) Dispersion Attraction Potential

To a good approximation the charge distributions of krypton and methane can be considered to be spherically symmetric. Thus these sorbate molecules should possess no appreciable permanent dipole or multipole moments. Nevertheless the dispersion attraction still arises from the long range interactions of instantaneous dipoles and multipoles mutually induced by the sympathetic fluctuations of electron distribution densities. (Lennard-Jones 1932, Margenau 1939, Young & Crowell 1962a, Crowell 1966)

For a sorbate molecule that is electrically neutral and chemically inert, the attraction potential function is given by

$$U_D(\underset{\sim}{r}) = -\sum_i \left[\frac{C_i^{(6)}}{r_i^{6}} + \frac{C_i^{(8)}}{r_i^{8}} + \frac{C_i^{(10)}}{r_i^{10}} + \cdots\cdots \right] \qquad (6.2.1)$$

where $\underset{\sim}{r}$ is the position vector of the sorbate molecule,

r_i is the distance between this molecule and the i th atom of the zeolite sorbent,

and $C_i^{(6)}$, $C_i^{(8)}$, $C_i^{(10)}$,... are respectively the constants for the interactions involving induced dipole-dipole, dipole-quadrupole, quadrupole-quadrupole plus dipole-octapole, and for those involving multipoles of higher orders.

The summation in (6.2.1) is over all the atoms and ions of the zeolite sorbent.

The constants $C^{(6)}$, $C^{(8)}$, $C^{(10)}$,... can in principle be calculated from the wave functions of the interacting species. Quantum-mechanical analyses based on the perturbation theory and the variational principle have led to some useful expressions for these. (London 1930, Slater & Kirkwood 1931, Kirkwood 1932, Müller 1936) The Slater-Kirkwood formula for $C^{(6)}$ is used in this work, and this is given by

$$C_{12}^{(6)} = - \frac{3eh}{4\pi m_e^{\frac{1}{2}}} \frac{\alpha_1 \alpha_2}{(\alpha_1/N_1)^{\frac{1}{2}}+(\alpha_2/N_2)^{\frac{1}{2}}} \qquad (6.2.2)$$

where e is the electronic charge, m_e the electronic mass, h the Planck constant, k the Boltzmann constant, $\alpha_i (i=1,2)$ the polarizability of the i th interacting species, and N_i its effective number of electrons.

For the interaction between like species, (6.2.2) gives

$$C_{11}^{(6)} = - \frac{3eh}{8\pi m^{\frac{1}{2}}} \alpha^{3/2} N_1^{1/2} \qquad (6.2.3)$$

The interaction parameters used are given in Table 6.3. Each N_i is taken to be the arithmetic mean of the total number and the subshell number of electrons in the atom or ion concerned. (Pitzer 1959) The polarizabilities of Na and Ca cations, with the charges indicated, are taken from Landolt-Bornstein's Tabellen (a). The relevant data for the O anion is lacking. The value given, based on a refractivity measurement of K-felspar, has been used by several authors for the O anions in zeolites. (Barrer & Peterson 1964, Rees & Williams 1964) This appears to be a reasonable choice. For a useful comparison the following polarizabilities ($\AA^3$) may be noted : 0.15 for neutral O, 3.88 for O^{2-}, and 1.77, 2.35 & 2.7 for the O anions in MgO, CaO & CrO, respectively. (Pauling 1927, Ramberg 1954, Yamashita & Kurosawa 1954, Barrer & Stuart 1959)

From the dispersion constant $C^{(6)}$ the interaction parameter ε was deduced by using the relation:

$$\varepsilon = \tfrac{1}{2} C^{(6)} r_0^{-6} \qquad (6.2.4)$$

where r_0 is the equilibrium separation. The values of r_0 for the sorbent atoms are given in Section 6.2(c). The relevant parameters for krypton and methane are given in Section 6.4. For any interaction between unlike species ε_{12} was calculated by using the combination rule (6.3.4). In Tables 6.3 and 6.4 the calculated interaction parameters are presented.

Theoretical expressions for $C^{(8)}$, $C^{(10)}$, etc., are available in the literature. (Margenau 1938, Heller 1941, Hornig & Hirschfelder 1952, Fontana 1961) However, these will not be discussed further here; and as regards the dispersion attraction potentials used in the statistical mechanical calculation of Chapter 7, only the contributions from $C^{(6)}$ will be taken into account. For the present purpose this simplification should not introduce any additional inaccuracy. It is clear that the uncertainty in the most significant contribution involving induced dipole-

dipole interactions can itself be quite appreciable. Owing to the lack of accurate data for the relevant parameters α and N in (6.2.3), the possible inaccuracy of the results for ε/k presented in Tables 6.3 and 6.4 may be as high as 10 % and 5 % respectively. Nonetheless it should be mentioned that, in a general case, the dipole-quadrupole term can contribute of the order of 10 %, and the quadrupole-quadrupole term of the order of 1 %, to the total value of the dispersion energy. (Young & Crowell 1962a, Crowell 1966)

TABLE 6.3 Interaction Parameters for Linde 5A

Atom	Charge	N_1	α_1 (Å^3)	ε_{11}/k (°K)
O	-0.25	11.25	1.65	409.9
Na	1	9	0.196	209.3
Ca	2	13	0.50	307.5

TABLE 6.4 Sorbate-Sorbent Interaction Parameters ε_{12}/k (°K)

Species 2	Species 1	
	Krypton	Methane
O	254.5	246.5
Na	181.9	176.1
Ca	220.4	213.5

(b) Electrostatic Induction Potential

The ions of the zeolite framework give an electrostatic field in the sorption cavity, and this can interact with the permanent and induced dipoles of the sorbate molecules. For non-polar krypton and methane, however, only the effects on induced dipoles need be taken into account. This is given by

$$U_I(\underset{\sim}{r}) \quad = \quad -\alpha F^2(\underset{\sim}{r}) \tag{6.2.5}$$

where α is the polarizability of the sorbate molecule, and $F(\underset{\sim}{r})$ is the magnitude of the electrostatic field intensity vector due to the sorbent ions, $\underset{\sim}{F}(\underset{\sim}{r})$, at the point $\underset{\sim}{r}$ where the reference sorbate molecule is located.

It is clear that the electrostatic induction energy is not additive. In calculating it the intensity vector $\underset{\sim}{F}(\underset{\sim}{r})$ has first to be evaluated by summing the space components of the electrostatic field vectors of all individual ions interacting with a unit charge at the specific location $\underset{\sim}{r}$. Induced multipoles of higher orders interact with the space derivatives of various orders of the electrostatic field, e.g., the quadrupole with $\underset{\sim}{\nabla}.\underset{\sim}{F}(\underset{\sim}{r})$. Quantitative studies of these derivatives certainly present a very difficult problem. For practical purposes, however, their contributions to the total potential are expected to be quite insignificant. So they will not be considered further here.

In calculating the electrostatic field intensity inside a sorption cavity the charge distribution of the zeolite framework can be approximated as follows. The Na and Ca exchangeable cations are given electrostatic charges of e and 2e respectively, where e is the electronic charge; and the neutralizing negative charges are then distributed equally among the O anions, so that each has a negative charge of 0.25e. As the sorption cavity is approximately spherical, it is expected that only the 8 (Na,Ca) cations and the 72 O anions lining the surface of each cavity should make any significant contribution to the electrostatic field. The Si and Al atoms are more distant from the cavity centre than these ions. So for the present purpose they need not be taken into account.

It is well known that when any quantity of charges is uniformly distributed on a closed surface, the electric field intensity at any point in the resulting cavity is identically zero. This is, of course, a direct consequence of Gauss's theorem in electrostatics. (Reitz & Milford 1960, Panofsky & Phillips 1962) In the cases of interest, on the other hand, the charges are not uniformly distributed in the above sense, but are assumed to be concentrated at the ion centres. As a result the field intensity inside a sorption cavity can be expected to be practically zero in the major part of the cavity, nevertheless in the regions close to the wall a considerable field intensity does appear.

The potentials due to the interactions of the induced dipoles of a sorbate molecule with the electrostatic field of Linde 5A were calculated on the digital computer along the symmetry axes: $3C_4$ ([100] direction), 6 C_2 ([110] direction) and 4 C_3 ([111] direction). The field intensity at each point was calculated from the formula:

$$\underset{\sim}{F}(\underset{\sim}{r}) = \sum_i e_i \frac{\underset{\sim}{r}_i}{r_i^{\,3}} \qquad (6.2.6)$$

where $\underset{\sim}{r}_i$ is the vector from the i th ion of the sorbent to the reference point $\underset{\sim}{r}$,

r_i is the magnitude of $\underset{\sim}{r}_i$,

and e_i is the charge (including sign) of the i th ion.

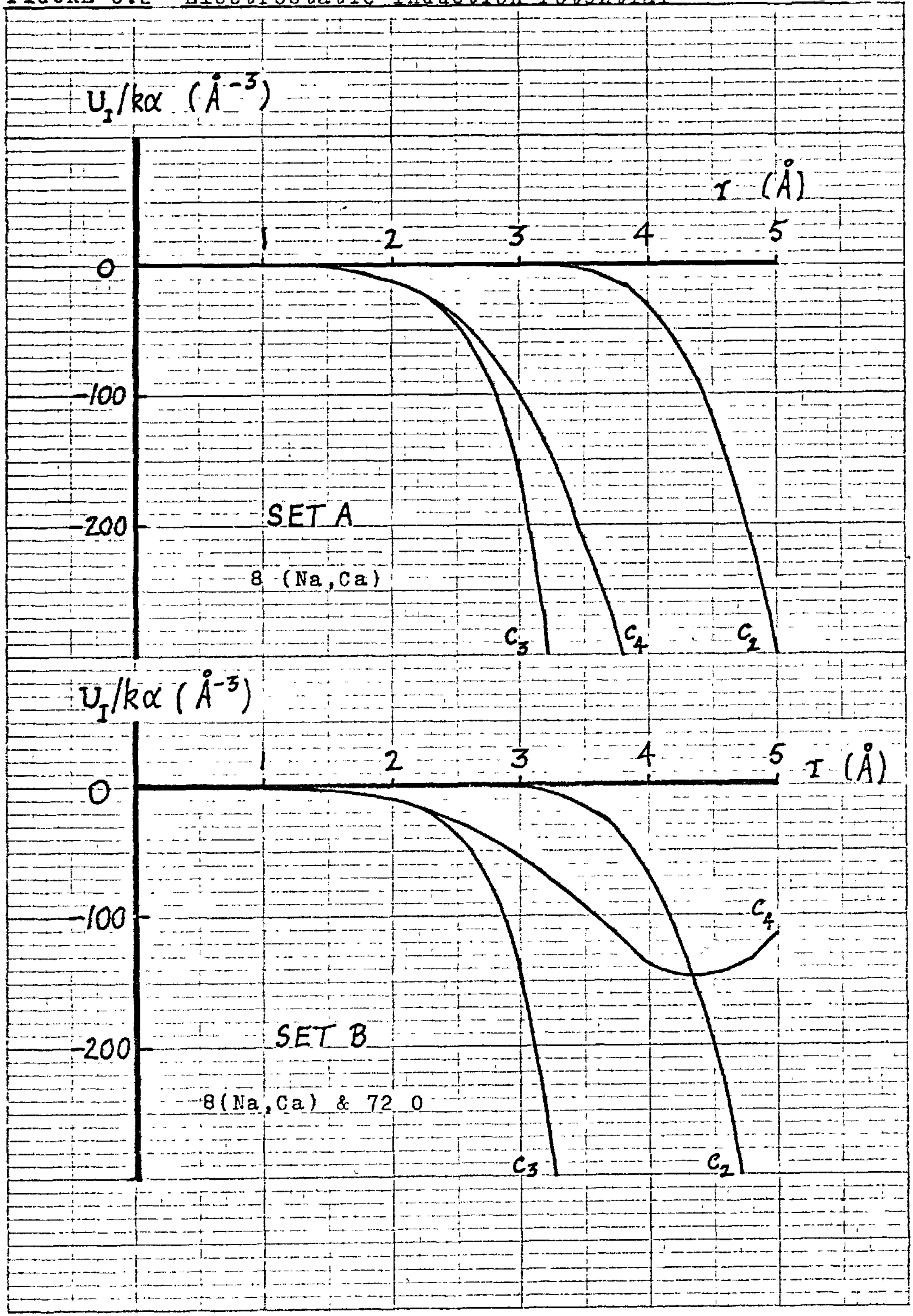
For convenience it was assumed that the 8 cations were each of charge 1.5e, and were all located at different points along the 4 C_3 axes, at distances 6.5032 Å from the cavity centre. This then gives the cubic symmetry which is particularly convenient to deal with in the calculation. The values of the polarizabilities α chosen for krypton and methane were 2.47 and 2.58 Å^3, respectively. (Young & Crowell 1962b)

Results for $U_I/k\alpha$ are presented in Figure 6.2. In calculating the potentials given in Set A only the contributions from 8(Na,Ca) cations were taken into account in the summation of (6.2.6), whereas in Set B those from the 72 O anions were also included. As expected, the electrostatic induction potential is most significant along the C_3 axis directly approaching an exchangeable cation.

The C_4 axis passes through the centres of two opposite 8-membered rings of O anions; consequently there appears to be a considerable difference between the C_4 curves in Set A and Set B.

It should be pointed out that the use of (6.2.5) and (6.2.6) implies that the electrostatic charges have been treated as discrete points at the relevant ion centres. This tends to exaggerate the magnitude of the electrostatic induction potential. In the actual system, on the other hand, the charges of the sorbent ions are non-uniformly distributed over finite volumes, and the resulting electrostatic field does vary significantly over the space occupied by a sorbate molecule. Therefore it cannot be expected that the electrostatic effect has thereupon been accurately taken into account. It would of course be more satisfactory to assume some reasonable charge distribution for each atom and ion, and to perform an integration over the volume occupied by this for the purpose of estimating its interaction with the induced dipole of the reference sorbate molecule. (Lenel 1933) However, in view of the ensuing mathematical difficulties such an approach does not appear to be really practicable.

FIGURE 6.2 Electrostatic Induction Potential of Linde 5A



(c) Repulsion Potential

The repulsion potential arises from an interpenetration of electronic orbitals of the atoms and molecules at short distances. For mathematical convenience the form of the repulsion potential used in this work is chosen to be Rr^{-12}. The constant R can in principle be calculated directly for each atomic species of the sorbent by requiring that the minimum in the resulting total potential be at the proper equilibrium separation. In practice, however, this problem is not really straightforward. The electrostatic induction energy, unlike the dispersion effect which involves only induced dipole-dipole interactions, is not pairwise-additive. As a result the total attraction potential is expected to be direction-dependent.

To a good approximation, therefore, it is reasonable first to obtain the 'averaged' attraction potential for each atomic species simply by taking the arithmetic mean of a large number of such potentials for the random directions, generated on the computer, within a reasonably chosen solid angle subtended at the centre of an exchangeable cation. Then the repulsion constant could be calculated by minimizing the resulting 'averaged' total potential at the equilibrium separation. Although it is obviously more satisfactory to use a Boltzmann average instead of just the arithmetic mean of the total potentials, the latter estimate is used here, since thereby the complication due to a temperature-dependent potential can conveniently be avoided.

The equilibrium distances chosen were 3.04 Å for the O anions (Van der Waals radius; Bondi 1964), 1.96 Å for the Na cations (ionic radius; Kiselev & Lopatkin 1967) and 2.36 Å for the Ca cations (univalent radius; Pauling 1960a)

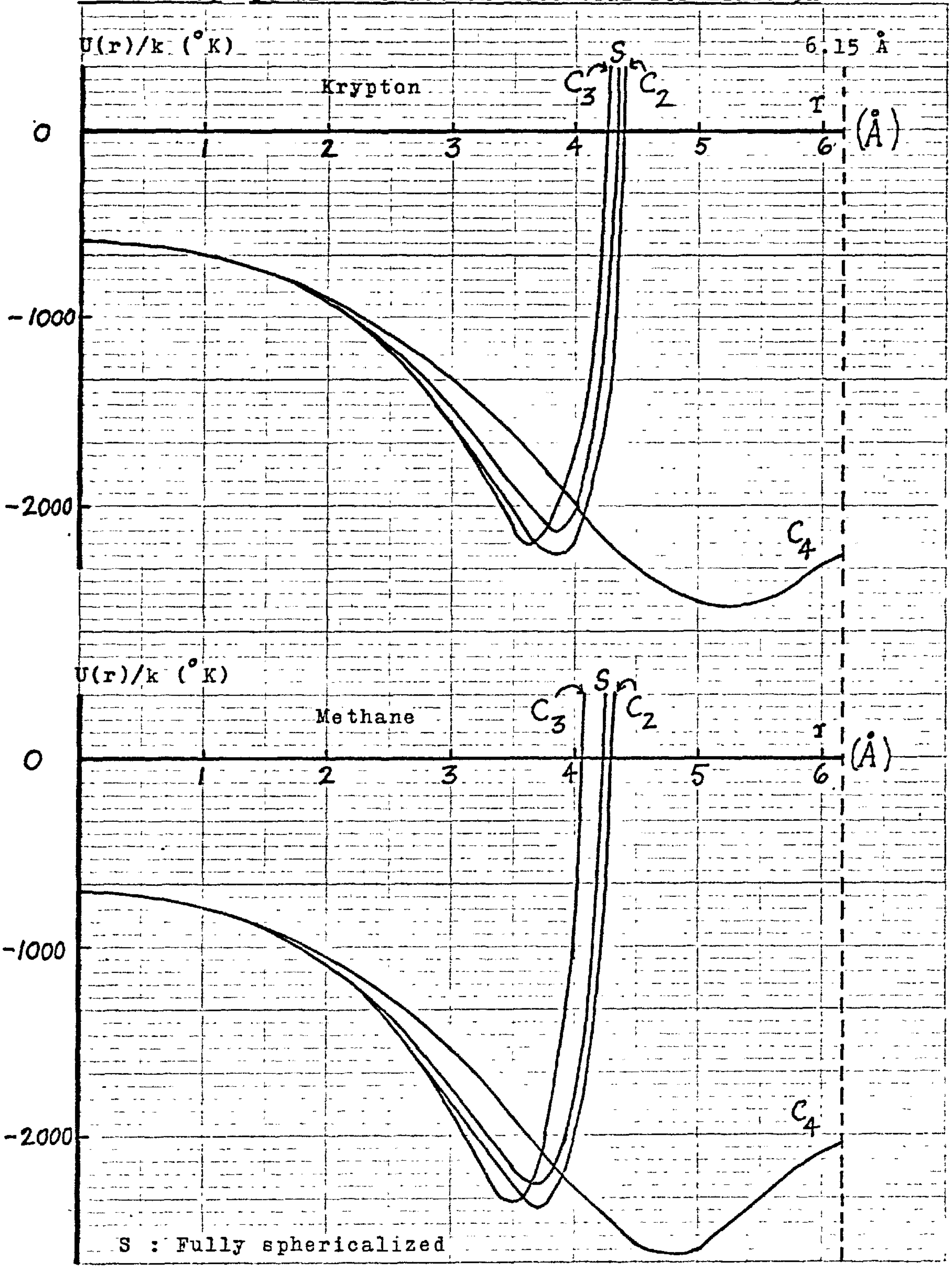
(d) Total Potential

The total sorbate-sorbent potential of a sorbate molecule at a specified point within any sorption cavity can be calculated by summing the contributions from dispersion, induction and repulsion potentials over all atoms of the zeolite sorbent. However, it appears that to a good approximation only the 72 O atoms and the 8 exchangeable cations lining the surface of each Linde 5A cavity need be taken into account in this summation. If higher accuracy is required, a correction can subsequently be made for the background potential due to all other atoms and ions outside the approximately spherical cavity surface. For this purpose the method described in Section 6.5 can be used.

Calculation of the total potentials was carried out on the computer for various distances of the sorbate molecules along the C_4, C_2 and C_3 symmetry axes. The results are presented in Figure 6.3. The value of the repulsion constant R certainly has some indefiniteness associated with the rather arbitrary choice of the solid angle subtended at the relevant cation. Fortunately the total potential does not appear to be very sensitive to this choice. Thus the appropriate value could be obtained quite conveniently by using the method of trial and error on the computer.

It is interesting to note that the interaction along the C_4 axis is rather unique. This is in fact the direction through the centres of the 8-membered rings of O anions, which form the large openings between any two neighbouring sorption cavities. Of course, this potential is very sensitive to the variations in the interaction parameters of sorbate molecules. Accordingly it can give a useful indication of the ease with which a sorbate molecule goes from one cavity to another. From these results it can be seen that the potential barriers opposing the passage of krypton and methane through the openings of Linde 5A sorption cavities are relatively small.

FIGURE 6.3 Total Interaction Potential for Linde 5A



S : Fully sphericalized Potential

6.3 SPHERICALIZATION

The 72 O anions lining the surface of every sorption cavity in Linde 5A are more or less uniformly distributed. If the electrostatic effect of these is not taken into account, the interaction of each anion with a sorbate molecule is given approximately by a potential function of the Lennard-Jones (12,6) form:

$$u_{LJ}(r) = 4\mathcal{E}\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}}\right) \qquad (6.3.1)$$

where r = the distance between the reference sorbate molecule and the anion concerned,

σ = the effective collision diameter, such that $u_{LJ}(\sigma) = 0$,

and $\mathcal{E}$ = the magnitude of the negative interaction energy at equilibrium separation.

The interaction of the sorbate molecule, located at a point $\underset{\sim}{r}$ in the cavity, with the 72 anions is then given as a sum of the $u_{LJ}(r_i)$ over all these anions:

$$U_0(\underset{\sim}{r}) = \sum_i u_{LJ}(r_i) \qquad (6.3.2)$$

where r_i is the distance between the sorbate molecule and the i th O anion.

In the subsequent statistical mechanical calculation, however, it is mathematically more convenient to approximate $U_0(r)$ by a spherically symmetric Lennard-Jones & Devonshire (LJD) potential function (Lennard-Jones & Devonshire 1937, 1938) :

$$U_{LJD}(r) = \Lambda^{*}\left[\left(\frac{v^{*}}{v_0}\right)^4 l\left(\frac{r^2}{a^2}\right) - 2\left(\frac{v^{*}}{v_0}\right)^2 m\left(\frac{r^2}{a^2}\right)\right] \qquad (6.3.3)$$

where $l(x) = (1+12x+25.2x^2+12x^3+x^4)(1-x)^{-10}$

$m(x) = (1+x)(1-x)^{-4}$

a = radius of the spherical cavity,

r = distance of the sorbate molecule from the cavity centre,

Λ^{*} = the energy parameter, given by 72ε in this case,

$v^{*} = \sigma^3$

and $v_0 = a^3 2^{-\frac{1}{2}}$.

The form of the LJD potential is well known and has been studied in detail by Wentorf et al. (1950). It has been used extensively in the cell theories of liquids and dense gases. (Barker 1963, Levelt & Cohen 1964)

The relevant data for the sorption of krypton and methane in Linde 5A are given in Table 6.5. The value for the cavity radius is the arithmetic mean of distances from the cavity centre of the 3 types of O anions as given in Table 6.2. In choosing the values for ε and σ , which characterize the interactions between unlike atoms and molecules, the following combination rules (Winter 1950, Rowlinson & Townley 1953) were used :

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{\frac{1}{2}} \qquad (6.3.4)$$

and

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11}+\sigma_{22}) \qquad (6.3.5)$$

In view of (6.2.4) it is clear that ε can also be deduced directly from the dispersion attraction parameter $C^{(6)}$ by using

$$C^{(6)} = 4\varepsilon\sigma^{6} \qquad (6.3.6)$$

where

$$\sigma = 2^{-1/6}r_0 \qquad (6.3.7)$$

r_0 being the equilibrium separation. The values for ε are given in Table 6.4. The relevant parameters for estimating σ are given in Sections 6.2(c) and 6.4.

Figure 6.4 presents the total potentials along the three symmetry axes : C_2, C_3 and C_4. In this calculation the spherically symmetric LJD potential just described was used for the interaction of the sorbate molecules with the 72 O anions. On the other hand, the 8(Na,Ca) cations were treated as discrete atoms with point charges, and the electrostatic induction energy arising from these were fully taken into account. The computation was carried out on a digital computer. The space components of the electrostatic field were summed in a manner similar to that already described in Section 6.2.

The results are in general agreement with those given by the more accurate potentials in Figure 6.3. However, it may be observed that the use of the LJD potential here causes the potential along the rather unique C_4 direction to change markedly. Physically this means that the sorption cavity is now bounded by a spherical surface of infinite repulsion potential, of radius a.

For practical reasons, it is necessary in the subsequent calculations involving more than two sorbate molecules in a subsystem to use a less accurate form of the sorbate-sorbent interaction potential. In this case the contributions from the 8 (Na,Ca) cations, as well as those from the 72 O anions are sphericalized. The appropriate interaction parameters are given in Table 6.6. As in the previous case, these were obtained by using the relevant data from Tables 6.2 and 6.4, and from Sections 6.2(c) and 6.4. Results are presented as curves S in Figures 6.3 and 6.4. From these it appears that the fully sphericalized potentials actually give quite a reasonable approximation of the more elaborate potentials for which some or all of the sorbent atoms are treated as discrete interaction centres.

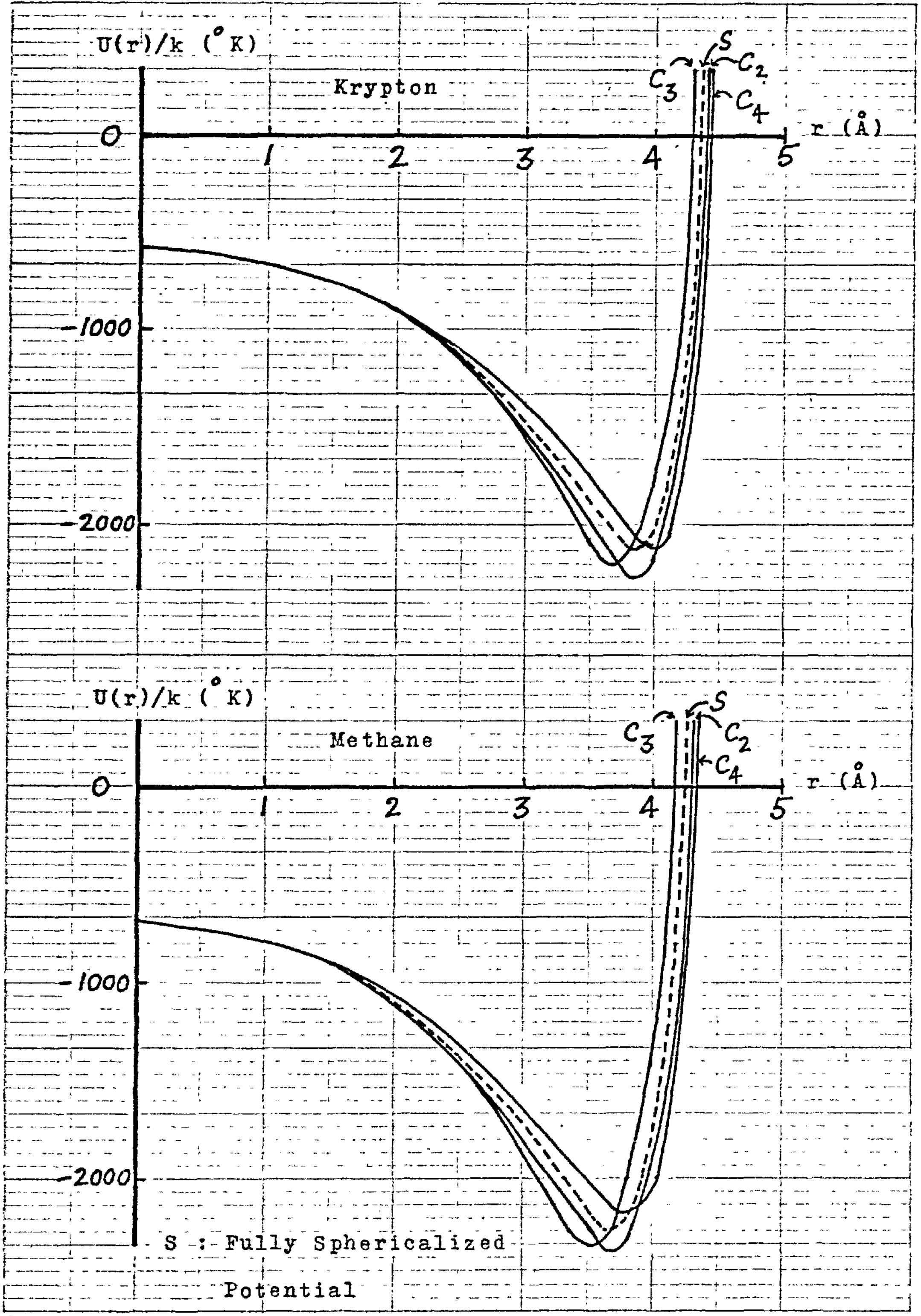
TABLE 6.5 LJD Parameters for the 72 O Anions

Parameter	Unit	Krypton	Methane
Λ^*/k	degs.K.	18325	17748
a	Å	7.066	7.066
σ	Å	3.153	3.263
v^*	$Å^3$	31.34	34.73
v_0	$Å^3$	249.5	249.5

TABLE 6.6 LJD Parameters for the 72 O Anions and 8 (Na,Ca) Cations

Parameter	Unit	Krypton	Methane
Λ^*/k	degs.K.	19934	19304
a	Å	7.010	7.010
σ	Å	3.114	3.224
v^*	$Å^3$	30.20	33.49
v_0	$Å^3$	243.6	243.6

FIGURE 6.4 Sphericalized Potential for Linde 5A



6.4 SORBATE-SORBATE INTERACTIONS

For the cases of sorption of krypton and methane in Linde 5A it is reasonable to assume that the sorbate-sorbate interactions are pairwise additive. The Lennard-Jones (12,6) potential of the form (6.3.1) was chosen for these interactions. The interaction parameters used were: $\varepsilon/k = 158^{\circ}$ and 148.2° K, $\sigma = 3.597$ and 3.817 Å, for krypton and methane, respectively. These values are based on experimental measurements of the second virial coefficients. (Hirschfelder et al. 1954a, Barker & Leonard 1964)

It may be of interest to note that in using the Lennard-Jones potential with the above empirical constants the dispersion effects which involve higher multipole interactions are partially taken into account. Strictly speaking, the Lennard-Jones potential should be used only in studying molecular systems in the gas phase. It is not expected to be a good approximation for a dense phase of highly polar molecules. In such circumstances the molecular interactions cannot be accurately represented by pairwise additive potential functions. As for the subsequent use in statistical mechanical calculations of the sorption of non-polar sorbate molecules in zeolite, however, the present simplification should not introduce any appreciable error. At least it can be expected that the possible inaccuracy in this case is much less than that of the previous estimates for sorbate-sorbent interaction energy. The primary reason for using the Lennard-Jones potential here is certainly one of mathematical convenience.

6.5 BACKGROUND POTENTIAL

A general expression can be derived for the potential of a reference sorbate molecule interacting with a system of identical molecules that are randomly distributed with a uniform density in the infinite region surrounding a spherical space to which the reference molecule is confined. This result can then be used to estimate the 'background potential' due to the presence of molecules and atoms outside the shells of 8(Na,Ca) cations and 72 O anions forming the wall of a sorption cavity. This cavity wall is regarded here as the immediate environment of the subsystem, and thus do not directly contribute to the 'background potential' of interest. For definiteness the interaction potential between the reference molecule and a 'background' molecule is chosen to be of the Lennard-Jones (12,6) form as given by (6.3.1).

The interaction potential between the reference molecule located at a distance r from the cavity centre and all the randomly distributed molecules outside the spherical space of radius a is given by (Figure 6.5)

$$\psi(r) = 8\pi\varepsilon\rho \int_a^\infty dx \int_0^\pi d\theta \; \left[F^2(x,\theta) - F(x,\theta) \right] x^2 \sin\theta \quad (6.5.1)$$

where $F(x,\theta) = \sigma^6/(r^2+x^2- rx\cos\theta)^3, \quad (r<a),$

ε and σ are the relevant Lennard-Jones parameters,

and ρ is the number density of the 'background' molecules.

The integration with respect to θ is over the volume elements each constituted of an infinitesimal circular ring any diameter of which subtends a parametric angle 2θ at the cavity centre. Also, the straight line passing through the reference molecule and the cavity centre is normal to the plane of the infinitesimal ring. In consequence every point of this ring is at the same distance x from the cavity centre. The integration with respect to x is over the infinitesimal spherical shells, any representative one of which is of radius x and is formed by the previous integration over θ .

By integrating by parts it is easy to show that (6.5.1) leads to

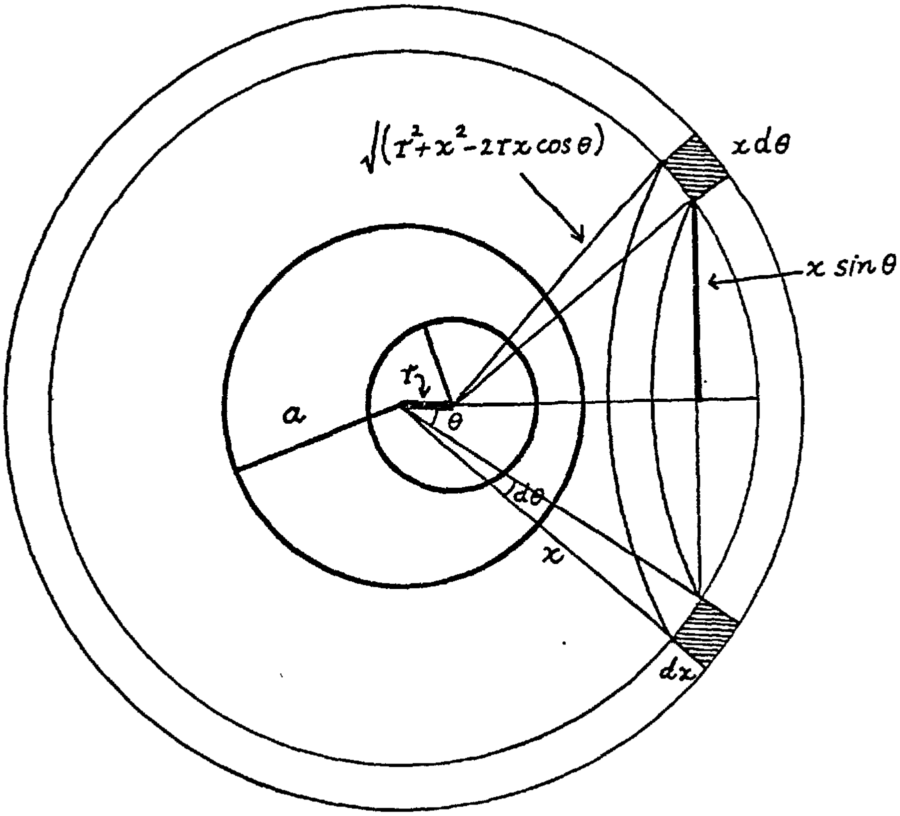
$$\psi(r) = \frac{16\pi}{3}\rho^{*}\varepsilon\left[\frac{1+9y+12.6y^{2}+3y^{3}}{3a^{*^{9}}(1-y)^{9}} - \frac{1}{a^{*^{3}}(1-y)^{3}}\right] \qquad (6.5.2)$$

where $y = (r/a)^2$. The 'reduced' quantities are defined by $a^{*} = a/\sigma$, $r^{*} = r/a$, $\rho^{*} = \rho\sigma^{3}$, and $\psi^{*}(r) = \psi/\rho^{*}\varepsilon$.

A slightly variant form of (6.5.2) has been given by Barrer & Stuart (1959) and by Barrer & Reucroft (1960). The reduced potential $\psi^{*}(r)$ was calculated at various values of the parameter a^{*}. These results are presented in Figure 6.6.

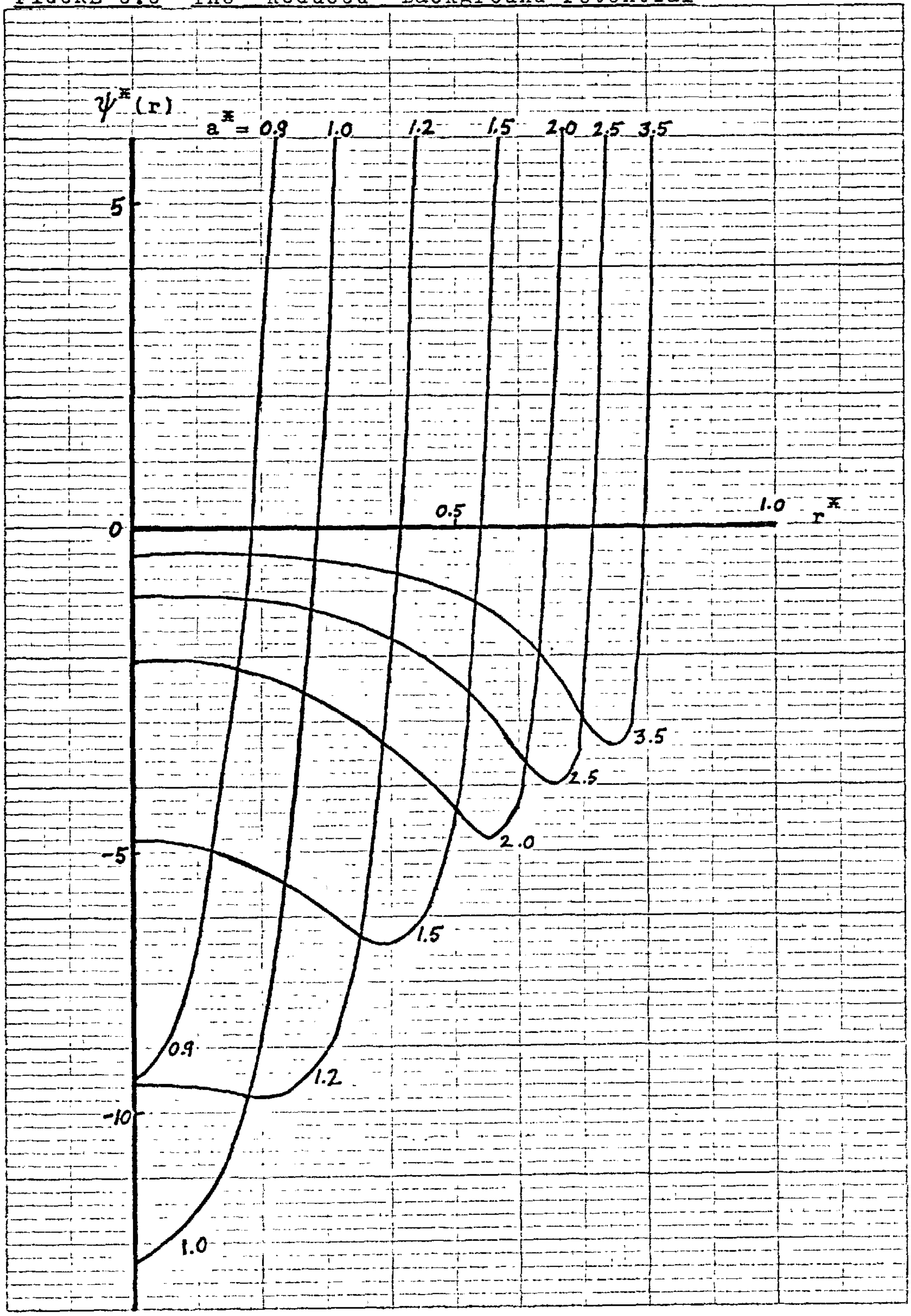
It is observed that the magnitude of $-\psi^{*}(r)$ near the cavity centre decreases gradually as a^{*} increases. In the case of sorption of krypton and methane in Linde 5A at saturation, the appropriate parameters for $\psi(r)$ are: $a^{*} \sim 2.5$, $\rho^{*} \sim 1$, and $\varepsilon/k \sim 200$ °K. Accordingly the contribution from 'background potential' to the total sorbate-sorbent and sorbate-sorbate interactions is expected to be only about 10 %.

FIGURE 6.5 Integrations of the 'Background Potential'



This means that at moderate sorbate concentration, to a fair approximation, the configurational energy of a subsystem is simply the sum of sorbate-sorbate interactions within the single cavity concerned and the interactions of these sorbate molecules with their immediate environment already described. In Section 9.2 this fact will be further discussed in relation to the assumption of quasi-independence of the subsystems.

FIGURE 6.6 The 'Reduced' Background Potential



CHAPTER 7

RESULTS FOR THE SUBSYSTEMS

7.1 ANALYTICAL RESULTS

Quantitative studies of the statistical mechanics of a subsystem with one or two molecules in the spherically symmetric potential field of a zeolite sorption cavity can be conveniently achieved by means of analytic methods together with some standard techniques of numerical analysis. The choice of the relevant parameters for the sorption of krypton and methane in Linde 5A has already been considered in Chapter 6. The Lennard-Jones & Devonshire potentials, with the contributions from the 72 O anions and 8 (Na,Ca) cations fully sphericalized, will be used to represent the sorbate-sorbent interactions. The sorbate-sorbate interaction potentials are assumed to be of the Lennard-Jones (12,6) form. By performing the Simpson's rule integrations on a digital computer, various statistical thermodynamic quantities of interest can be calculated from the following analytical expressions.

(a) One Molecule in a Subsystem

The configuration integral for this sorbate molecule is given by

$$Q(1,T) = 4\pi \int_0^a \exp\left[-U(r)/kT\right] r^2 \, dr \qquad (7.1.1)$$

where $U(r) = U_{LJD}(r)$ as given by (6.3.3).

As a consequence

$$\frac{\partial}{\partial T} Q(1,T) = 4\pi \int_0^a \frac{U(r)}{kT^2} \exp\left[-U(r)/kT\right] r^2 \, dr \qquad (7.1.2)$$

and

$$\frac{\partial^2}{\partial T^2} Q(1,T) = 4\pi \int_0^a \frac{U(r)}{kT^2}\left[\frac{U(r)}{kT^2} - \frac{2}{T}\right] \exp\left[-U(r)/kT\right] r^2 \, dr \qquad (7.1.3)$$

(b) Two Identical Molecules in a Subsystem

The configuration integral concerned is

$$Q(2,T) = 8\pi^2 \int_0^a dr_1 \int_0^a dr_2 \int_0^\pi d\theta \, \exp\left[-U(\underset{\sim}{r}_1, \underset{\sim}{r}_2)/kT\right] \cdot r_1^2 r_2^2 \sin\theta \qquad (7.1.4)$$

where $U(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = U_{LJD}(r_1) + U_{LJD}(r_2) + u_{LJ}(r_{12})$,

$U_{LJD}(r_i)$ $(i = 1,2)$ is given by (6.3.3),

$u_{LJ}(r_{12})$ is given by (6.3.1),

r_1 and r_2 are the magnitudes of the vectors $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$

from the cavity centre to the two molecules,

θ is the angle between the vectors $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$,

and r_{12} is the intermolecular distance, which is given by

$$r_{12} = (r_1^2 + r_2^2 - 2r_1r_2 \cos\theta)^{\frac{1}{2}} .$$

It follows that

$$\frac{\partial}{\partial T} Q(2,T) = 8\pi^2 \int_0^a dr_1 \int_0^a dr_2 \int_0^\pi d\theta \; \frac{U(\underset{\sim}{r}_1,\underset{\sim}{r}_2)}{kT^2} \cdot \quad (7.1.5)$$

$$\exp\left[-U(\underset{\sim}{r}_1,\underset{\sim}{r}_2)/kT\right] \, r_1^2 r_2^2 \sin\theta$$

and

$$\frac{\partial}{\partial T^2} Q(2,T) = 8\pi^2 \int_0^a dr_1 \int_0^a dr_2 \int_0^\pi d\theta \; \frac{U(\underset{\sim}{r}_1,\underset{\sim}{r}_2)}{kT^2} \left[\frac{U(\underset{\sim}{r}_1,\underset{\sim}{r}_2)}{kT^2} - \frac{2}{T}\right] \quad (7.1.6)$$

$$\exp\left[-U(\underset{\sim}{r}_1,\underset{\sim}{r}_2)/kT\right] \, r_1^2 r_2^2 \sin\theta$$

(c) Three Identical Molecules in a Subsystem

An analytical expression for the configuration integral of three identical sorbate molecules in the spherical potential field is

$$Q(3,T) = 8\pi^2 \int_0^a dr_1 \int_0^a dr_2 \int_0^a dr_3 \int_0^{\pi} d\theta_{12} \int_0^{\pi} d\theta_{13} \int_0^{2\pi} d\phi \tag{7.1.7}$$

$$\cdot \exp\left[-U(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3)/kT\right] r_1^2 r_2^2 r_3^2 \sin\theta_{12} \sin\theta_{13}$$

where

$$U(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) = \sum_{i=1}^{3} U_{LJD}(r_i) + \sum_{i=1}^{3} \sum_{j<i} u_{LJ}(r_{ij}) \quad ,$$

r_1, r_2 and r_3 are the magnitudes of vectors $\underset{\sim}{r}_1$, $\underset{\sim}{r}_2$ and $\underset{\sim}{r}_3$ from cavity centre to the three molecules labelled by 1, 2 and 3, respectively,

θ_{ij} is the angle between two vectors $\underset{\sim}{r}_i$ and $\underset{\sim}{r}_j$, $(i\neq j;\ i,j=1,2,3)$,

and ϕ is the angle that the vector $\underset{\sim}{r}_1$ makes with the plane of $\underset{\sim}{r}_2$ and $\underset{\sim}{r}_3$.

It is easy to show that ϕ is related to θ_{23} by

$$\cos\theta_{23} = \cos\theta_{12}\cos\theta_{13} - \sin\theta_{12}\sin\theta_{13}\cos\phi \quad .$$

Likewise expressions for $\frac{\partial}{\partial T} Q(3,T)$ and $\frac{\partial^2}{\partial T^2} Q(3,T)$ can be written as finite integrals with respect to the variables r_1, r_2, r_3, θ_{12}, θ_{13}, and ϕ . However, as the integral in (7.1.7) is 6-dimensional, the Simpson's rule integration is inevitably time-consuming, and in practice was not found to give any satisfactory result within a reasonable limit of computing time, On the other hand, it appears that the Monte Carlo methods can in general give much more reliable estimates in the cases of three of more sorbate molecules in a subsystem. These alternatives will be considered in the subsequent sections.

(d) Statistical Thermodynamic Quantities

When the configuration integral Q(n,T) and its first two partial derivatives with respect to T are known, statistical thermodynamic functions of interest can be evaluated by using the following standard formulae:

$$A(n,T) = -kT\left[\ln \frac{Q(n,T)}{n!} - \frac{3}{2}\ln\Lambda\right] \qquad (7.1.8)$$

$$u(n,T) = kT^2 \frac{\partial}{\partial T}\ln Q(n,T) - \frac{3}{2}nkT \qquad (7.1.9)$$

$$s(n,T) = \frac{1}{T}\left[u(n,T) - A(n,T)\right] \qquad (7.1.10)$$

and

$$C(n,T) = kT^2\left[\frac{\partial}{\partial T^2}\ln Q(n,T) - \frac{2}{T}\frac{\partial}{\partial T}\ln Q(n,T)\right] - \frac{3}{2}nk \qquad (7.1.11)$$

where n is the number of identical molecules in a cavity.

It is useful to define the configurational thermodynamic functions (subscript cf) by the followings:

$$A_{cf}(n,T) = A(n,T) - \frac{3}{2}nkT\ln\Lambda \qquad (7.1.12)$$

$$u_{cf}(n,T) = u(n,T) - \frac{3}{2}nkT \qquad (7.1.13)$$

$$s_{cf}(n,T) = s(n,T) - \frac{3}{2}nk(1 - \ln\Lambda) \qquad (7.1.14)$$

and

$$C_{cf}(n,T) = C(n,T) - \frac{3}{2}nk \qquad (7.1.15)$$

(e) Details of Simpson's Rule Integration

In evaluating the integrals characterizing two identical molecules in a subsystem, efficiency of the Simpson's rule integration on the computer was improved by

(1) Using the symmetry properties of the integrands with respect to the interchange of molecular coordinates,

(2) Storing the required values of $\sin\theta$ and $\cos\theta$ at the beginning of each Program-execution,

(3) Using the Taylor's series expansion to approximate the factor $\exp(-U/kT)$ for small values of the exponent,

and (4) Reducing the ranges of integration with respect to r_1 and r_2, and thereby ignoring the contribution from configurations with very high potential energy near the cavity wall.

For one sorbate molecule in a cavity the calculation was performed with respect to 1000 - 10000 quadratures, and for two molecules in a cavity with respect to 40 - 100 quadratures for each dimension of the integral. Results for statistical thermodynamic quantities of krypton and methane in Linde 5A are presented in Figures 7.1 - 7.5.

FIGURE 7.1 Configurational Free Energy of One Sorbate Molecule in a Linde 5A Cavity

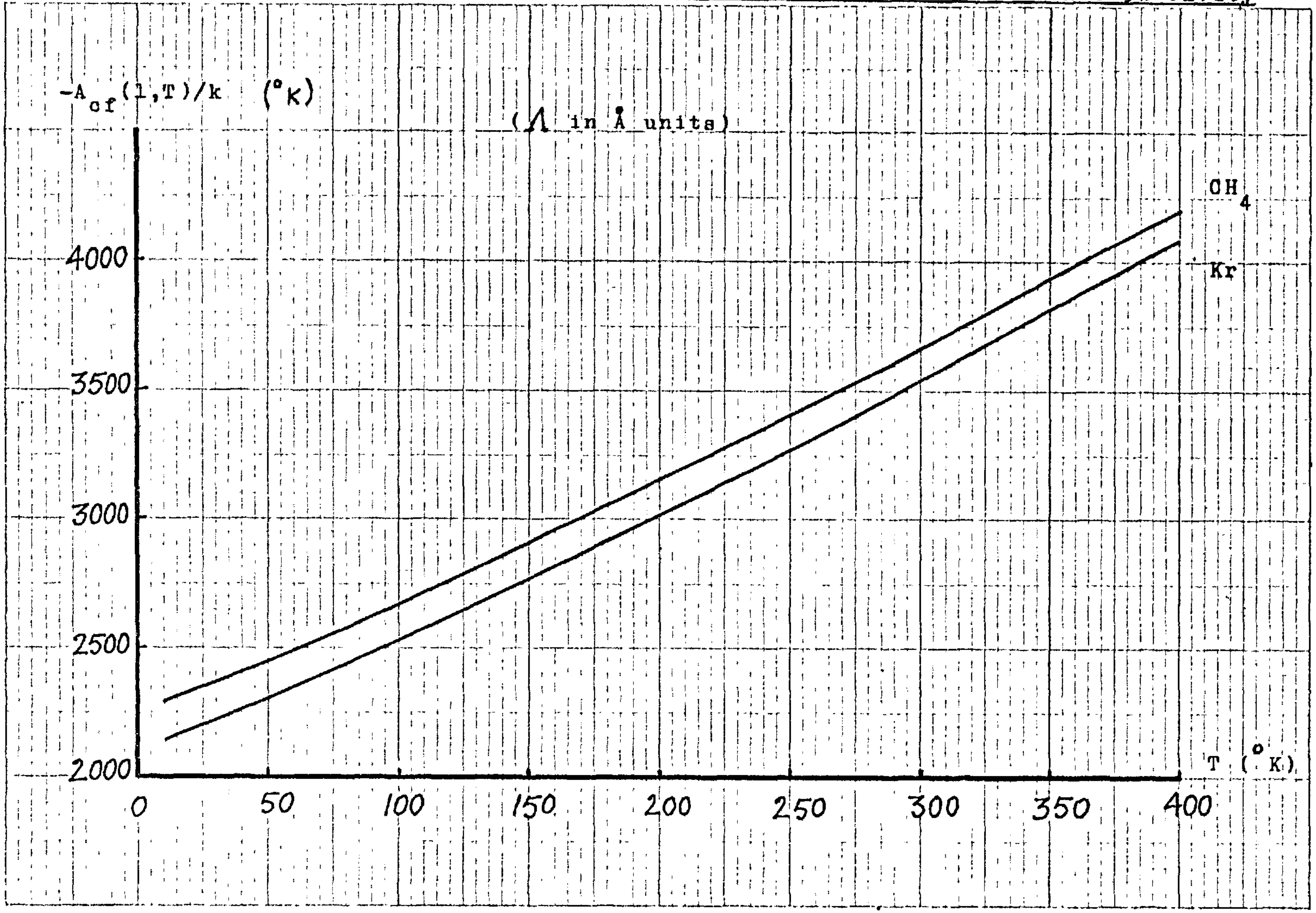


FIGURE 7.2 Configurational Free Energy of Two Sorbate Molecules in a Linde 5A Cavity

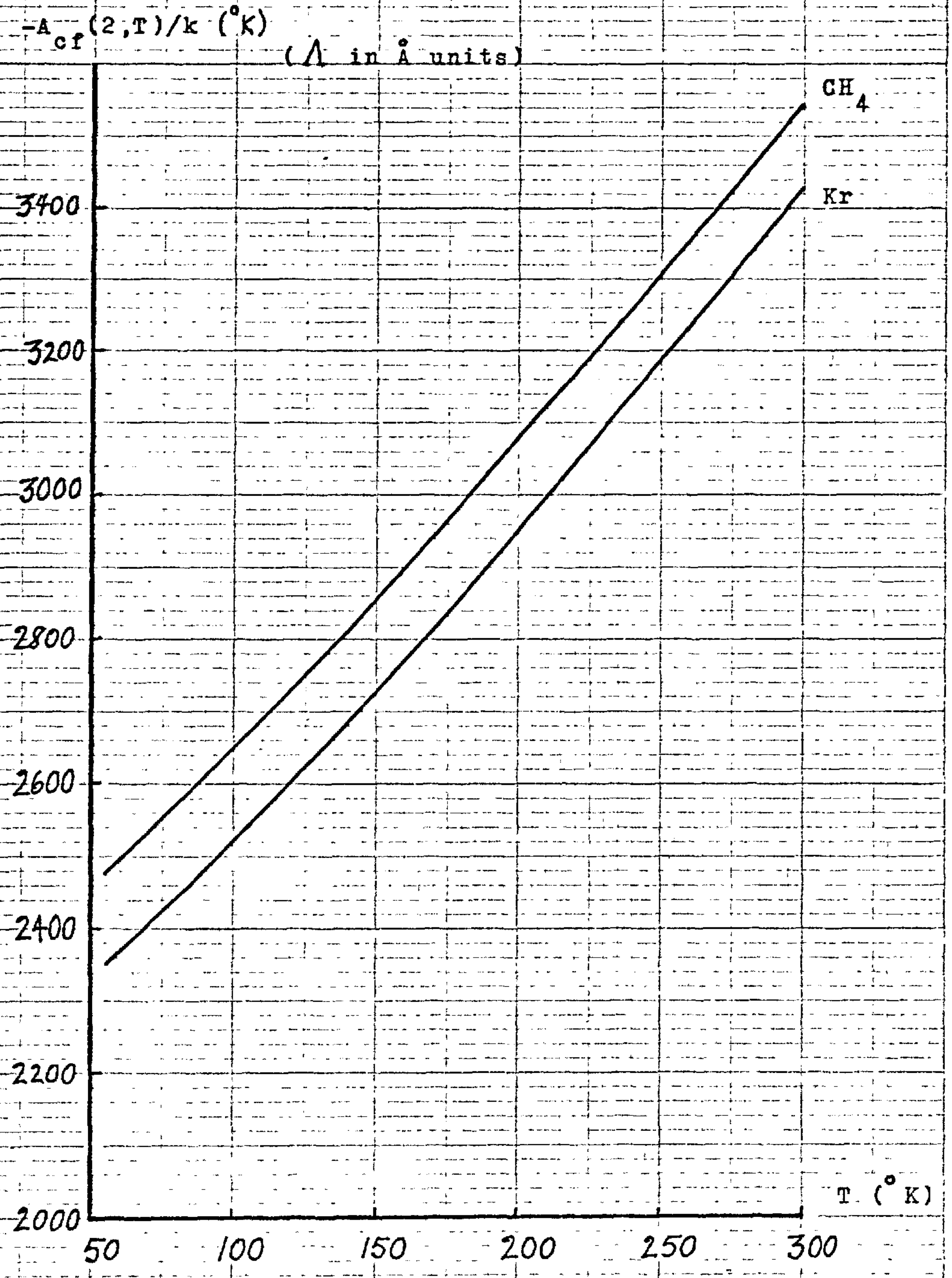


FIGURE 7.3 Internal Energy of One and Two Sorbate Molecules in a Linde 5A Cavity

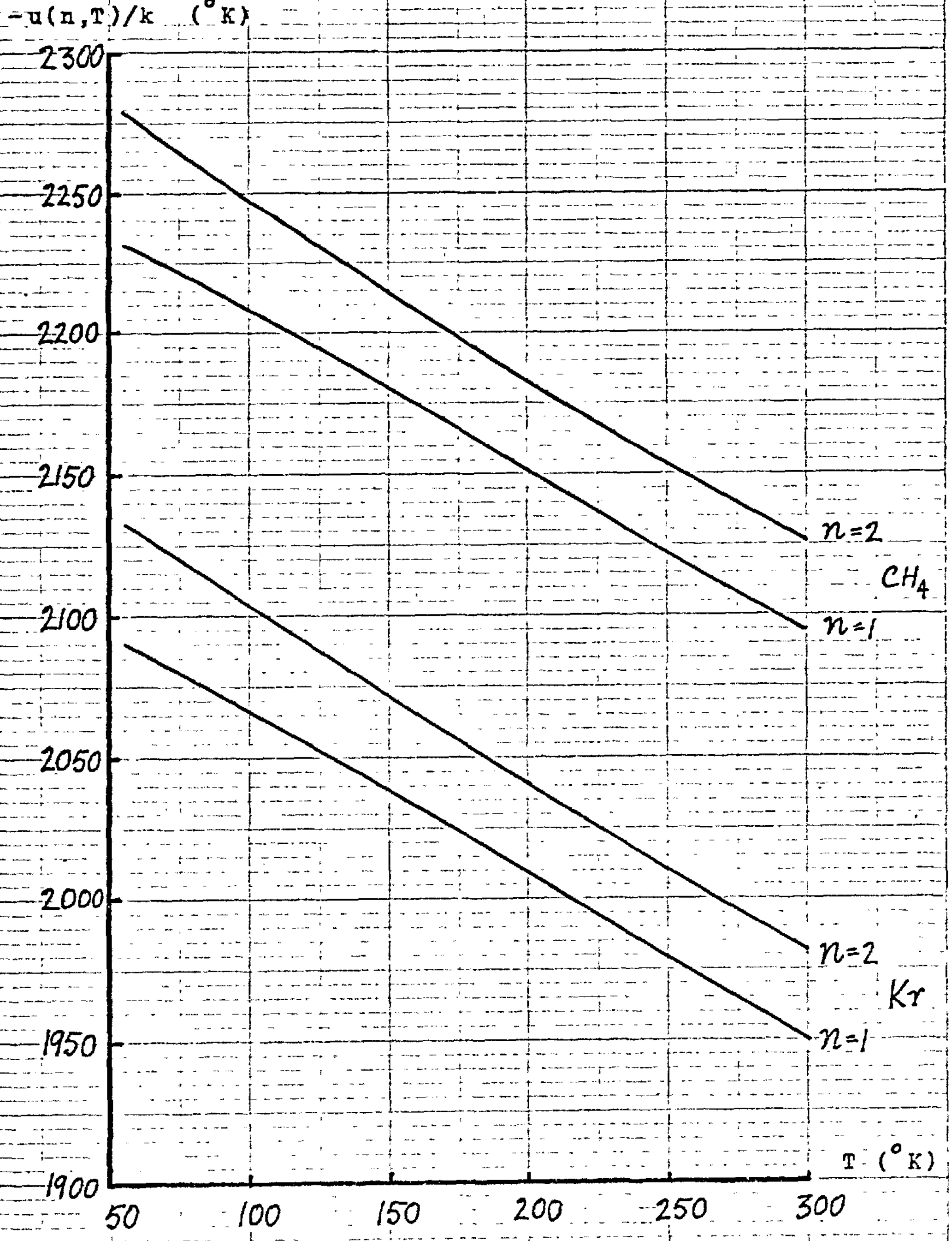


FIGURE 7.4 Configurational Heat Capacity of One Sorbate Molecule in a Linde 5A Cavity

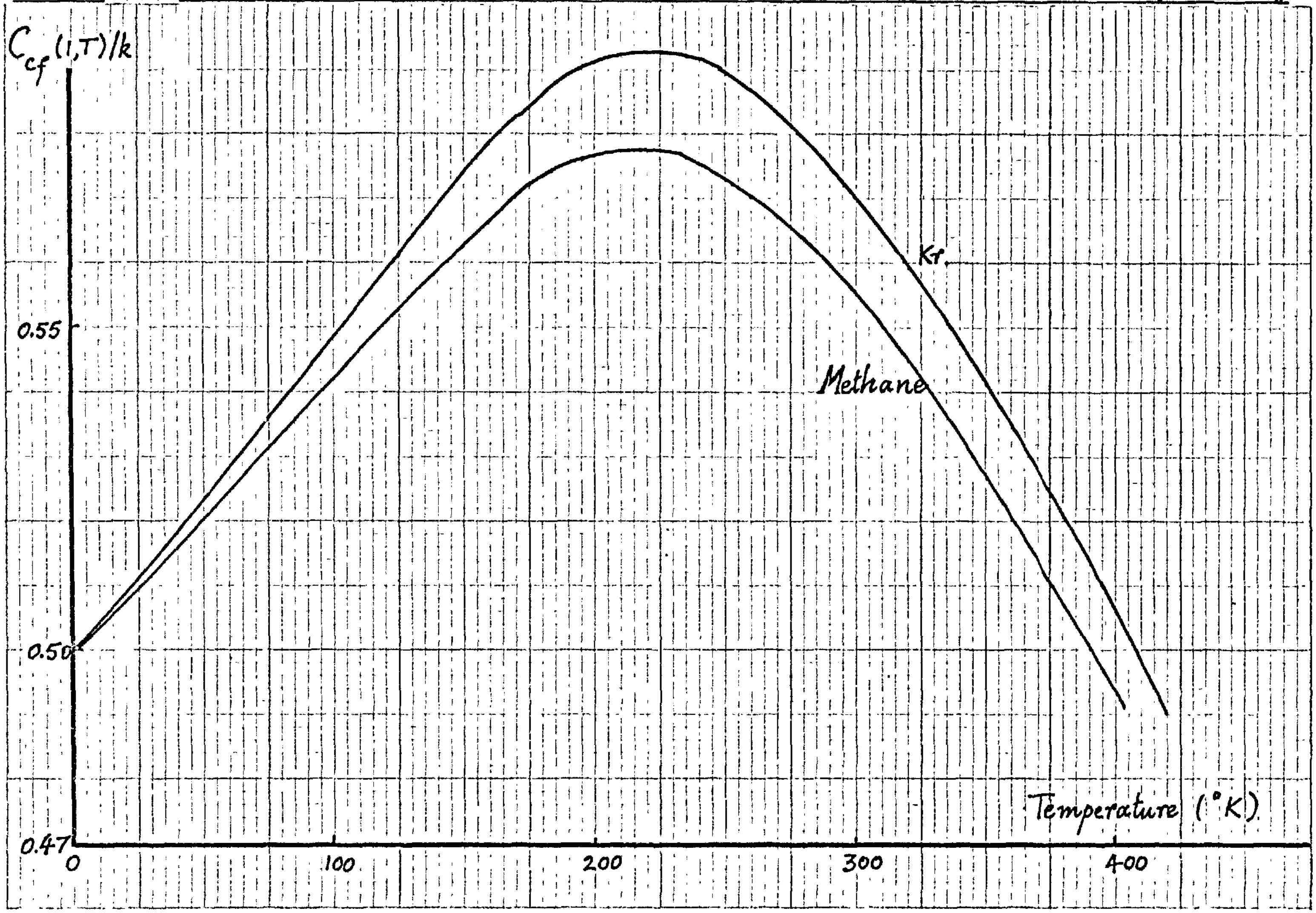
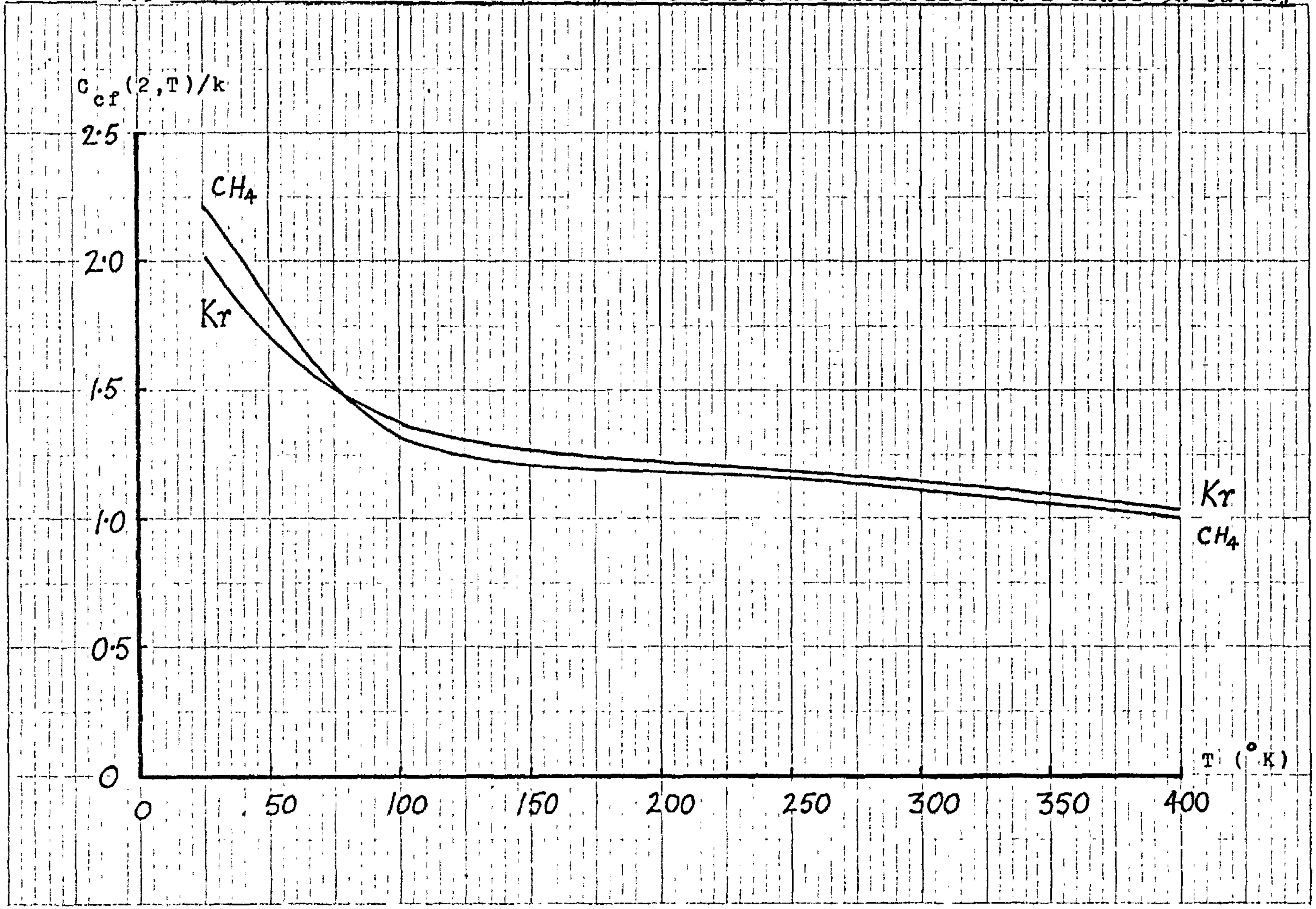


FIGURE 7.5 Configurational Heat Capacity of Two Sorbate Molecules in a Linde 5A Cavity



7.2 SIMPLE MONTE CARLO RESULTS

The canonical partition functions for specific sorption systems of n molecules ($n \leqslant 5$) and their partial derivatives with respect to temperature were calculated by using the simple Monte Carlo methods. Following the computational techniques described in Section 5.3, some mathematical expectations of multidimensional integrals of interest were estimated from the arithmetic means of integrand values calculated for a large number of trial sets of molecular configurations. For such a purpose, however, it is clear that the point density distribution of randomly chosen configuration sets in the 3n-dimensional configuration space had to be rectangularly uniform. In practice the required distribution was efficiently generated on the computer by applying the method of independent random trials introduced in Section 5.4. The detail of the computation is on the whole quite straightforward.

As regards computer-programming mention should be made of the following important points. Special care was taken in choosing a way to nest together the various cycle-settings, since in general even a slight modification in this could effectively save much valuable computing time. In particular it can be expected that the evaluation of each interaction potential with respect to a specified set of molecular configurations tends to be very time-consuming. So this step was arranged to be outside the computing cycle inside which the integrand was evaluated at a number of temperatures. Superficially this method should be very advantageous in that the configuration integrals and their derivatives could be evaluated for a large number of temperatures without having to increase proportionately the length of computing time. In reality, however, it is clear that fluctuations of the resulting estimates for a particular integral at different temperatures do correlate, and thereby systematic errors can be introduced. To obtain the most reliable estimates within limited computing time, therefore, an optimum number of temperatures for which each integral was evaluated by means of a single sequence of random configuration sets had to be chosen rather carefully. In this connection a detailed study of fluctuations in the quantities being estimated with respect to the number of trial configuration sets could give much useful information. More reliability was subsequently obtained by using the techniques just described in conjunction with other independent methods which do not imply the same type of correlation.

The sequence of pseudo-random numbers generated by the computer was of course identical in each Program-execution. So in order to minimize any systematic error that would be caused by subsequent correlation of the sampling procedures in separate computations, an arbitrarily chosen length of the sequence was generated and rejected at the beginning of each Program-execution, before this sequence was used to determine the sets of random molecular configurations. At convenient stages in the computation similar rejections of arbitrarily chosen lengths of the sequence currently generated were also effected whenever these seemed desirable.

Efficiency of the calculation was found to be much improved by using appropriately chosen hard-core cut-offs in the potential functions concerned as a means of reducing variance of the estimates. In dealing with the sorption of krypton and methane in Linde 5A, the cut-offs chosen for the Lennard-Jones & Devonshire potentials were at 4.6 - 4.8 Å and 4.5 - 4.7 Å from the cavity centre, and those for the Lennard-Jones potentials between like molecules at 3.1 - 3.4 and 3.2 - 3.6 Å, respectively.

Typical numbers of the trial configuration sets in these computations were 40,000 - 80,000 for $n = 1$, 2 or 3, and 20,000 - 40,000 for $n = 4$ or 5. Fluctuations of each estimate were carefully studied; and in general the convergence was found to be very reasonable. An attempt was also made to estimate $Q(6,T)$ and $Q(7,T)$, but because of the rather slow rates of convergence in these cases no satisfactory result was obtained. For practical reasons the case of $n = 5$ appears to be the upper limit of available capacity of the computer used. As expected, estimates for $Q(2,T)$ and their derivatives are in good agreement with the results previously obtained by the Simpson's rule integration. Thus the reliability and usefulness of the technique of independent random trials with appropriate variance reduction have been demonstrated.

Monte Carlo calculations of Q(n,T) and their partial derivatives with respect to temperature, where n = 2, 3 and 4, were also carried out by using the method of stochastic sequence as described in Section 5.3 to generate the sequence of trial configuration sets. Again the computation was fairly straightforward, and similar attention was also paid to the manner in which the most efficient programming was effected. The results are in accordance with those previously obtained by applying the method of independent random trials. Accordingly the mutual consistency of these computational techniques has been checked.

As pointed out in Section 5.4, when the method of stochastic sequence is used with interactions involving hard-core cut-off potential functions, it is necessary to know numerical values of the relevant Q_n^o explicitly. The configuration integral Q_1^o for one hard-sphere molecule of diameter σ in a spherical cavity of radius a and of effective wall thickness σ' is clearly just the accessible volume Δ' of that cavity, which is given by

$$\Delta' = \frac{4}{3}\pi R^3 \qquad (7.2.1)$$

where $R = a - \sigma'$ is the free radius of the cavity. Also an elementary geometrical consideration leads to the following result for Q_2^o : (Appendix 1)

$$Q_2^o = \pi^2\left(\frac{16}{9} R^6 - \frac{16}{9} R^3\sigma^3 + R^2\sigma^4 - \frac{1}{18}\sigma^6\right) \qquad (7.2.2)$$

Analytical expressions for Q_n^o with $n > 2$, on the other hand, involve complicated multidimensional integrals which cannot be easily partitioned into directly integrable parts. So their numerical values were estimated on the computer by applying the method of independent random trials.

Generally speaking, fluctuations, and hence the rate of convergence, of estimates resulting from the method of random trials and from the method of stochastic sequences were found to be comparable. However, it turns out in practice that the latter method requires a careful study of the effects of changing initial configuration sets, which tends to make the necessary computation and analysis very tedious. For this reason, in the present work most of the numerical values for the canonical partition functions and their derivatives were obtained by means of the method of independent random trials. Typical fluctuation plots are shown in Figure 7.6.

At this stage statistical thermodynamic functions for specific subsystems with $n < 6$ could be derived from the above results by applying the appropriate formulae given in Section 7.1(d). These values are presented in Figures 7.7 - 7.14. Results for the cases when $n = 1$ and 2 are of course identical with those previously obtained by the Simpson's rule integrations. Results for $A(n,T)$, $u(n,T)$ and $s(n,T)$ with $n = 6$ and 7 were obtained by extrapolating the plots of known results up to $n = 5$ versus n. In the statistical thermodynamic calculation of Chapter 8, accurate results for $A_{cf}(n,T)$ ($n = 1$ to 7) will be needed. So these are presented in Tables 7.1 and 7.2.

FIGURE 7.6 Fluctuations of Simple Monte Carlo Estimates

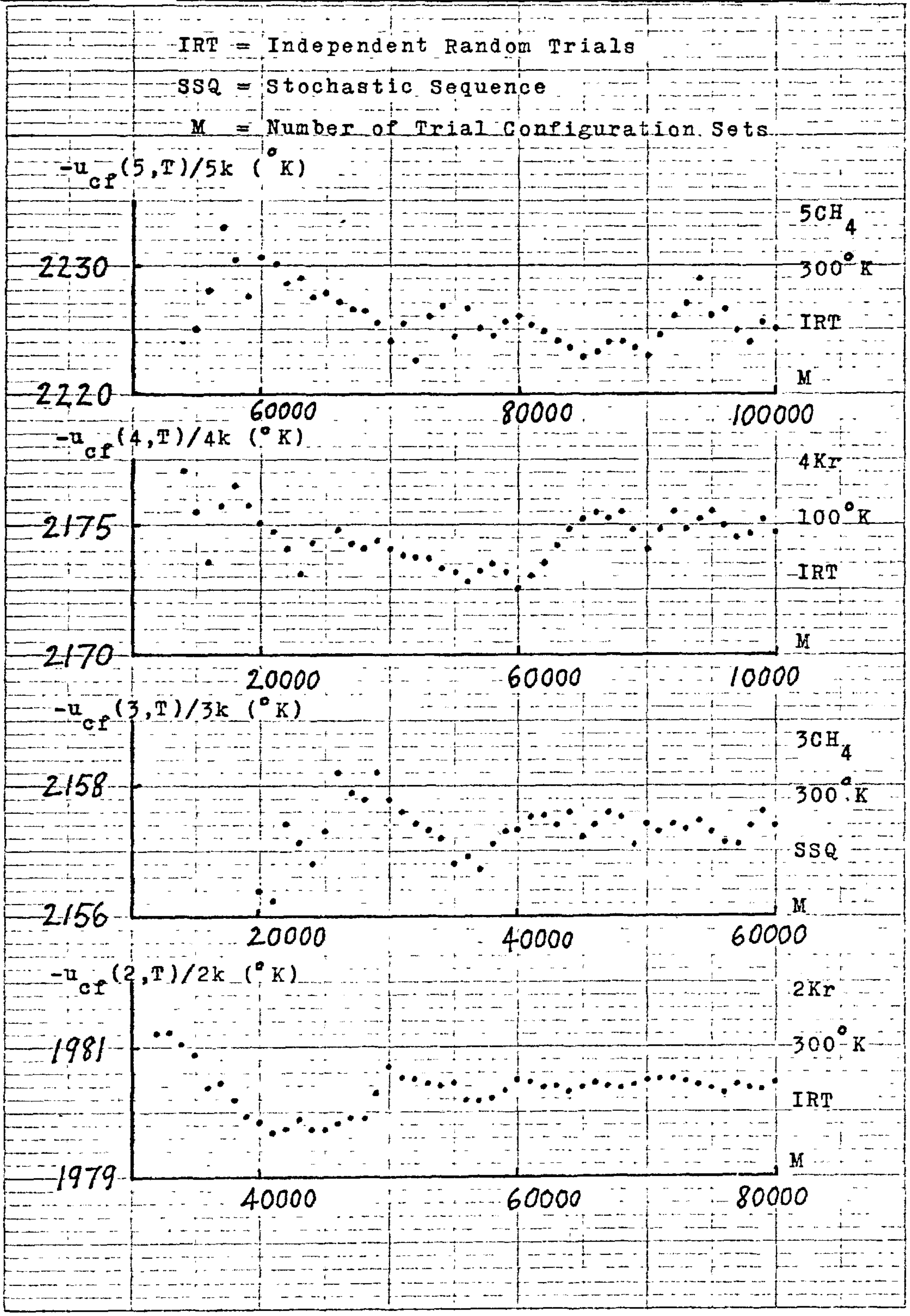


FIGURE 7.7 Free Energy of n Krypton Molecules in a Linde 5A Cavity

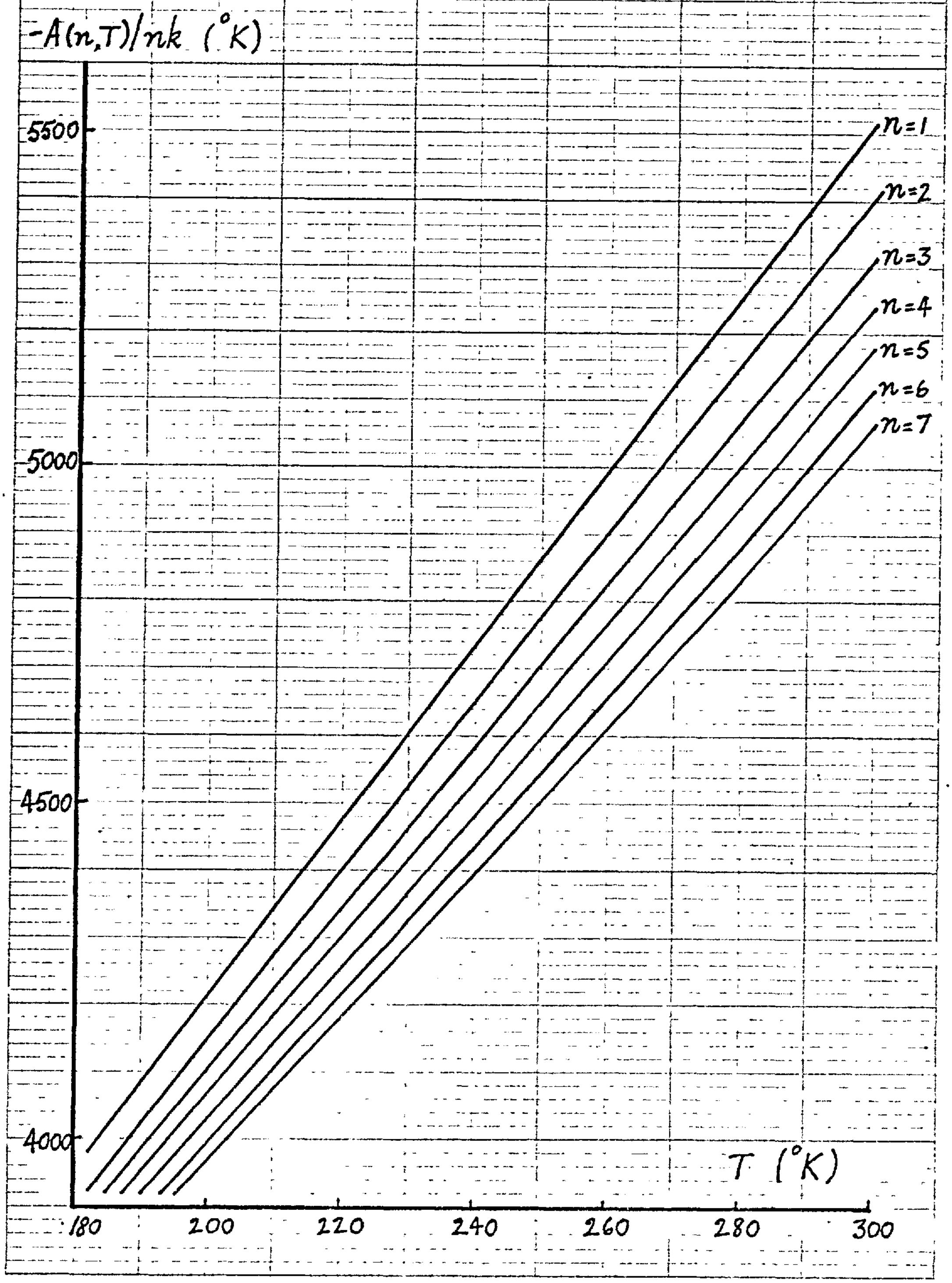


FIGURE 7.8 Free Energy of n Methane Molecules in a Linde 5A Cavity

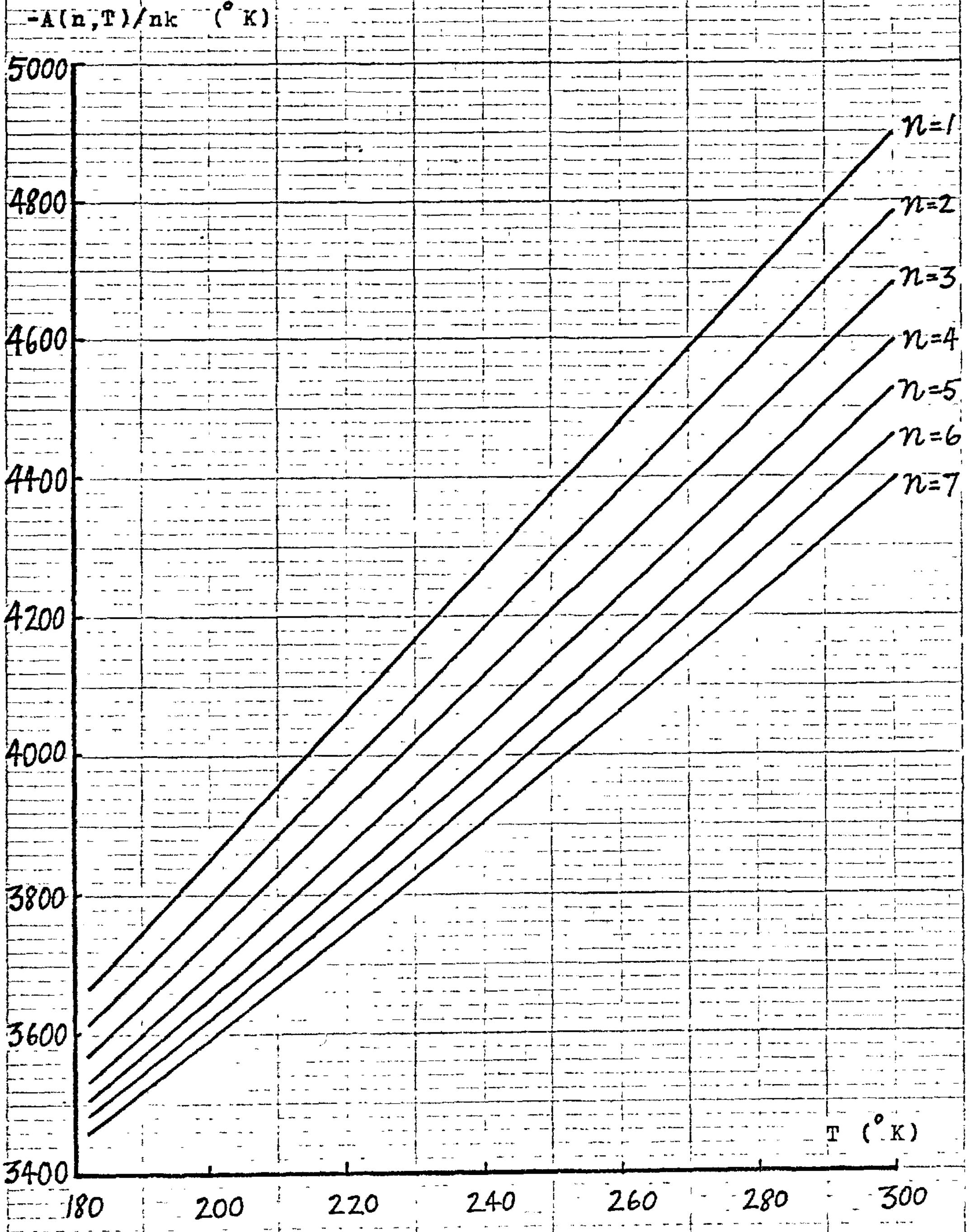


FIGURE 7.9 Internal Energy of n Krypton Molecules in a Linde 5A Cavity

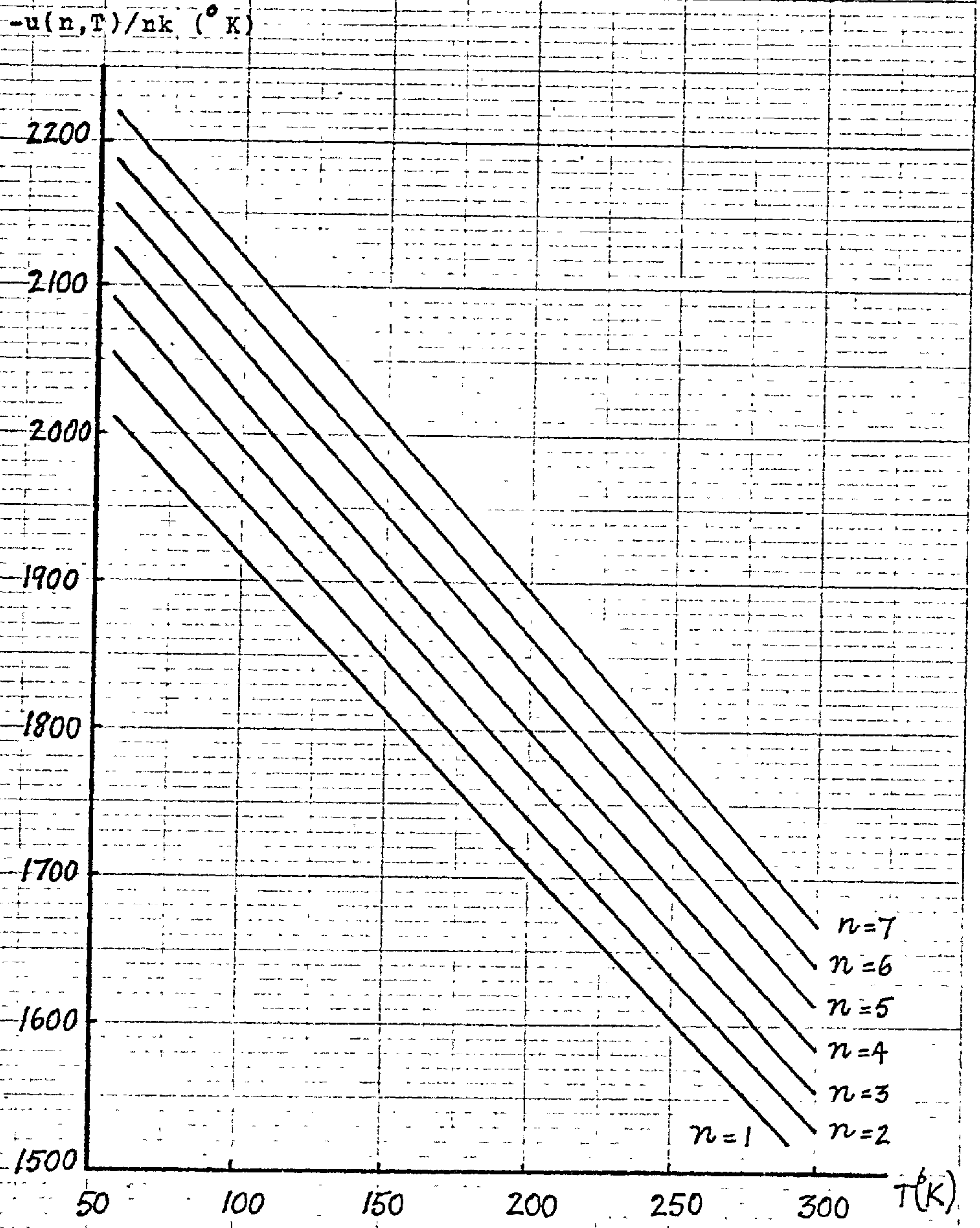


FIGURE 7.10 Internal Energy of n Methane Molecules in a Linde 5A Cavity

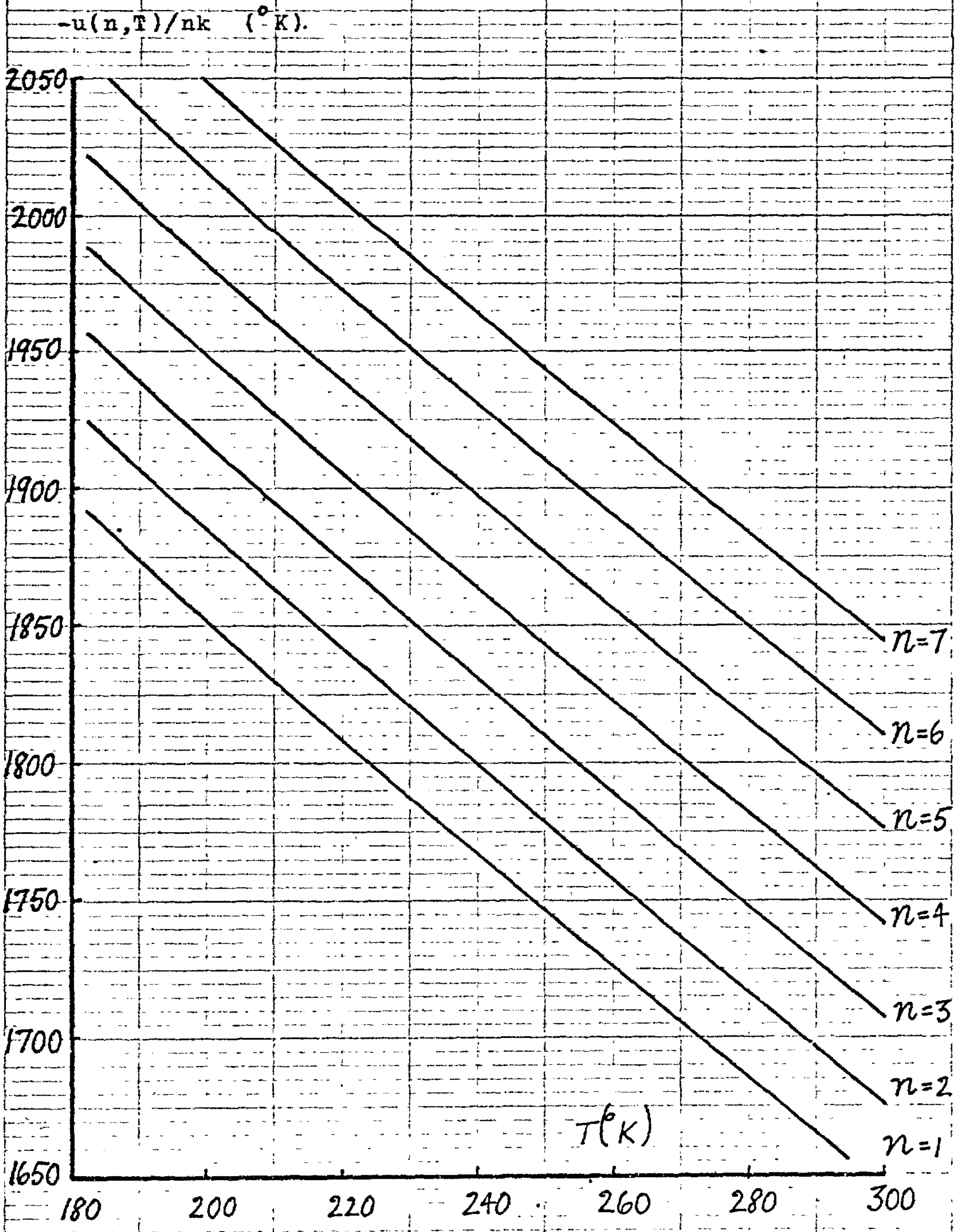


FIGURE 7.11 Entropy of n Krypton Molecules in a Linde 5A Cavity

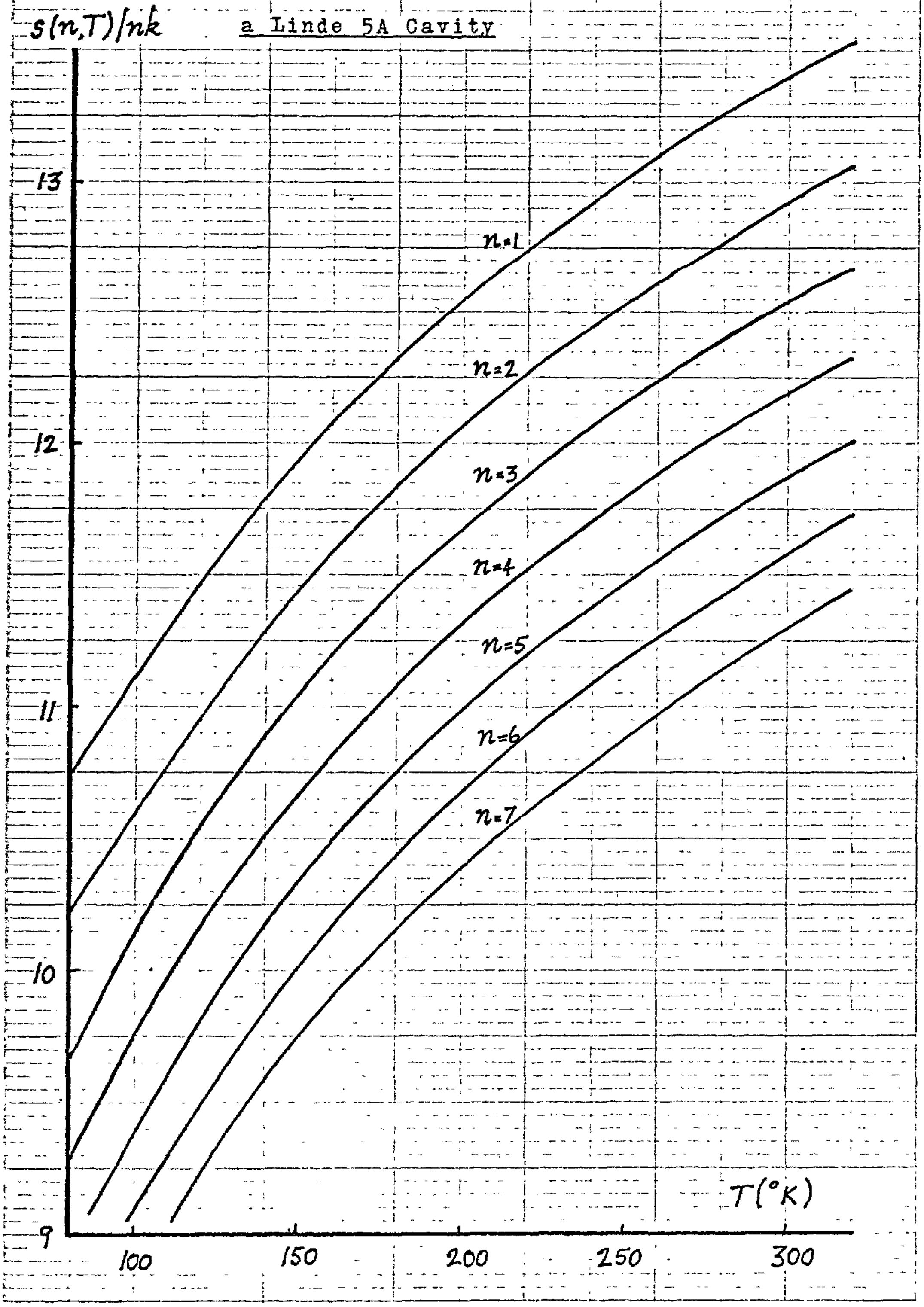


FIGURE 7.12 Entropy of n Methane molecules in a Linde 5A Cavity

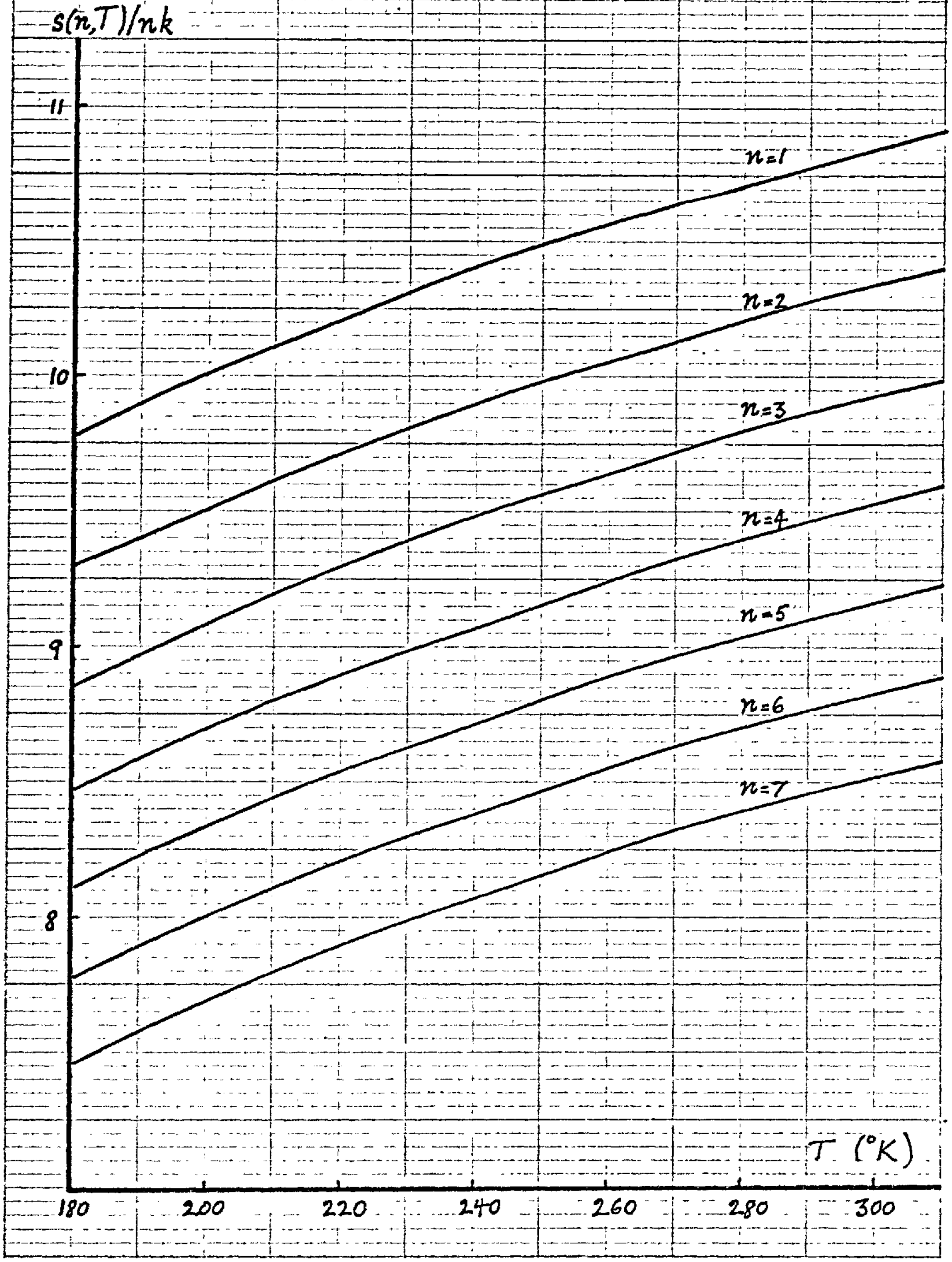


FIGURE 7.13 Heat Capacity of n Krypton Molecules in a Linde 5A Cavity

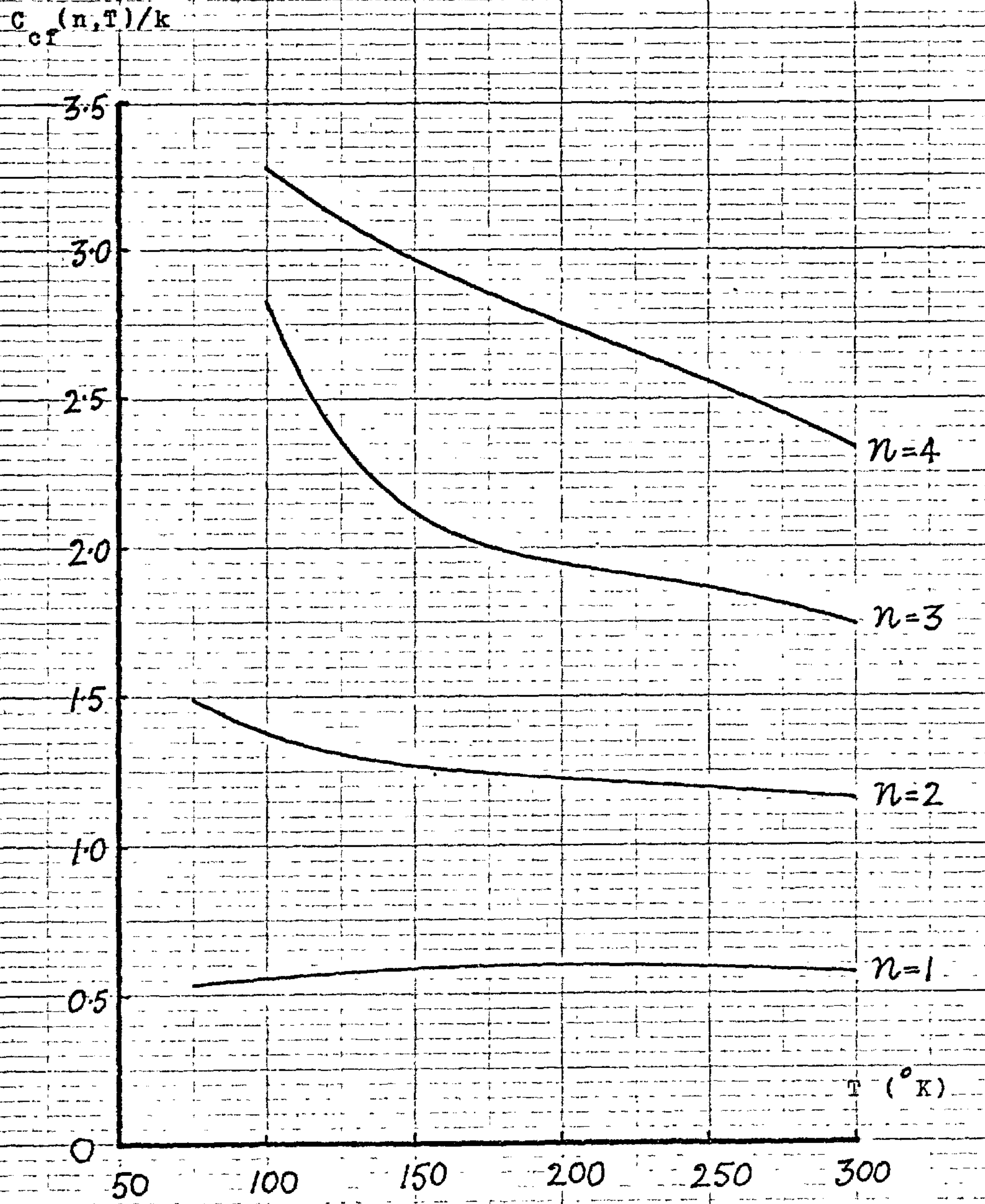


FIGURE 7.14 Heat Capacity of n Methane Molecules in a Linde 5A Cavity

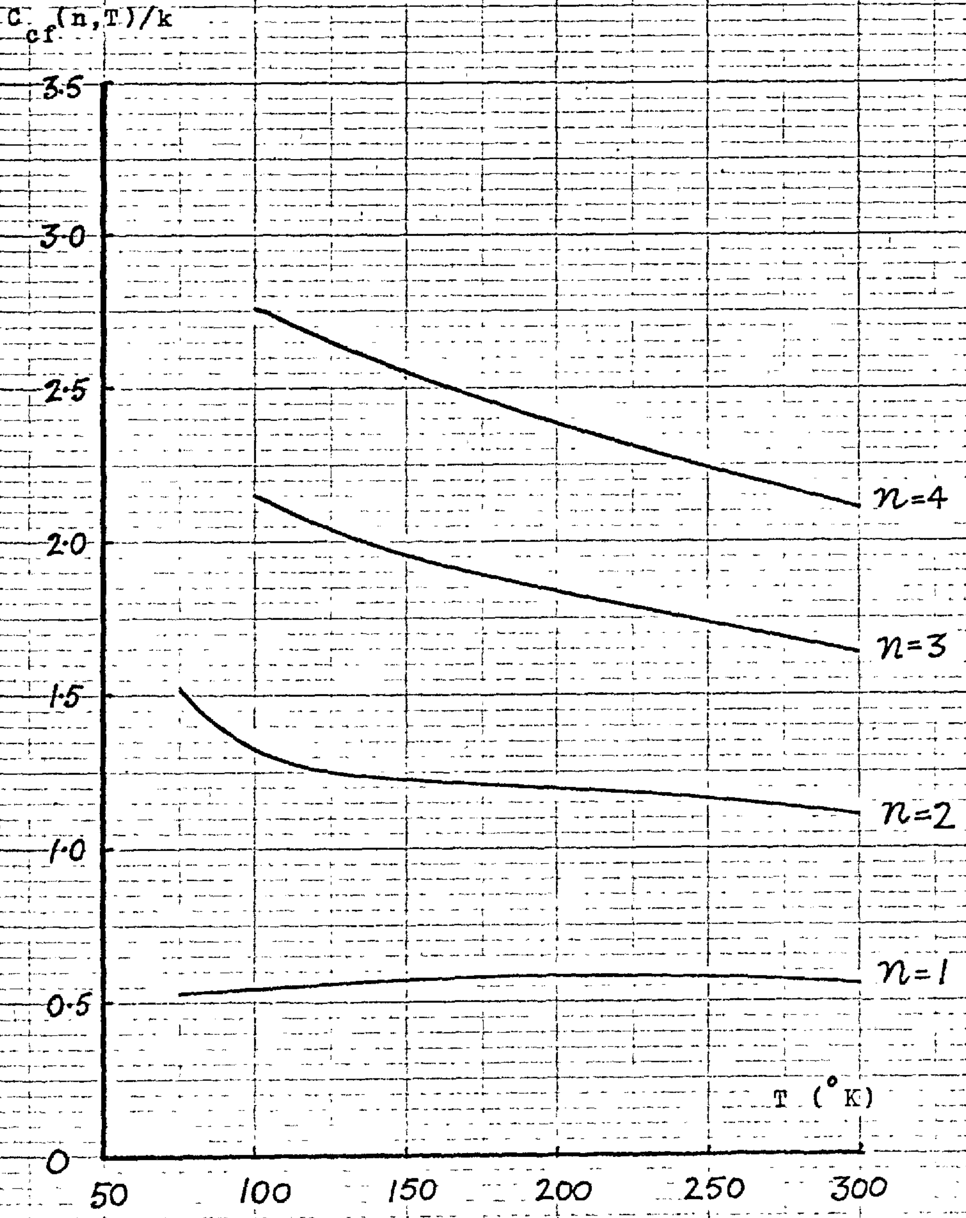


TABLE 7.1 Configurational Free Energy of Krypton in Linde 5A

T ($^\circ$K)	$-A_{cf}(n,T)/nk$ ($^\circ$K)(Λ in Å units)						
	n=1	n=2	n=3	n=4	n=5	n=6	n=7
300.00	3532.4	3420.6	3330.8	3255.3	3189.3	3130.0	3078.2
288.15	3470.1	3363.9	3278.7	3207.3	3145.4	3083.0	3032.5
273.15	3391.5	3292.5	3213.1	3147.0	3090.2	3029.7	2979.2
253.15	3287.6	3198.0	3126.4	3067.3	3017.2	2963.3	2922.0
233.15	3184.5	3104.4	3040.7	2988.6	2945.1	2899.5	2861.5
218.15	3107.9	3035.0	2977.2	2930.4	2891.5	2848.0	2814.3
194.65	2989.1	2927.4	2878.9	2840.5	2808.7	2776.5	2752.0
150.00	2768.3	2728.1	2697.6	2675.5	2655.5	2642.0	2631.5
100.00	2530.2	2515.1	2506.2	2502.9	2500.2	2500.0	2500.0

TABLE 7.2 Configurational Free Energy of Methane in Linde 5A

T ($^\circ$K)	$-A_{cf}(n,T)/nk$ ($^\circ$K)(Λ in Å units)						
	n=1	n=2	n=3	n=4	n=5	n=6	n=7
300.00	3657.3	3538.5	3443.4	3358.0	3286.0	3220.5	3159.0
288.15	3595.7	3482.9	3392.8	3312.0	3243.8	3180.0	3124.5
273.15	3518.1	3412.8	3329.0	3254.2	3189.5	3131.5	3082.5
253.15	3415.4	3320.1	3244.7	3177.8	3120.5	3071.5	3025.0
233.15	3313.5	3228.3	3161.3	3102.3	3054.0	3010.5	2970.0
218.15	3237.8	3160.2	3099.5	3046.3	3000.5	2964.0	2928.0
194.65	3120.4	3054.6	3003.8	2959.9	2924.5	2895.5	2868.5

7.3 RESULTS FROM IMPORTANCE SAMPLINGS AND OPTIMUM SAMPLINGS

It has been shown in Sections 5.5 - 5.7 how statistical thermodynamic parameters characterizing specific sorption subsystems could be calculated by using the techniques of importance sampling and optimum sampling. As applied to studying the sorption of krypton and methane in Linde 5A, these methods were found to be very efficient; and in general very accurate estimates of the quantities of interest could be obtained within a comparatively short computing time. However, it is clear from (5.6.1) and (5.7.1) that the partition functions themselves cannot be conveniently evaluated by such means, since these functions are implicit in the normalizing factors of relevant Markov transition probabilities. Indeed these methods can only give an estimate of the ratio of two integrals, such as the Boltzmann average defined by (5.5.2), but not the estimate of each of these. On the other hand, reasonably accurate values of the internal energy could easily be obtained by using the methods of importance sampling and optimum sampling even when the number of molecules in a subsystem is as high as 10.

Because of the temperature-dependence of the transition probabilities, there is undoubtedly a stringent limitation on the use of importance samplings and optimum samplings in regard to computing time. The primary object in employing these methods here is for improving the reliability of estimates previously obtained by other techniques which are less tedious. Following (3.3.7)

$C_{cf}(n,T)$ was estimated from fluctuations of the total configurational energy of the subsystem under investigation. Results for u(n,T) and $C_{cf}(n,T)$ for small n are in accordance with those already obtained in the last two sections. These are presented together in Figures 7.9, 7.10, 7.13 and 7.14. For subsequent use in Chapter 8 the most accurate values of $u_{cf}(n,T)$ obtained are given in Tables 7.3 and 7.4. Again, in these calculations it was found that studies of fluctuations with respect to the number of trial configuration sets could give valuable information concerning the reliability of various estimates. Typical plots of fluctuations are presented in Figure 7.15.

As remarked in Section 5.7, the Fosdick method of optimum sampling can most suitably be applied as an iteration procedure for increasing the reliability of Monte Carlo estimates. So this technique was used for the purpose of obtaining the values of the internal energy of specific subsystems to the maximum accuracy attainable, particularly when a subsystem contains more than 5 or 6 molecules. Some typical results are presented in Table 7.5. From this it may be observed that the internal energy per sorbate molecule does not vary significantly from $n = 1$ to $n = 10$. This is so because in the case of sorption of krypton and methane in Linde 5A the sorbate-sorbate interaction energy is relatively small. Also the approach of sorption saturation (at $n \sim 13$) is indicated by the fact that $-u_{cf}(n,T)/nk$ reaches its maximum value when $n = 8$ or 9.

FIGURE 7.15 Fluctuations of Monte Carlo Estimates

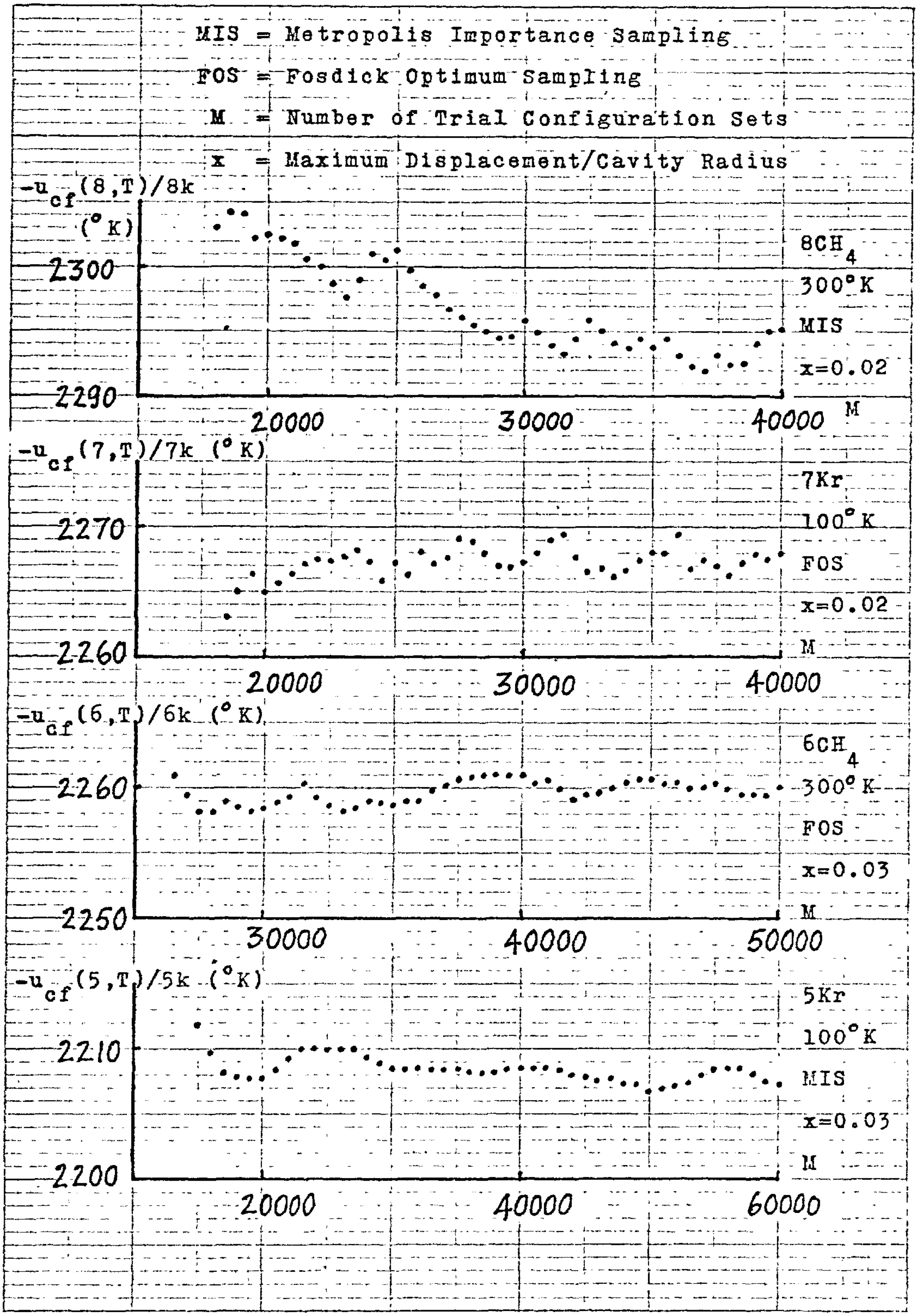


TABLE 7.3 Internal Energy of Krypton in Linde 5A

T (°K)	-u(n,T)/nk (° K)						
	n=1	n=2	n=3	n=4	n=5	n=6	n=7
300.00	1500.2	1530.4	1557.3	1586.5	1614.5	1642.8	1671.2
288.15	1524.8	1555.0	1582.0	1611.3	1640.5	1669.3	1698.1
273.15	1556.0	1586.3	1613.5	1642.9	1671.4	1700.3	1729.1
253.15	1597.7	1628.1	1655.7	1685.3	1715.0	1744.7	1774.2
233.15	1639.5	1670.2	1698.1	1728.2	1759.3	1790.6	1821.7
218.15	1670.9	1701.8	1730.1	1760.7	1792.9	1824.0	1854.6
194.65	1720.0	1751.4	1780.3	1812.0	1843.0	1873.7	1904.5
150.00	1813.1	1846.1	1877.3	1911.1	1943.3	1975.4	2008.1
100.00	1916.2	1953.5	1991.2	2024.7	2058.2	2088.5	2118.2

TABLE 7.4 Internal Energy of Methane in Linde 5A

T (°K)	-u(n,T)/nk (° K)						
	n=1	n=2	n=3	n=4	n=5	n=6	n=7
300.00	1644.4	1676.0	1707.3	1740.8	1776.2	1810.0	1844.6
288.15	1668.8	1700.4	1731.6	1765.0	1799.3	1833.8	1868.3
273.15	1699.7	1731.3	1762.4	1795.6	1830.4	1863.8	1897.8
253.15	1741.1	1772.8	1803.8	1836.7	1870.8	1904.5	1938.9
233.15	1782.6	1814.4	1845.5	1878.0	1911.6	1944.7	1978.8
218.15	1812.8	1845.8	1876.9	1909.2	1943.5	1976.3	2010.6
194.65	1862.5	1895.0	1926.4	1958.0	1993.3	2026.5	2060.5

TABLE 7.5 Accurate Results for $-u_{cf}(n,T)/nk$ (°K)

n	Kr in Linde 5A, 100°K	CH_4 in Linde 5A, 300°K
1	2066.16 ± 0.05	2094.35 ± 0.03
2	2103.5 ± 0.3	2126.0 ± 0.2
3	2141.2 ± 0.5	2157.3 ± 0.3
4	2174.7 ± 1.0	2190.8 ± 0.6
5	2208.2 ± 1.5	2226.0 ± 1.0
6	2238.5 ± 2.0	2260.1 ± 1.5
7	2268 ± 3	2294.6 ± 2
8	2286 ± 6	2295 ± 3
9	2212 ± 10	2208 ± 7
10	2191 ± 15	2189 ± 10

N.B. The results for n = 1 were obtained by the Simpson's rule integrations. The uncertainty limits given above are only a rough guide, and were obtained by studying fluctuations of the Monte Carlo estimates with respect to the numbers of trial configuration sets, which varied from 20,000 to 100,000.

7.4 EFFECTS OF EXCHANGEABLE CATIONS

Thus far only certain subsystems with fully sphericalized sorbate-sorbent interaction potentials have been considered. Monte Carlo calculations of statistical thermodynamic quantities were also attempted for the subsystems of krypton and methane in Linde 5A in which the 8 exchangeable cations of each sorption cavity were treated as discrete interaction centres. The total potential for any specific molecular configuration set, including the electrostatic effect, was calculated in the manner described in Sections 6.2 and 6.3. As before, all contributions from the 72 O anions were sphericalized.

To obtain any reasonable result in this case it is inevitable that a very substantial computing time will be required. Consequently, in practice only a few rough estimates for the cases of one and two molecules in a subsystem could be made within the available computing time. Nevertheless from these results it becomes evident that, in general, there is not a significant difference between the values of any statistical thermodynamic quantity as estimated for the two cases of partially and fully sphericalized potentials. More specifically the internal energy difference was found to be only about 1 %. (Table 7.6)

It may therefore be concluded that in so far as statistical thermodynamic functions are concerned the sphericalization is indeed a good approximation. At least it is quite adequate for the present purpose. On the other hand, in regard to certain behaviours of the subsystems at the molecular level, the results of the next section will indicate that the representation of sorbate-sorbent interactions by fully sphericalized potential functions may not in some respects be physically realistic. However, this contrast should not cause any surprise here, for it is a common knowledge of statistical thermodynamics that the magnitudes of many thermodynamic functions are quite insensitive to the detailed nature of the laws governing intermolecular forces. The quantitative study of the interaction potentials in Chapter 6 should in particular help to clarify some of the foregoing remarks.

TABLE 7.6 Effects Of Exchangeable Cations on $-u_{cf}(n,T)/nk$ (°K)

T (°K)	n	Kr in Linde 5A		CH_4 in Linde 5A	
		Discrete	Sphericzd.	Discrete	Sphericzd.
300.00	1	1973	1950.2	2119	2094.4
	2	2003	1980.4	2153	2126.0
273.15	1	1988	1965.7	2134	2109.4
	2	2018	1996.0	2168	2141.0
194.65	1	2034	2012.0	2179	2154.5
	2	2066	2043.4	2214	2187.0
150.00	1	2061	2038.1	2205	2180.0
	2	2094	2071.1	2241	2214.1
100.00	1	2089	2066.2	2232	2207.7
	2	2127	2103.5	2272	2245.9

7.5 PROBABILITY DISTRIBUTION FUNCTIONS OF A SUBSYSTEM

This section is devoted to a quantitative study of the degrees of localization of sorbate molecules within specific subsystems of krypton and methane in Linde 5A. In this connection the effects of exchangeable cations are of special interest. Owing to limited computing time available, however, it was possible to investigate in some detail only the cases of one and two sorbate molecules in a subsystem. Qualitatively speaking it is expected that the sorbate molecules in any subsystem which is not too densely occupied should spend most of their time in regions near the cavity wall, and in particular around the 8 (Na,Ca) cations. Nevertheless, because of the complex nature of sorbate-sorbent and sorbate-sorbate interactions, the exact manner and extent of such localization may not in reality be easy to visualize.

For the present interest each sorption cavity is regarded as an isothermal closed quasi-independent subsystem. Mathematically the primary object is to study the distribution density of the canonical ensemble which represents the statistical mechanical behaviour of any subsystem in the relevant configuration space. However, instead of mapping out every detail of the distribution, one is merely interested in obtaining certain integrals of the density function which would subsequently find the most natural physical interpretation. These integrals are in effect the various probability distribution functions of a specific sorption system, some of which will now be introduced.

(a) Localization on Cavity Wall

A distribution function $P_n^{(s)}(r)$ is defined by the requirement that $P_n^{(s)}(r)dr$ be the probability of finding any sorbate molecule within the range dr at a distance r from the cavity centre of a subsystem containing n identical molecules. This function is normalized to unity:

$$\int_0^a P_n^{(s)}(r)\ dr = 1 \qquad (7.5.1)$$

It is obvious that $P_n^{(s)}(r)$ is related to the detailed molecular description of the subsystem by

$$P_n^{(s)}(r)\ dr = \frac{\int_{\Delta_n(dr)} \exp\left[-U(\{n\})/kT\right]\ d(\{n\})}{Q(n,T)} \qquad (7.5.2)$$

Here $\Delta_n(dr)$ represents the integrated region of the 3n-dimensional configuration space, in which any point specified by the generalized coordinates $n = (\underset{\sim}{r}_1, \underset{\sim}{r}_2, .., \underset{\sim}{r}_n)$ satisfies at least one of the following n conditions:

$$r \leqslant r_i \leqslant r + dr \qquad (i = 1,2,..,n) \qquad (7.5.3)$$

where r_i is the magnitude of the vector $\underset{\sim}{r}_i$ from the cavity centre to the i th molecule.

For the subsystem of one molecule in a fully sphericalized sorbate-sorbent potential, the distribution function concerned is simply given by

$$P_1^{(s)}(r) = \frac{4\pi r^2 \exp\left[-U(r)/kT\right]}{Q(1,T)} \qquad (7.5.4)$$

Typical plots of $P_1^{(s)}(r)$ versus r are presented in Figure 7.16. The physical interpretation of these results is quite clear. The maximum of the distribution function for one krypton molecule in Linde 5A is at 3.87 A, which is of course the distance from the cell centre that gives the lowest energy value for the fully sphericalized potential shown in Figures 6.3 and 6.4. It should also be observed that the distribution function becomes more sharply peaked as the temperature decreases.

For more complicated cases, however, there appears to be no useful relation equivalent to (7.5.4). Thus in practice $P_n^{(s)}(r)$ was calculated by applying the Monte Carlo techniques. The 8 exchangeable cations of each sorption cavity were treated as discrete interaction centres, whereas all contributions from the 72 O anions remained sphericalized. The electrostatic induction effect of the cations were fully taken into account. On the whole the computation was very similar to that carried out in Section7.4. Again the methods of independent random trials and importance sampling were used.

In evaluating $P_n^{(s)}(r)$ by the method of independent random trials the computer was used to generate a histogram the quadratures of which represented the sums of values of the integrand in (7.5.2) with respect to intervals of 0.01 - 0.05 A for the parameter r. When the Metropolis method of importance sampling was applied, a histogram of the numbers of accepted configuration sets satisfying (7.5.3) was constructed. Certainly these procedures were very time-consuming, and in order to achieve any reasonable result 20,000 - 100,000 trial configuration sets were required. Results are presented in Figures 7.17 and 7.18.

Superficially the general features of these plots closely resemble those of Figure 7.16. Also there seems to be no basic difference as regards $P_n^{(s)}(r)$ in the cases of n = 1 and n = 2. However, the presence of irregularities and smaller peaks in some of these curves may be noted. For comparison values of $P_2^{(s)}(r)$ for a fully sphericalized sorbate-sorbent potential are also shown in Figure 7.19.

(b) Localization on Cations

To clarify further the nature of localization of the sorbate molecules in a subsystem, it is appropriate to introduce another distribution function $P_n^{(c)}(r)$. By definition $P_n^{(c)}(r)$ dr is the probability of finding a sorbate molecule in the range dr at a distance r from a chosen exchangeable cation of the subsystem containing n identical molecules. Again this distribution function is normalized to unity. Calculations of $P_n^{(c)}(r)$ were carried out on the computer by constructing histograms with 200 - 400 quadratures. Typical results are presented in Figures 7.20-7.25.

As expected, the cases of one and two molecules in a subsystem do not differ fundamentally in so far as $P_n^{(c)}(r)$ is concerned. This reflects the fact that when the subsystem contains only a few molecules sorbate-sorbent interactions are generally more significant than sorbate-sorbate interactions. Of course, when the subsystem is more densely packed, the situation is very complicated and the same conclusion may not apply.

In contrast, the subsystems with fully sphericalized sorbate-sorbent potentials and those with discrete cation contributions do show some marked differences as regards $P_n^{(c)}(r)$. Physically $P_n^{(c)}(r)$ is expected to be peaked at those values of r which are approximately the same as the distances from the reference point to surfaces of minimum potential surrounding each of the 8 exchangeable cations. Looking along the C_3 symmetry axis, one sees immediately that the four peaks should be roughly at distances of 3.5, 7.0, 8.0 and 10.0 Å from the chosen cation. The detailed nature of the localization is clearly demonstrated by the results in Figures 7.20 - 7.23.

Unlike those of $P_n^{(s)}(r)$, the plots of $P_n^{(c)}(r)$ versus r are quite complicated even for a subsystem with fully sphericalized sorbate-sorbent potential. Mathematically, it is not difficult to see how such a complexity could arise as a consequence of the lower symmetry now associated with each integrated region of the canonical ensemble distribution in the relevant configuration space. A simple geometrical consideration shows that the volume of an infinitesimal region between two concentric spherical surfaces, which contains all points at the same parametric distance r from any fixed point on the outer surface of the finite spherical shell with outer radius a and inner radius b, is equal to

$$\pi r a(1 - b^2/a^2)\, dr \quad \text{when} \quad a - b \leqslant r \leqslant a + b$$

$$\text{and } \pi r^2(2 - r/a)\, dr \quad \text{when} \begin{cases} 0 \leqslant r \leqslant a - b \\ a + b \leqslant r \leqslant 2a \end{cases}.$$

Following this it is now possible to understand more clearly the relationship between $P_1^{(s)}(r)$ and $P_n^{(c)}(r)$ as far as a fully sphericalized sorbate-sorbent potential is concerned. Figure 7.26 illustrates how some relatively simple forms of $P_1^{(s)}(r)$ could generally result in quite intricate functions for $P_1^{(c)}(r)$ even in the spherically symmetric case.

Physically, however, the fine structures of these plots appear to have no obvious molecular interpretation. So they will not be studied further.

(c) Intermolecular Separation

In order to study the extent of sorbate-sorbate interactions quantitatively, it is convenient to use a pair distribution function $P_n^{(2)}(r)$ normalized to unity. By definition $P_n^{(2)}(r)\, dr$ is the probability of finding any pair of n identical sorbate molecules $(n \geqslant 2)$ in a subsystem at a distance r apart. In practice only $P_2^{(2)}(r)$ could be studied satisfactorily within reasonable computing time. As in the previous cases, this function was evaluated on the computer by constructing suitable histograms. Typical results are presented in Figures 7.27 and 7.28.

From the general features of these plots it is observed that the sorbate molecules indeed tend to be attracted towards each other, especially at lower temperatures. However, because the sorbate-sorbate interactions are comparatively weak, the $P_2^{(2)}(r)$ versus r plots are not sharply peaked. Again the detailed feature of the distribution can be quite complicated.

In concluding this section it may be remarked that in general the nature of localization of the sorbate molecules within any specific subsystem can be properly understood only in quantitative terms. As regards the sorption of krypton and methane in Linde 5A many interesting results have emerged from the foregoing studies. In particular the variation in the degree of localization with respect to temperature has been noted. In sorption studies it is customary to think of the sorbed phase as a mobile two-dimensional fluid, or as localized molecules on definite sorption sites, with or without sorbate-sorbate interactions. The results of this section have shown how far such familiar concepts can correctly be applied in studying the sorption in zeolites.

FIGURE 7.16 Localization of One Kr Molecule on the Wall of a Sphericalized Linde 5A Cavity

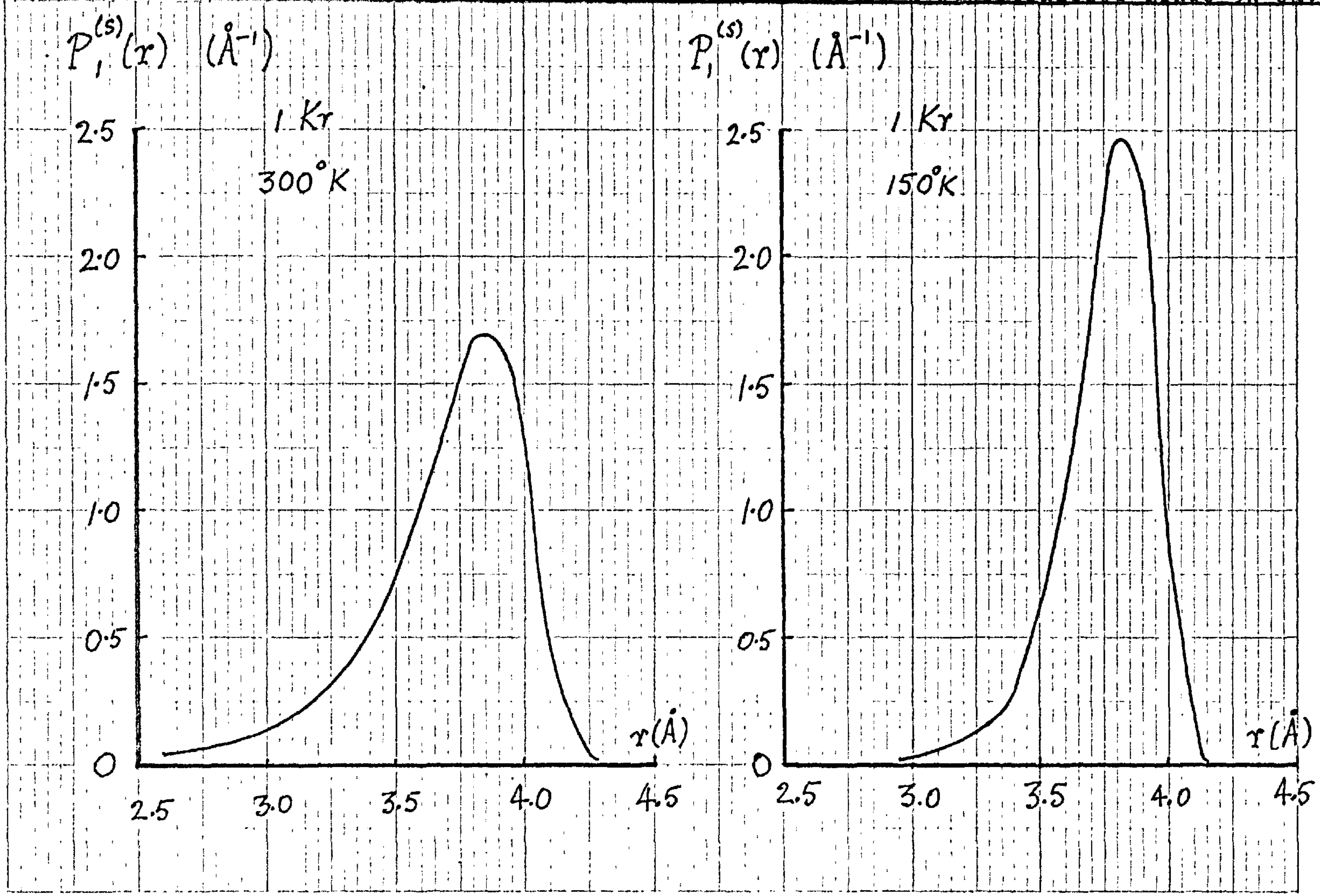


FIGURE 7.17 Localization of One Methane Molecule on the Wall of a Linde 5A Cavity with Discrete Cations

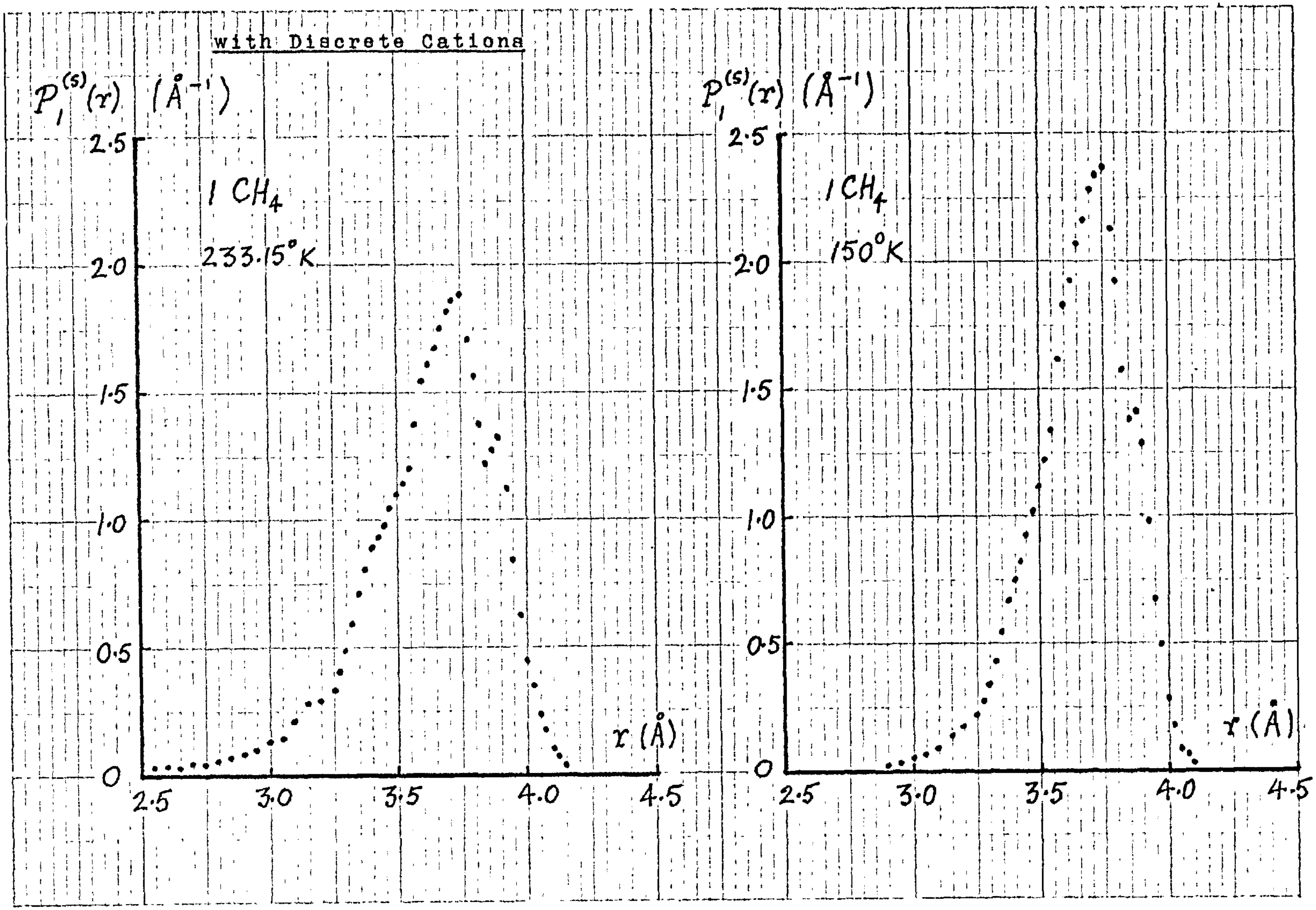


FIGURE 7.18 Localization of Two Methane Molecules on the Wall of a Linde 5A Cavity with discrete Cations

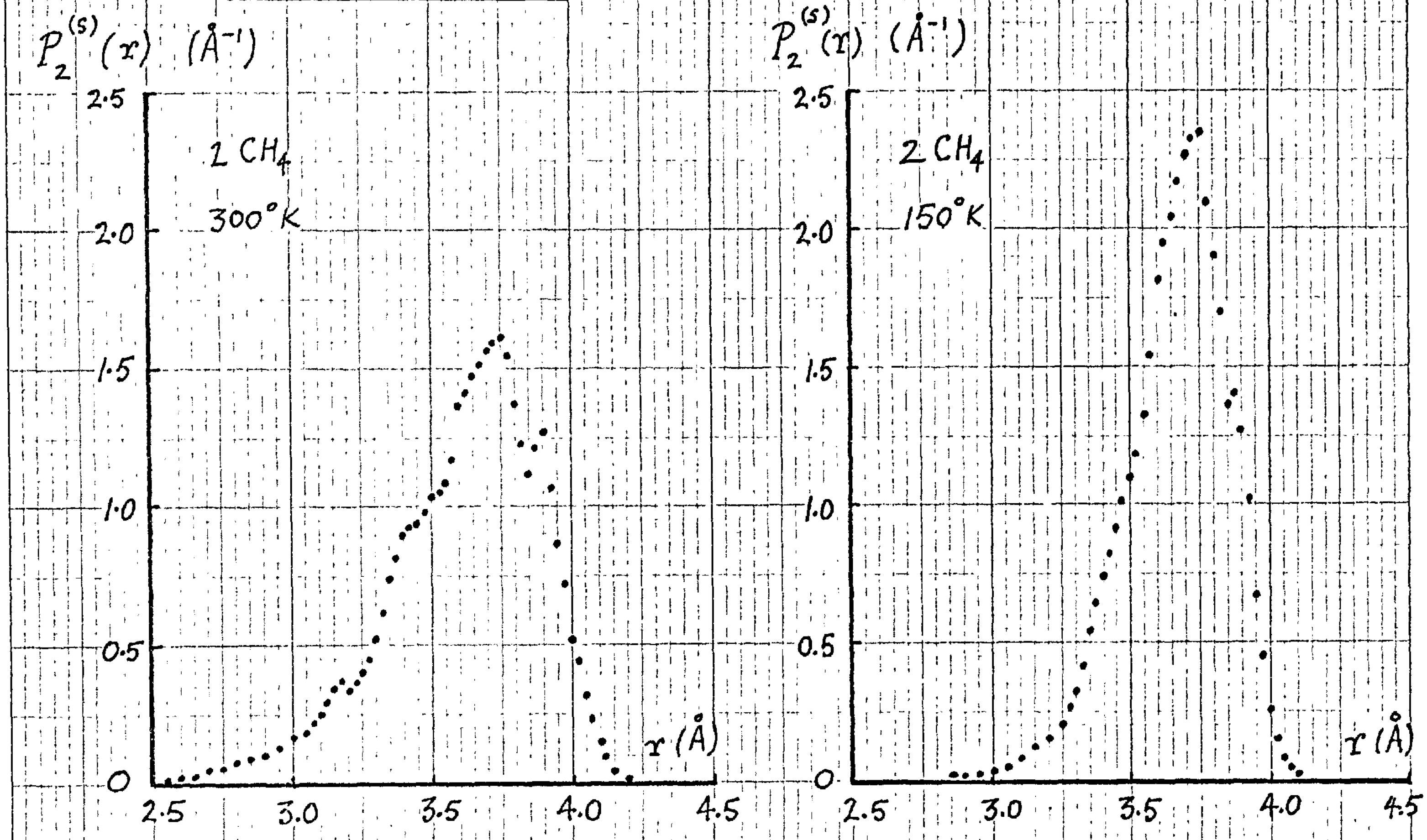


FIGURE 7.19 Localization of Two Methane Molecules on the Wall of a Sphericalized Linde 5A Cavity

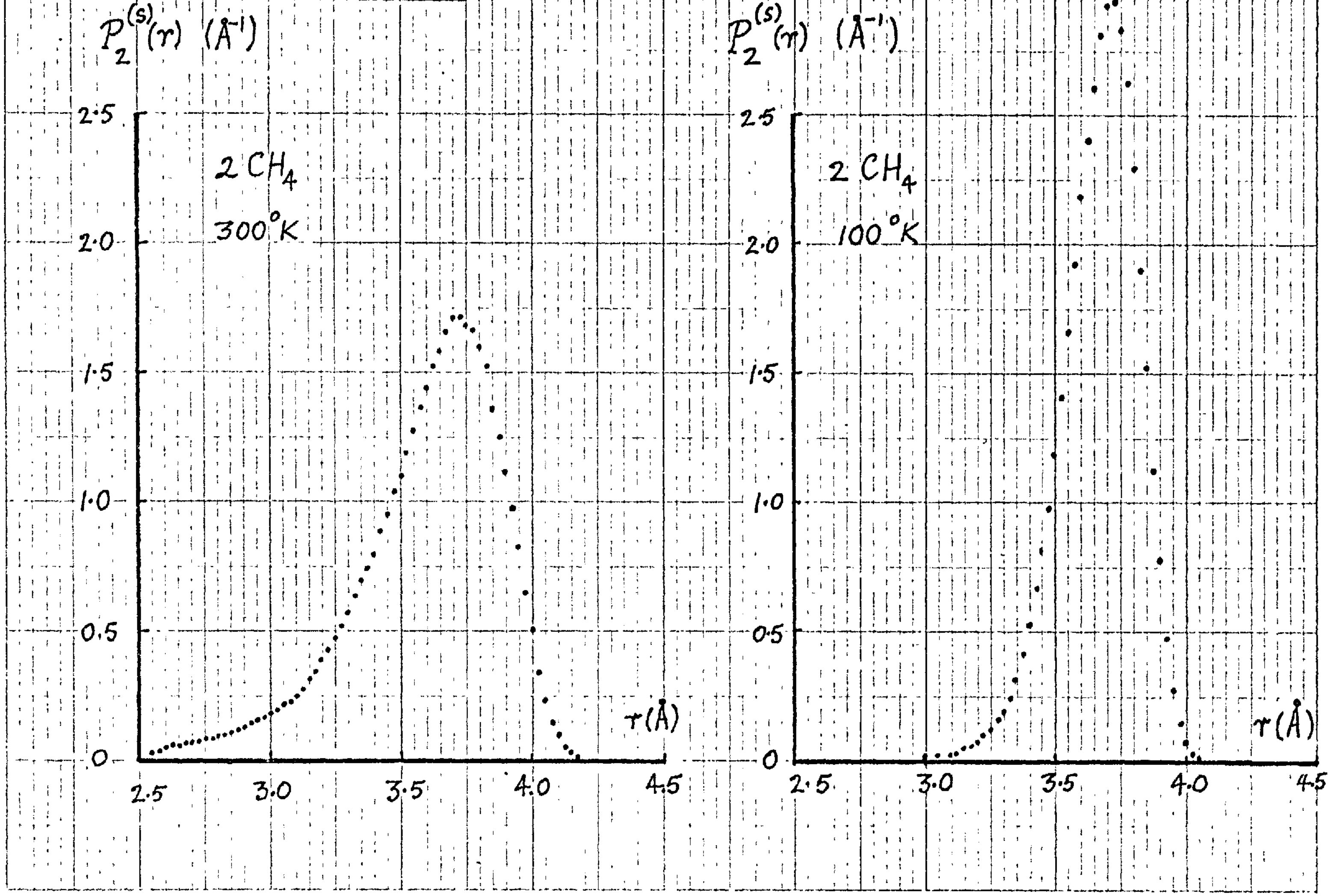


FIGURE 7.20 Localization of One Methane Molecule on the Discrete Cations of Linde 5A

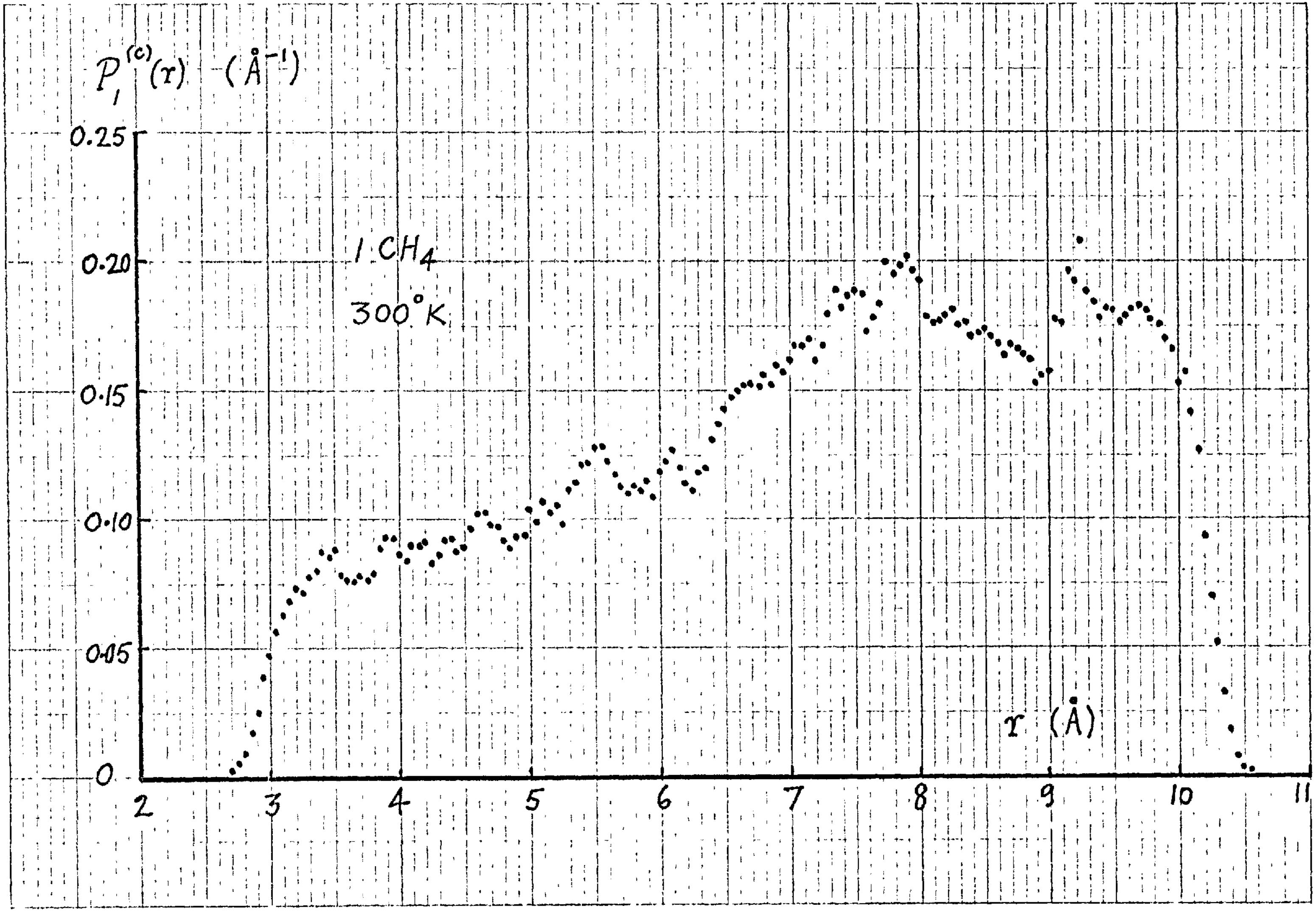


FIGURE 7.21 Localization of One Methane Molecule on the Discrete Cations of Linde 5A

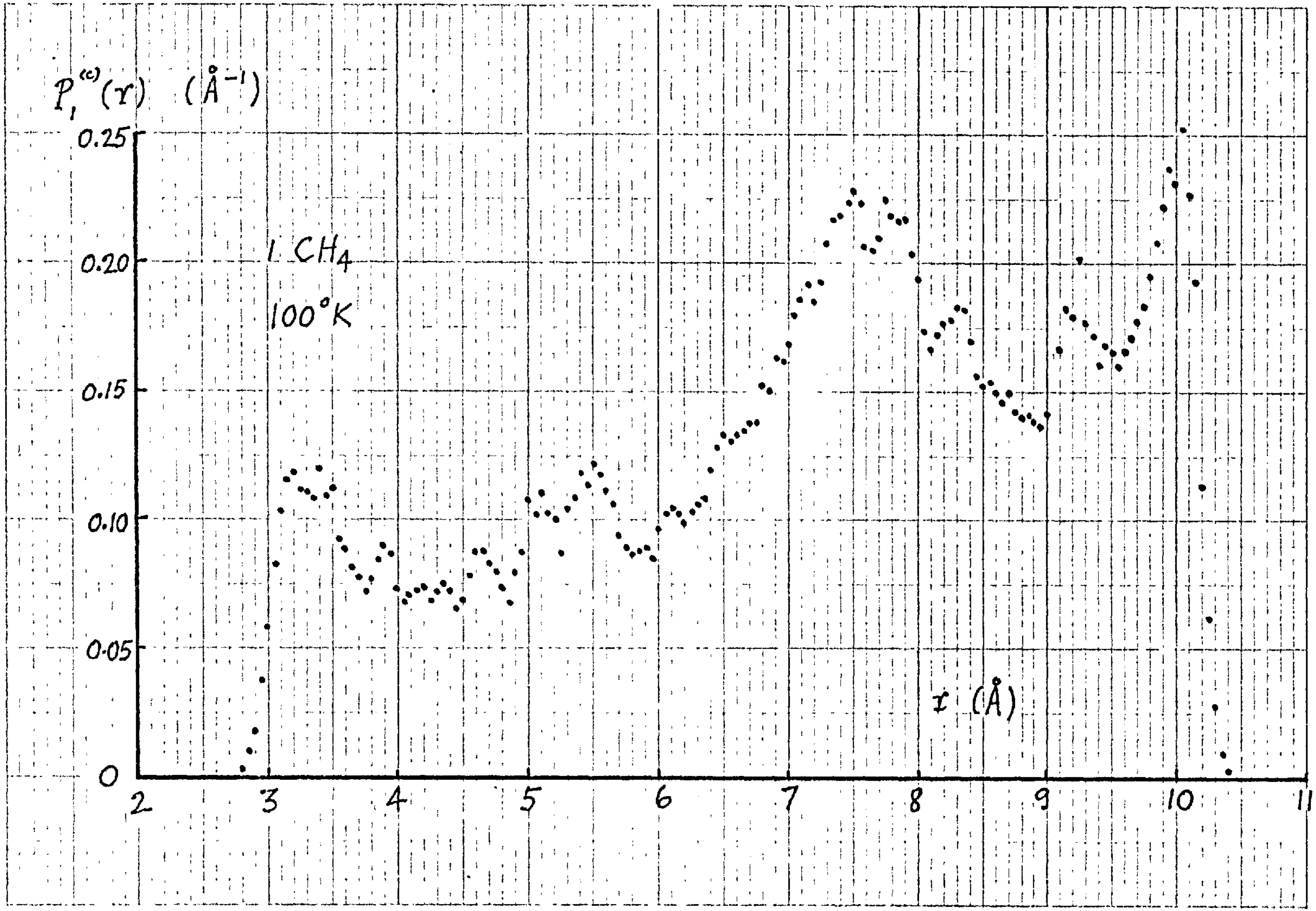


FIGURE 7.22 Localization of Two Methane Molecules on the Discrete Cations of Linde 5A

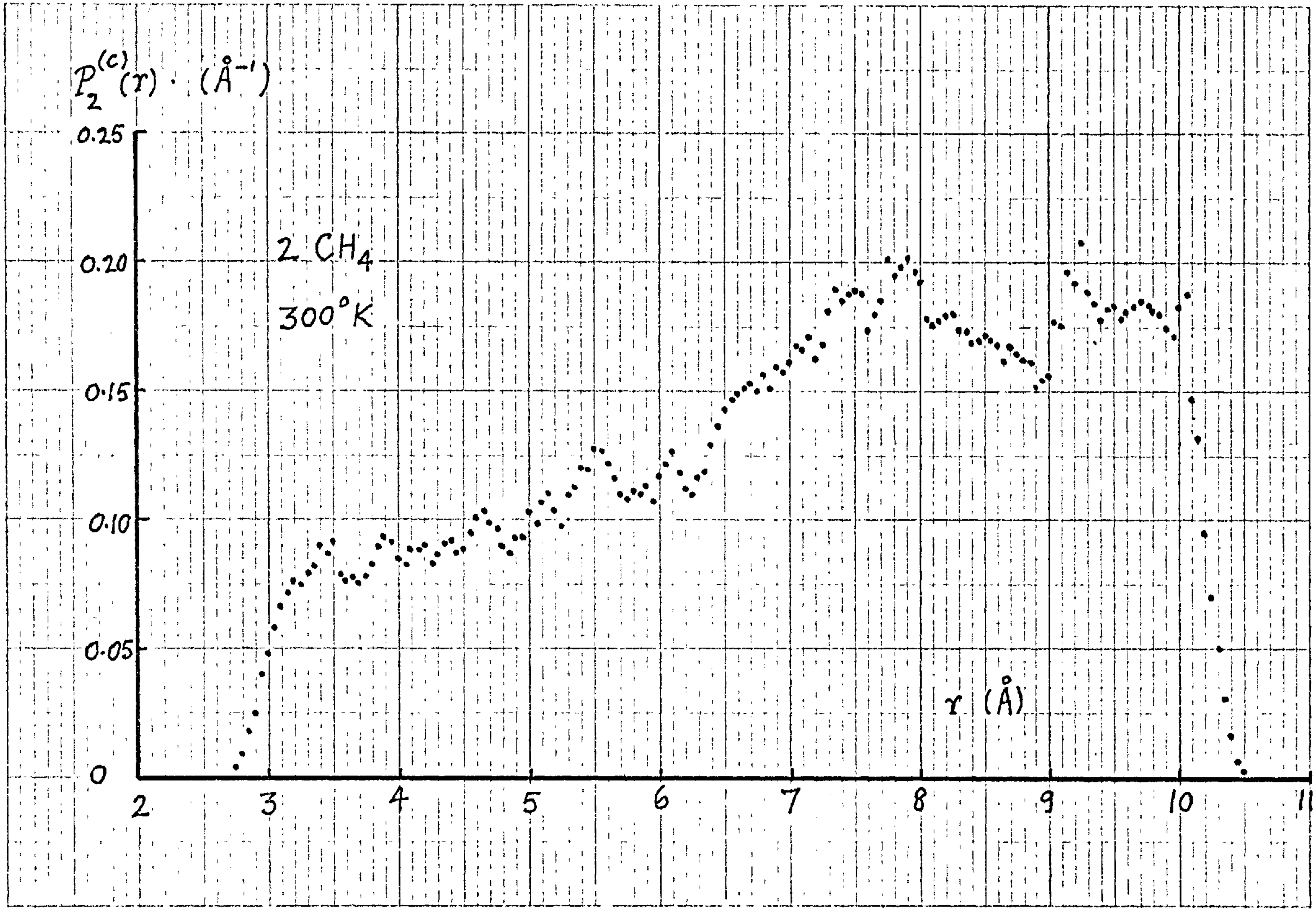


FIGURE 7.23 Localization of Two Methane Molecules on the Discrete Cations of Linde 5A

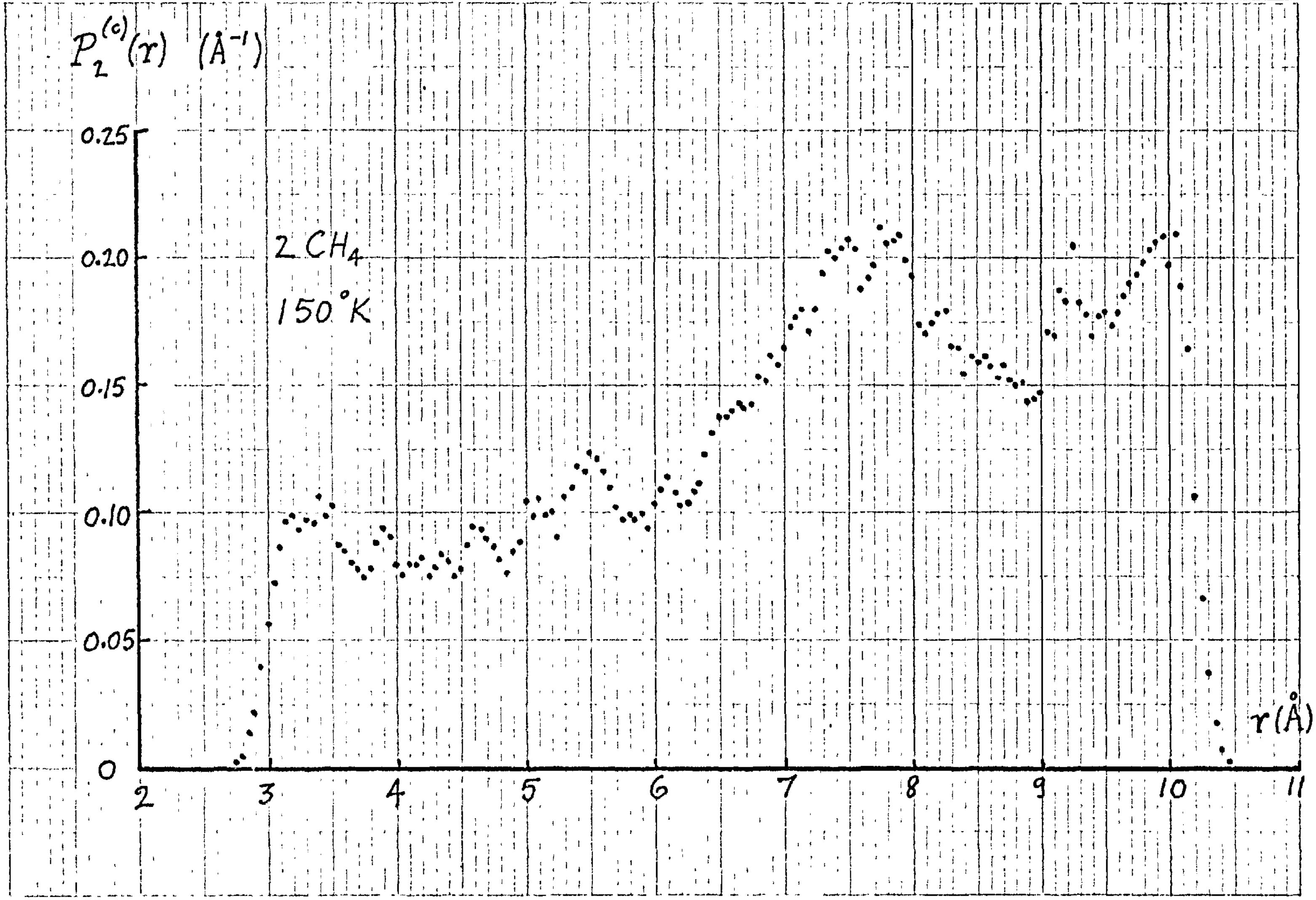


FIGURE 7.24 One Methane Molecule in a Sphericalized Linde 5A Cavity

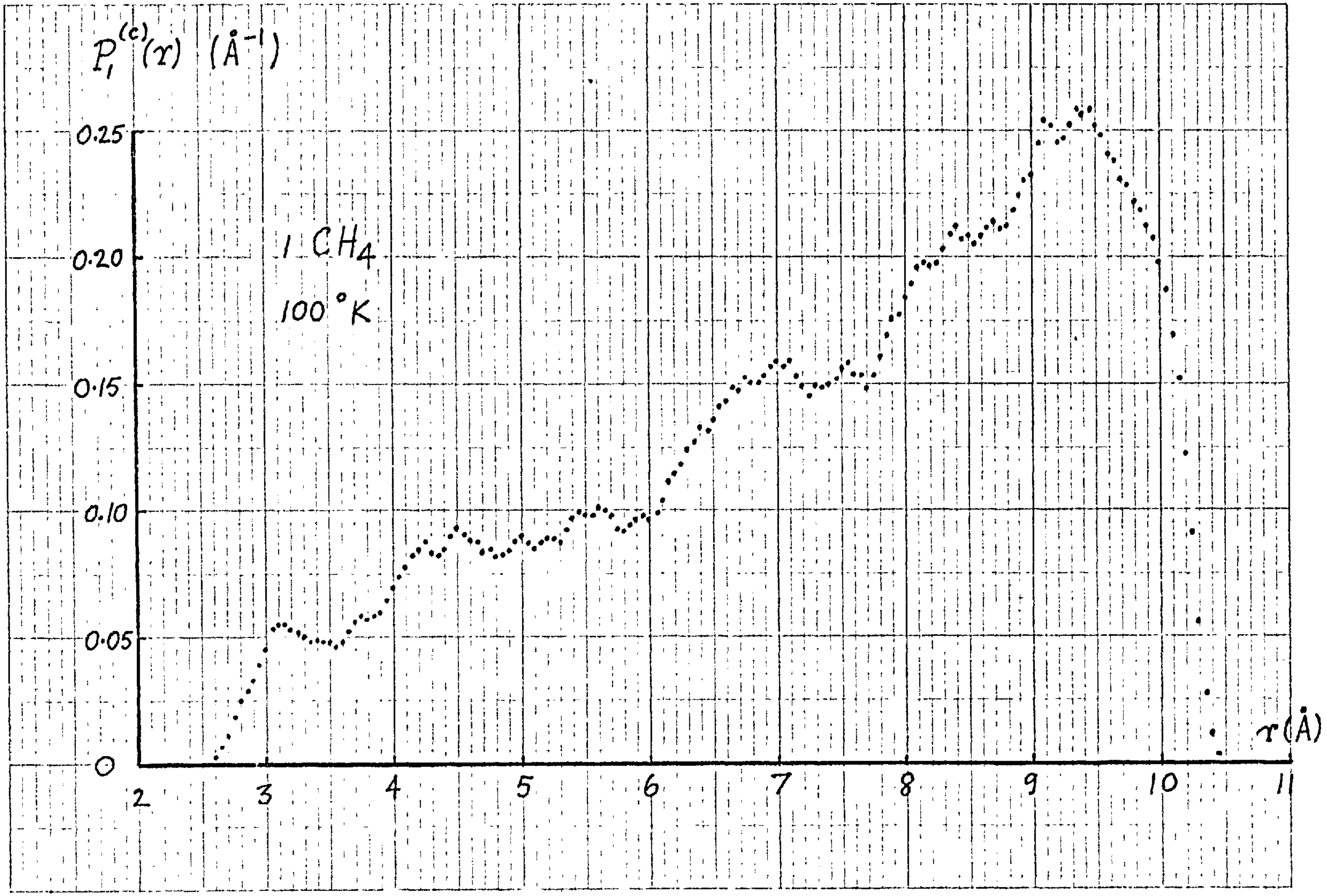


FIGURE 7.25 Two Krypton Molecules in a Sphericalized Linde 5A Cavity

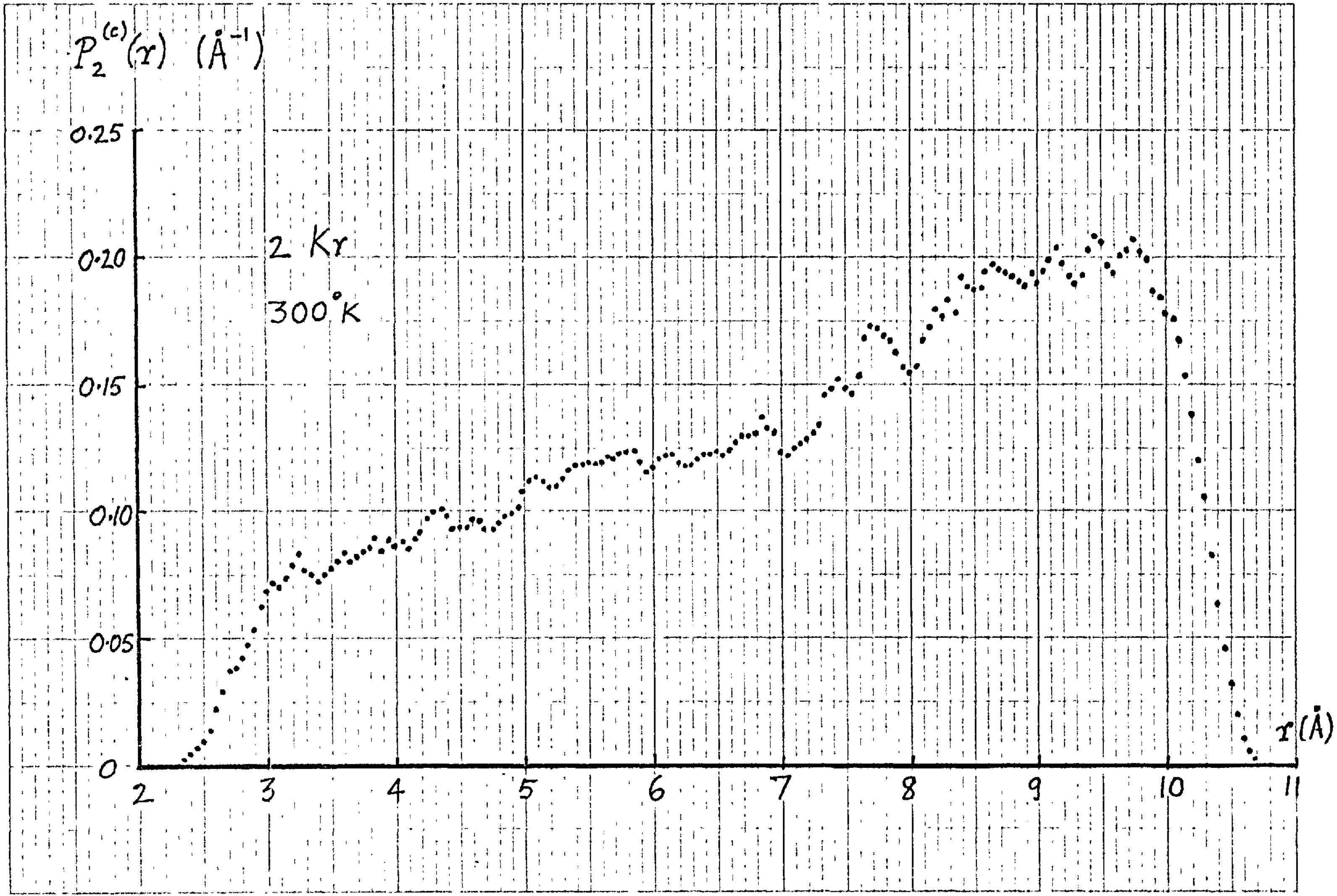
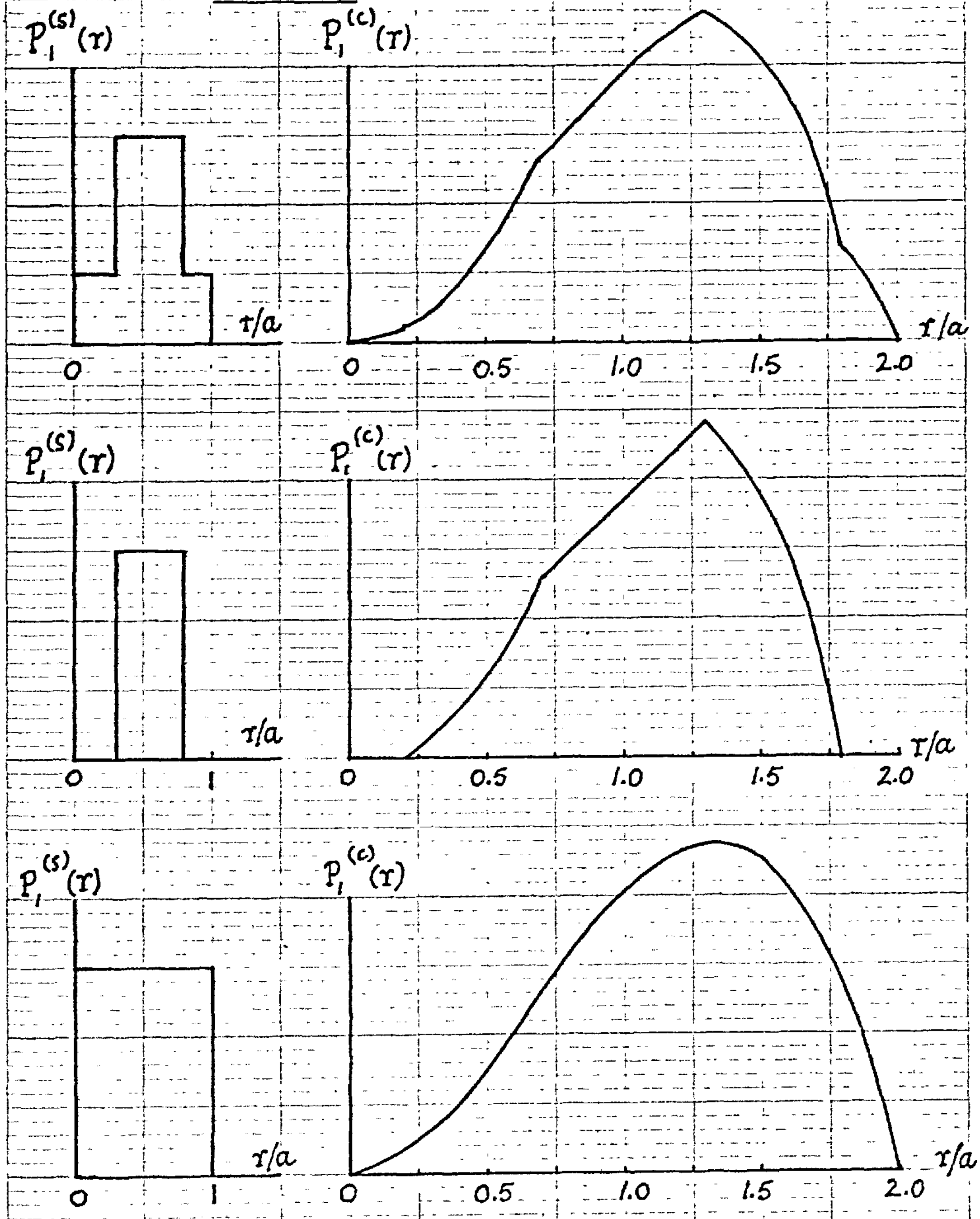


FIGURE 7.26 Relations between the Distribution Functions of One Molecule in a Spherically Symmetric Potential



N.B: These distribution functions have not been normalized.

a = cavity radius.

FIGURE 7.27 Pair Distribution Function of Two Sorbate Molecules in a Linde 5A Cavity

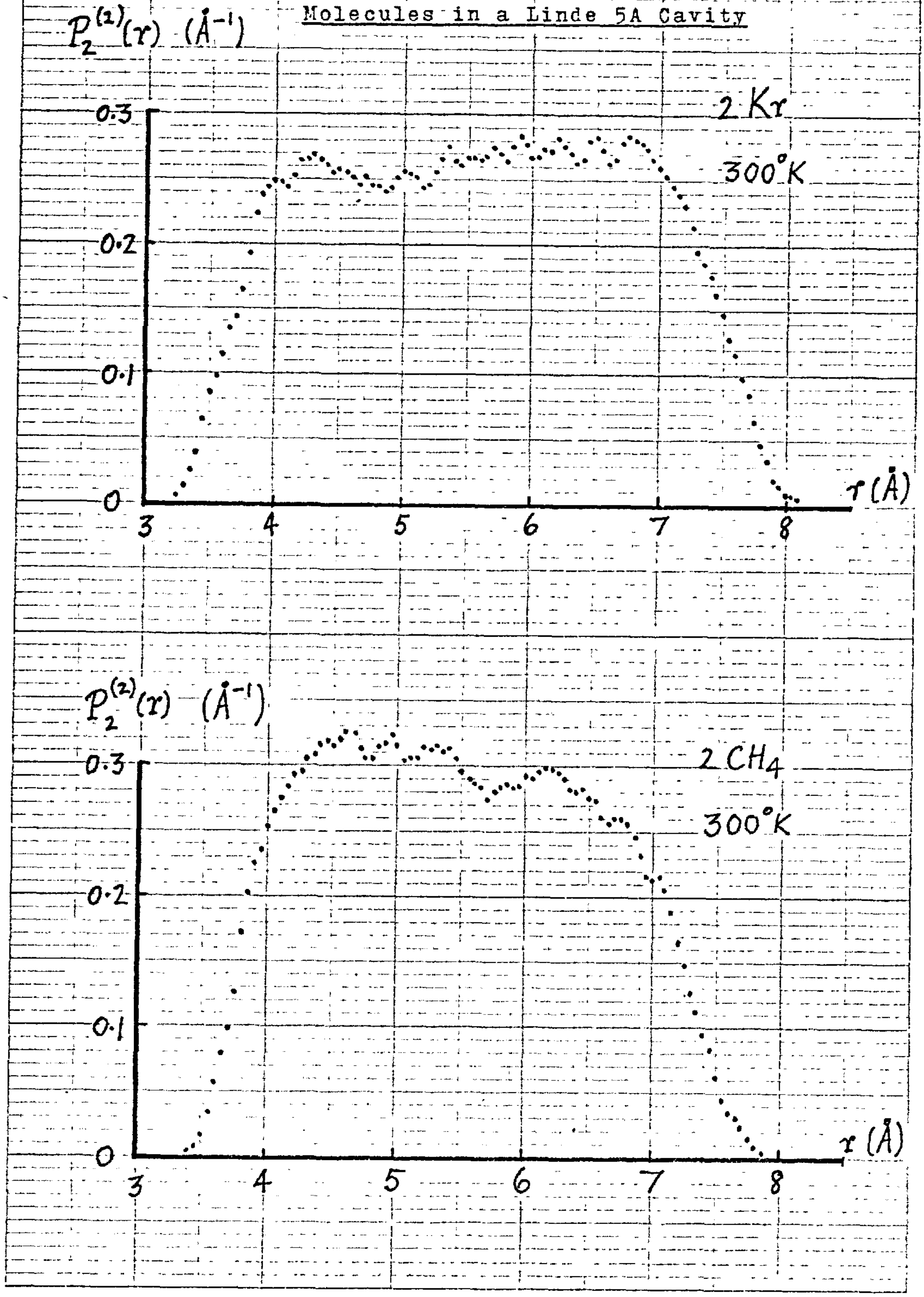
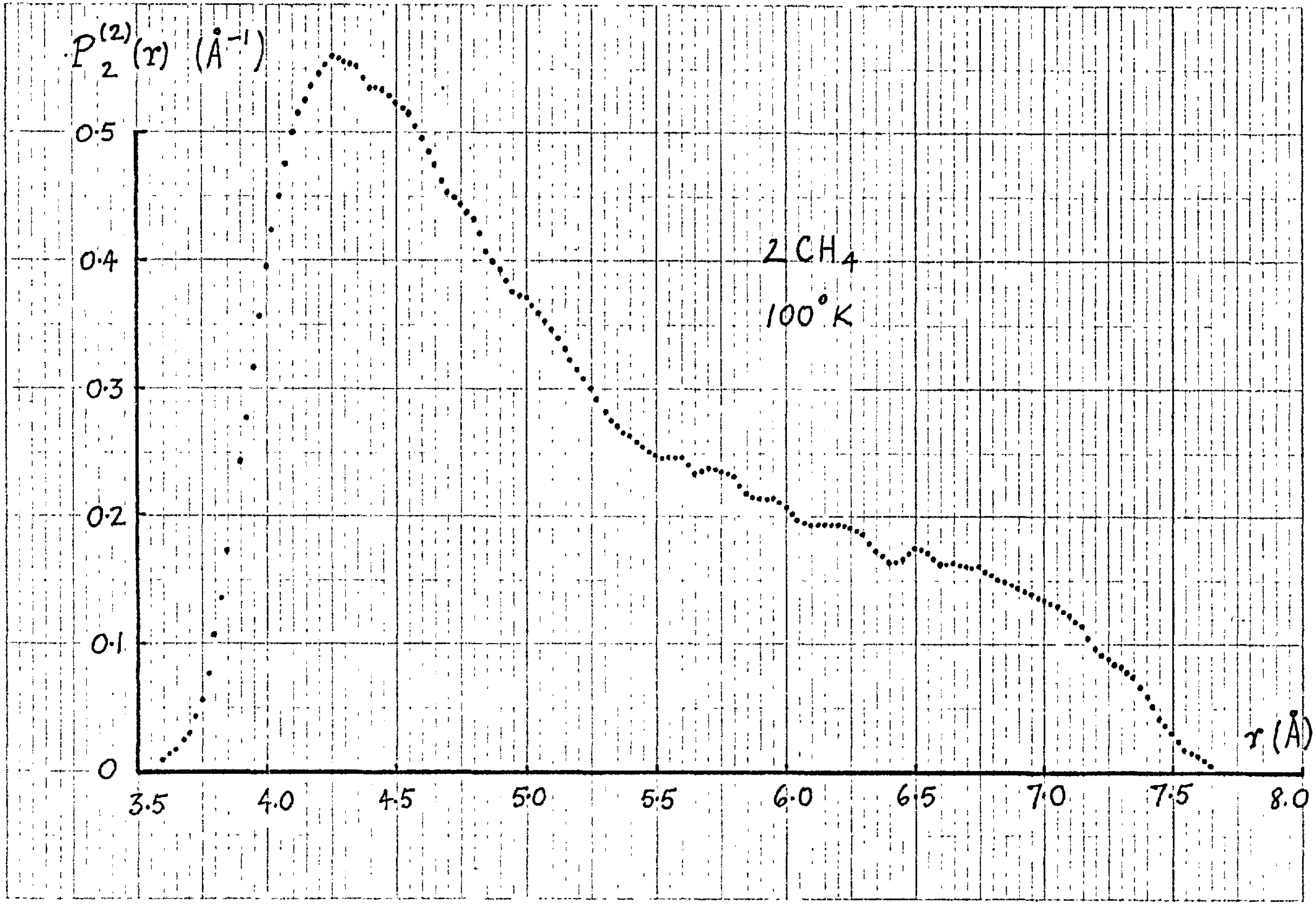


FIGURE 7.28 Pair Distribution Function of Two Methane Molecules in a Linde 5A Cavity



CHAPTER 8

RESULTS FOR THE MACROSCOPIC ASSEMBLY

8.1 DISTRIBUTION DENSITIES OF THE ASSEMBLY

The function $g(\underset{\sim}{n},T)$ as defined by (4.3.8) should give a very valuable information on how the N sorbate molecules are actually partitioned among the assembly of B zeolite cavities. For the specific case of a single-component system, it follows from (2.1.9), (4.3.8), (7.1.8) and (7.1.12) that

$$g(n,T) = \frac{\exp\left[-A_{cf}(n,T)/kT\right] z^n/n!}{E(T,z)} \tag{8.1.1}$$

where

$$E(T,z) = \sum_{n \geqslant 0} \exp\left[-A_{cf}(n,T)/kT\right] z^n/n! \tag{8.1.2}$$

Also (4.3.10) defines the mean molecular occupancy number of a sorption cavity as

$$\overline{n} = N/B = \sum_{n > 0} n\, g(n,T) \tag{8.1.3}$$

From (4.3.9) it is clear that the distribution function g(n,T) has been normalized. As a result (8.1.3) implies

$$\sum_{n \geqslant 0} g(n,T)\ (n - \overline{n}) = 0 \tag{8.1.4}$$

In calculating $g(n,T)$ and $\overline{n}$ on the computer the series in (8.1.2) and (8.1.3) were summed up to $n=7$ for each parametric value of the activity z. The appropriate values of $A_{cf}(n,T)$ for the sorption of krypton and methane in Linde 5A at various temperatures were obtained from Table7.1 & 7.2. Typical graphs of $g(n,T)$ versus $\overline{n}$ are presented in Figures 8.1 - 8.4. Evidently, these results confirm the previous conclusion that $g(n,T)$ are not sharply peaked at any particular value of $\overline{n}$, at least as regards the specific sorption systems studied within the temperature range 100 - 300 degrees K.

When it is known physically that N identical molecules are sorbed in the macroscopic assembly of B zeolite cavities, the variance $D(\overline{n},T)$ as defined by (4.5.5) should give a useful quantitative measure of the relative magnitudes of the molecular distribution function $g(n,T)$. Therefore pertinent results for $D(\overline{n},T)$ are presented in Figures 8.5 and 8.6. If any more detailed information concerning $g(n,T)$ is required, some higher moments of this distribution function should also be studied. Incidentally $g(n,T)$ can be completely characterized by all its moments.

In the present work it has not been found mathematically feasible to evaluate the partition function $Z(n,T)$ or the corresponding Helmholtz free energy $A(n,T)$ when $n \geqslant 8$. Nevertheless the essential behaviours of these functions, and hence also of $g(n,T)$ and $D(\overline{n},T)$, are known qualitatively. For physical reasons the sorption space of any Linde 5A sorption cavity cannot accommodate more than about 15 molecules of krypton or methane. A semi-quantitative description of the distribution function $g(n,T)$ for $0 \geqslant n \geqslant 12$ is given in Figure 8.7. From this it follows that the variance $D(\bar{n},T)$ should decrease monotonically when the average occupancy $\bar{n}$ is greater than about 6 and should vanish when $\bar{n}$ is equal to n^*, the maximum number of sorbate molecules which is allowed in any single sorption cavity at the given temperature. In the latter case every cavity within the assembly is known to have exactly the same number n^* of identical sorbate molecules in it.

FIGURE 8.1 Distribution Densities of Krypton Molecules in Linde 5A Assembly

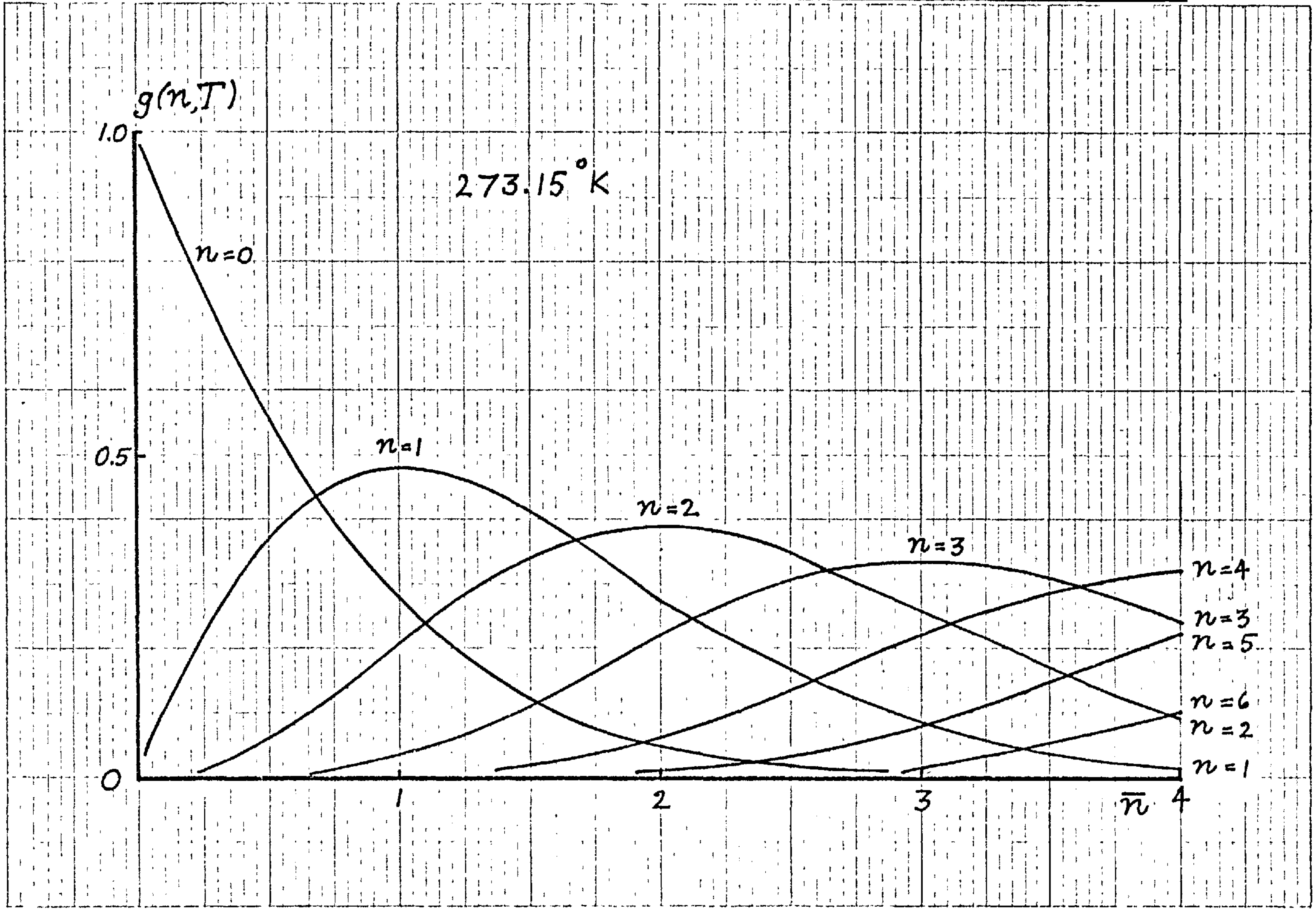


FIGURE 8.2 Distribution Densities of Krypton Molecules in Linde 5A Assembly

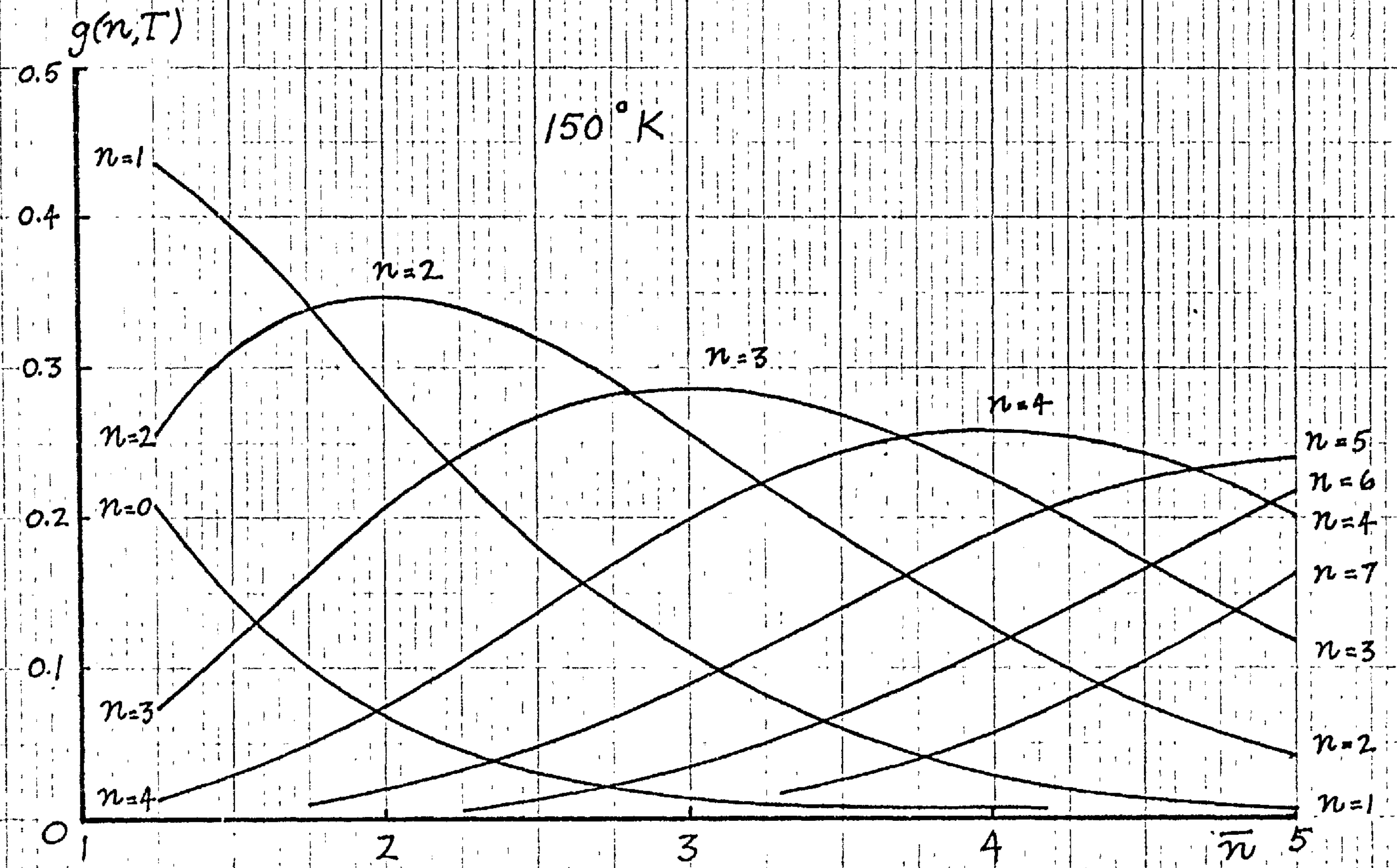


FIGURE 8.3 Distribution Densities of Methane Molecules in Linde 5A Assembly

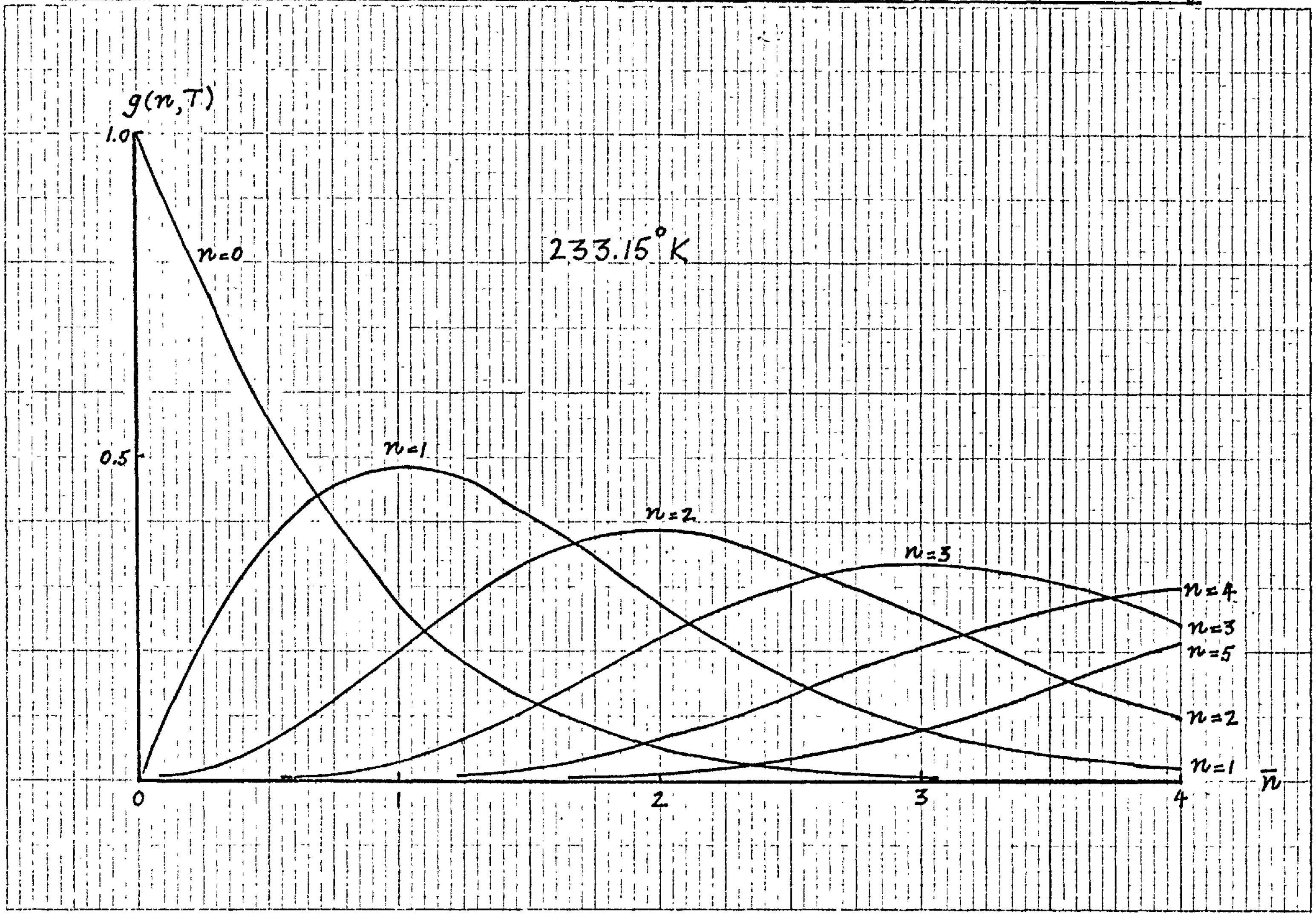


FIGURE 8.4 Distribution Densities of Methane Molecules in Linde 5A Assembly

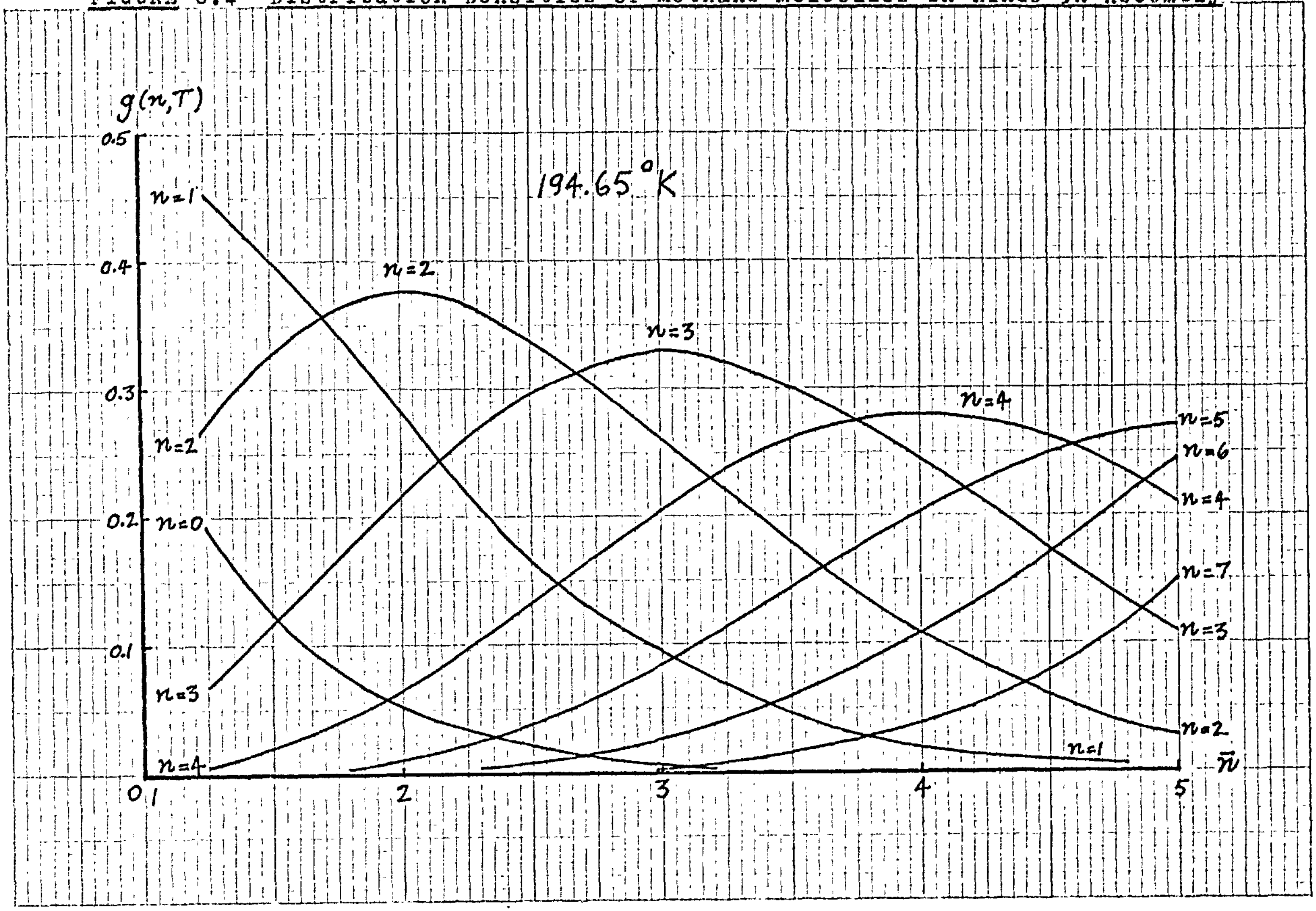


FIGURE 8.5 Variance of the Distribution of Krypton Molecules in Linde 5A Assembly

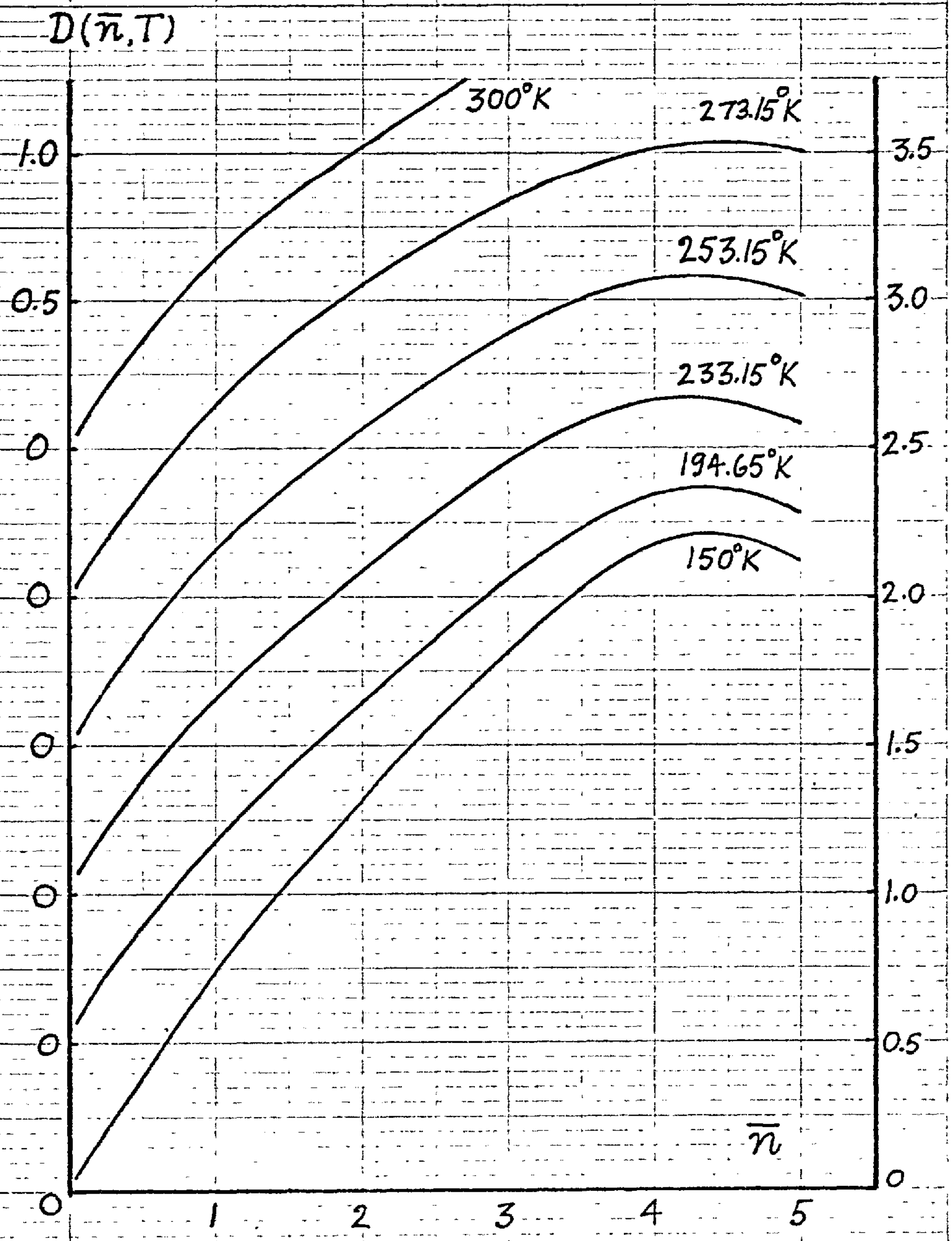


FIGURE 8.6 Variance of the Distribution of Methane Molecules in Linde 5A Assembly

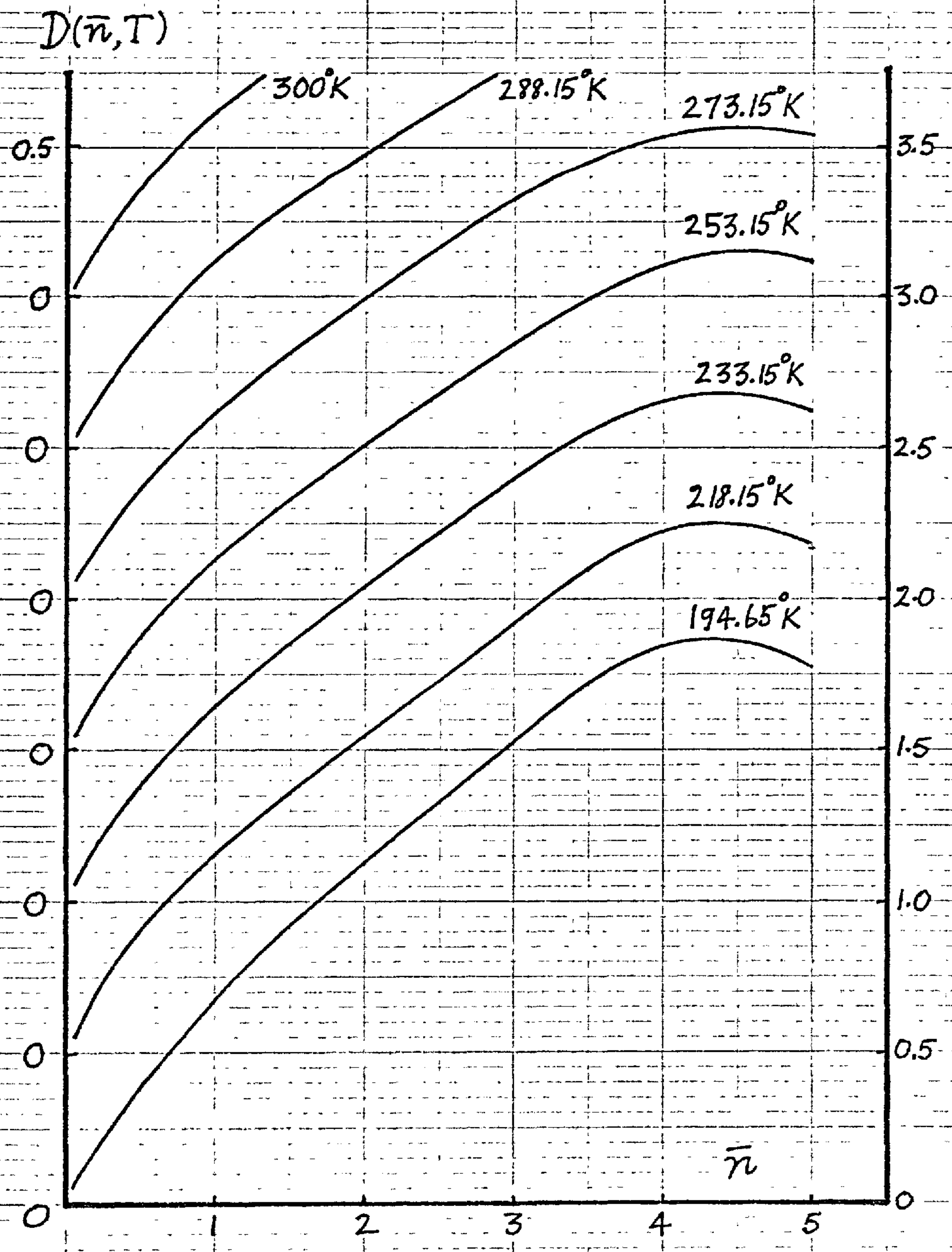
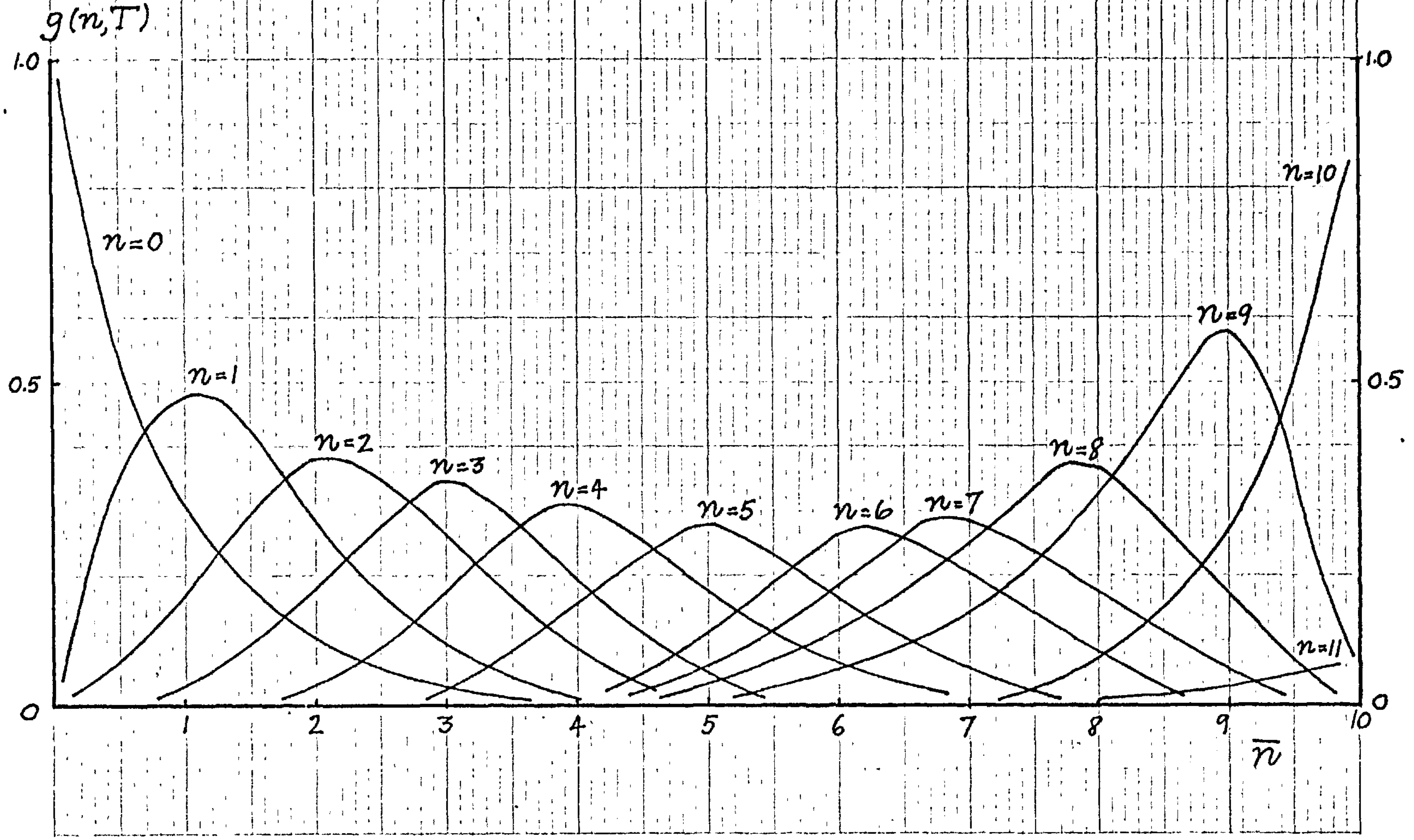


FIGURE 8.7 Expected Distribution Densities for an Assembly with $n^* = 11$ or 12

A semi-quantitative Description



8.2 ISOTHERMS

The sorption isotherms of a single-component sorbate in zeolite can be readily deduced from the results just obtained for $\overline{n}$. The hydrostatic pressure p of the single-component gas that is in thermodynamic equilibrium with the sorption system is related to the activity z of the sorbate by

$$p/kT \quad = \sum_{j \geq 1} b_j(T)\, z^j \qquad (8.2.1)$$

where each b_j is a function of the i th ($1 \leq i \leq j$) virial coefficients in the equation of state expansion of the gas. (Hill 1956c, Uhlenbeck & Ford 1962)

As regards krypton and methane in the pressure range of interest, it is sufficient for the present purpose to take only the first term of the series in (8.2.1) into account. When more accurate results are required, and especially for large molecules at high gas pressure, however, correction should be made with respect to the second and higher order virial coefficients. The calculated isotherms are presented as solid curves in Figures 8.8 and 8.9.

Sorption isotherms of krypton and methane in Linde 5A were experimentally determined by Stroud (To be published). These are presented as broken lines in Figures 8.8 and 8.9. No hysteresis was found, and the sorption and desorption curves all agree to within the limit of experimental accuracy. It can be observed that the agreement between the theoretical and the experimental isotherms is very satisfactory. This is perhaps rather remarkable in view of the fact that there is no adjustable parameter in the present molecular statistical theory.

FIGURE 8.8 Sorption Isotherms of Krypton in Linde 5A

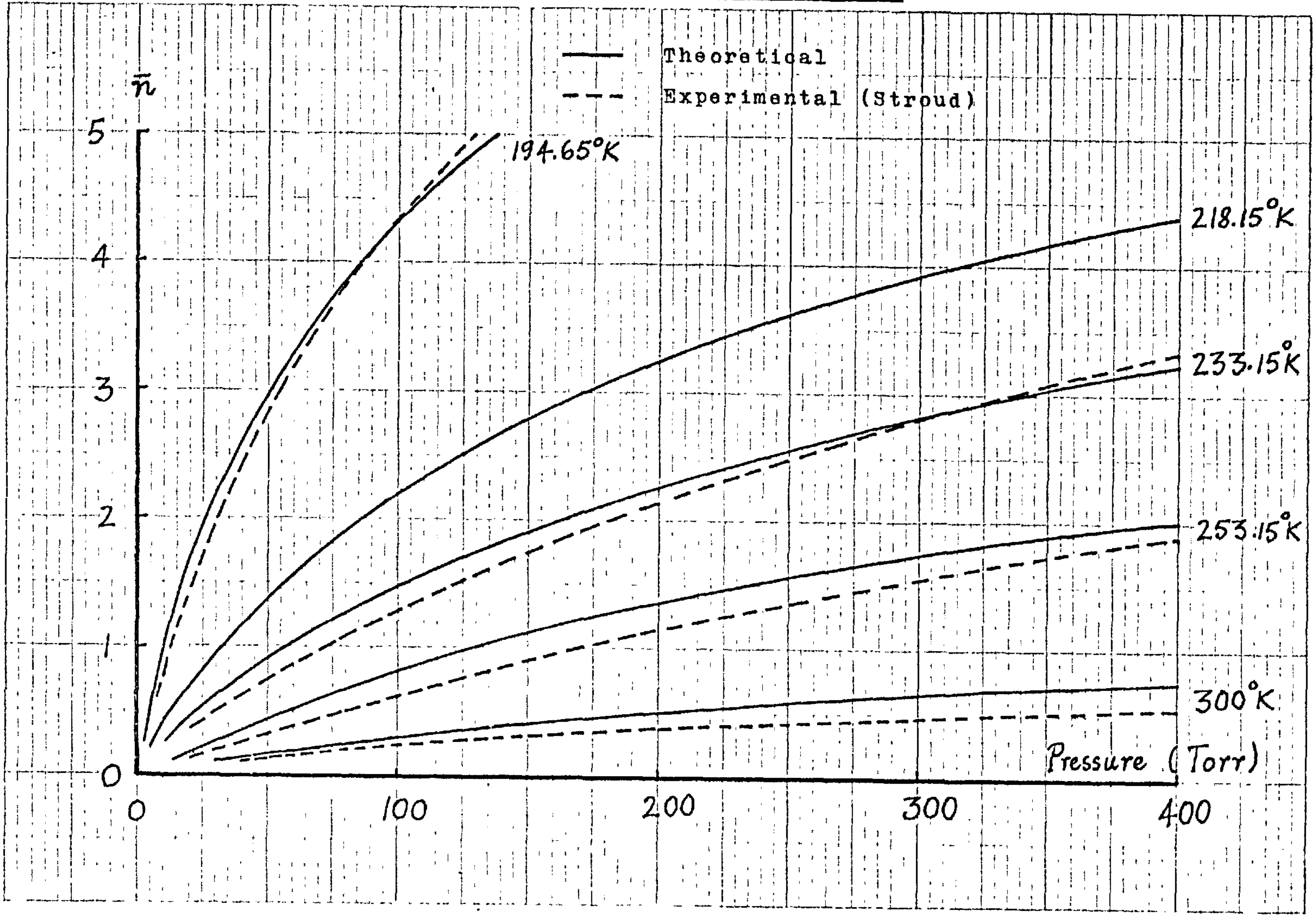
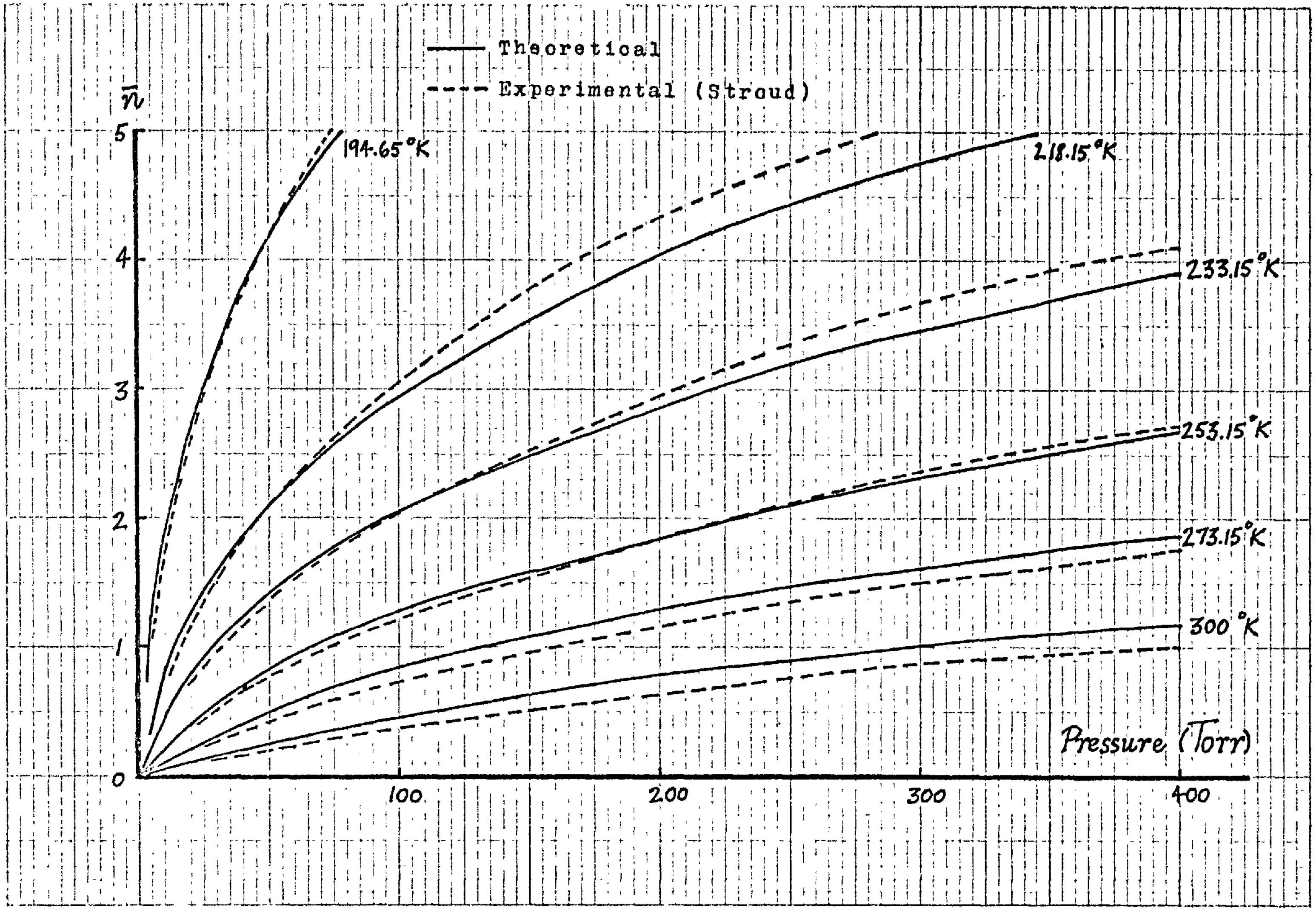


FIGURE 8.9 Sorption Isotherms of Methane in Linde 5A



8.3 ENTHALPIES AND ENTROPIES OF SORPTION

Integral enthalpies for the sorption of krypton and methane in Linde 5A were calculated by using the specialized form of (4.3.11) for a single-component system, viz.,

$$H/B = \sum_{n \geqslant 0} u(n,T)\ g(n,T) \qquad (8.3.1)$$

This series was summed on the computer up to n = 7 with respect to each set of the parametric values for z and T. The values of g(n,T) and $\bar{n}$ were calculated in the manner described in Section 8.1. The pertinent values for the statistical thermodynamic internal energies of individual subsystems, u(n,T), were obtained from Tables 7.3 and 7.4. In Figures 8.10 and 8.11 results for the integral enthalpies per mole of the sorbate, H/Nk, are plotted at several temperatures against the sorbate concentration $\bar{n}$.

The variation of H/Nk with respect to $\bar{n}$ and T should be of special interest in connection with the question of how far it is justified to use the Clausius-Clapeyron equation in analyzing isothermal data for the sorption in zeolites. By using this equation in its integrated form, viz.,

$$\ln \frac{p_1}{p_2} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad (8.3.2)$$

where p_1 and p_2 are the equilibrium pressures at constant sorbate concentration at T_1 and T_2 °K respectively, for the purpose of obtaining the isosteric heat ΔH of sorption, it is tacitly assumed that the integral enthalpy of sorption is constant over a reasonably small range, i.e. 20° - 30°, of temperature. The present results, however, do show some slight variation of H with respect to $\bar{n}$ and T. Following this it is clear that as regards the sorption in the microporous zeolite sorbent the use of (8.3.2) is on the whole a rather crude approximation. In general, therefore, provided that one is interested in the accuracy of the isosteric heat to not better than about 50 cals mole^{-1}, the integrated Clausius-Clapeyron equation is still useful as a means of estimating H. In this regard it should be observed that the integral enthalpies of krypton and methane in Linde 5A vary very smoothly with respect to both $\bar{n}$ and T.

The two distinct integral entropy contributions, S_1 and S_2, were calculated on the computer by summing the following series up to n = 7.

$$S_1/B = \sum_{n > 0} g(n,T)\, s(n,T) \qquad (8.3.3)$$

and

$$S_2/B = -k \sum_{n \geqslant 0} g(n,T) \ln g(n,T) \qquad (8.3.4)$$

These are, of course, the specialized forms of (4.3.15) and (4.3.16). The appropriate values of s(n,T) were obtained from Figures 7.11 and 7.12. Results for S_1/Bk, S_2/Bk, S_1/Nk, S_2/Nk and S/Nk are presented in Figures 8.12 - 8.21.

The physical interpretation of S_1 and S_2 has already been discussed in Section 4.4. At low sorbate concentration $\overline{n}$, it can be seen that the magnitudes of S_1 and S_2 are comparable. As expected, the latter contribution becomes less significant when the sorbate concentration is moderate. These results indicate that the molecular interpretation of the sorption based on the variation of the sorbate entropy with respect to $\overline{n}$ and T is in actuality not always straightforward. Accordingly, special care should be taken in drawing any direct conclusion from the shapes of the entropy curves, especially at low sorbate concentration. This applies in particular to the suggestions that have normally been made concerning the localization of sorbate molecules on the exchangeable cations, the specificity of sorbate-sorbent interactions, the extent of sorbate-sorbate interactions, and the degrees of freedom and the nature of movements of the sorbate molecules.

FIGURE 8.10 Enthalpy of Krypton in Linde 5A

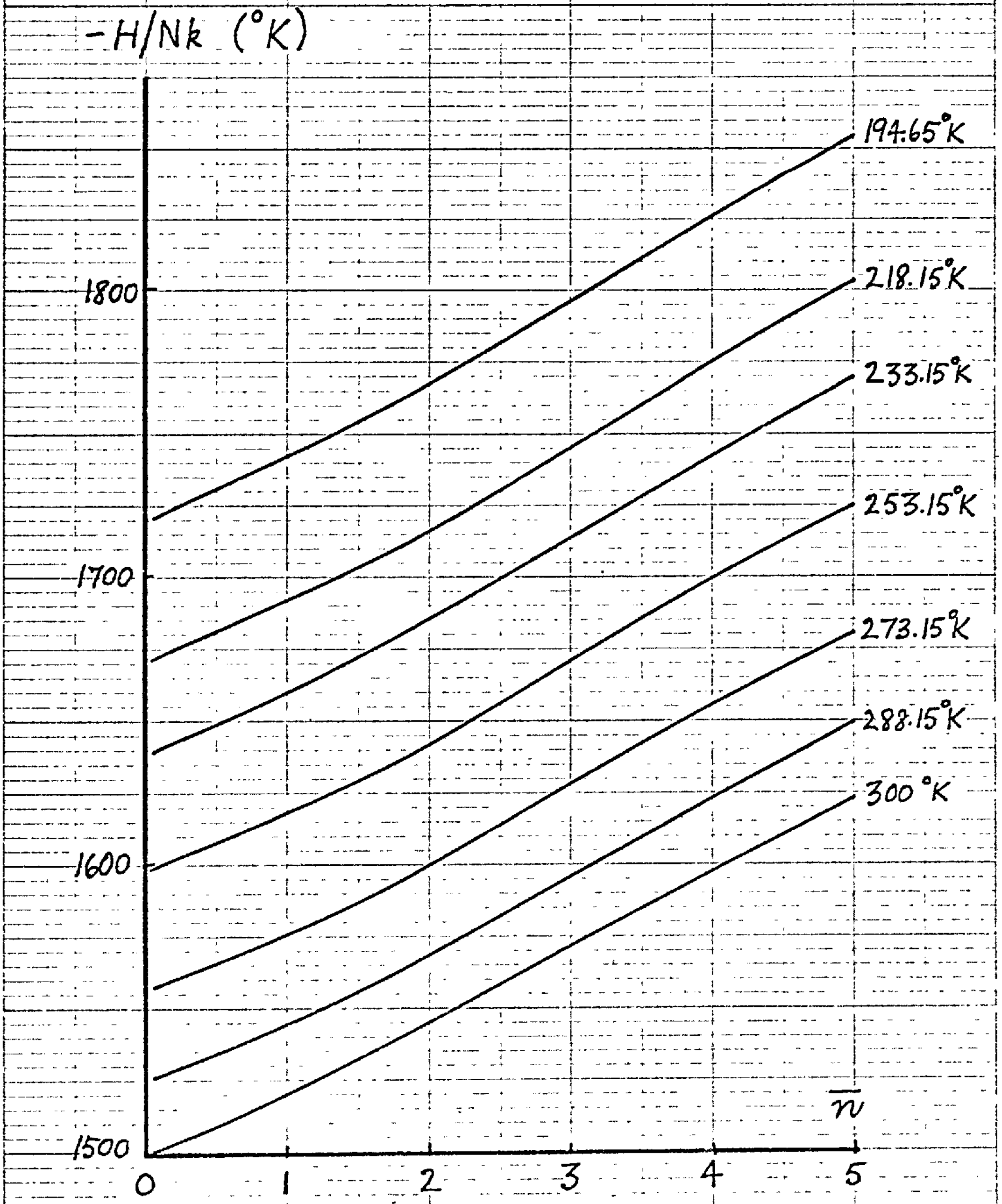


FIGURE 8.11 Enthalpy of Methane in Linde 5A

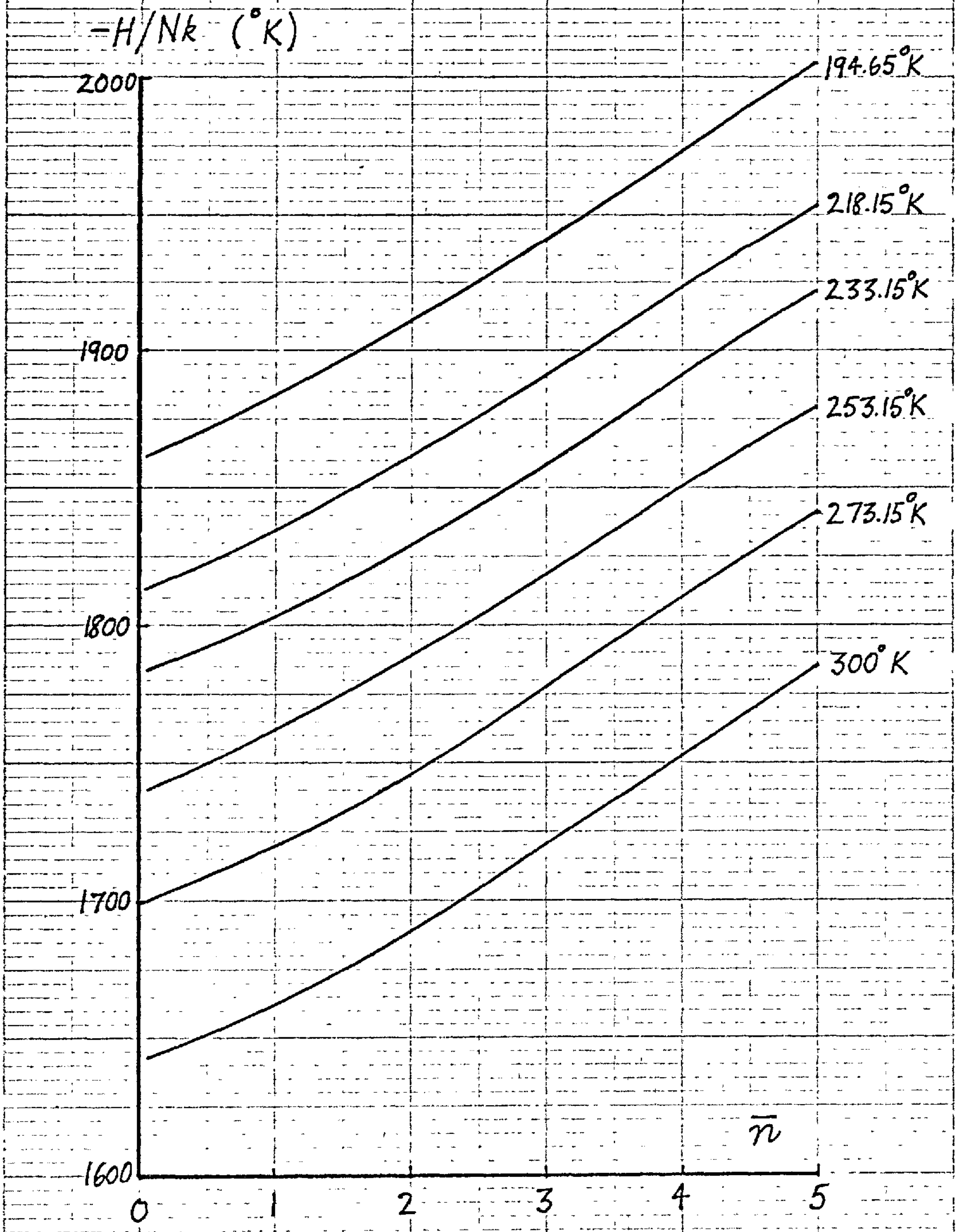


FIGURE 8.12 Entropy Contribution for Krypton in Linde 5A

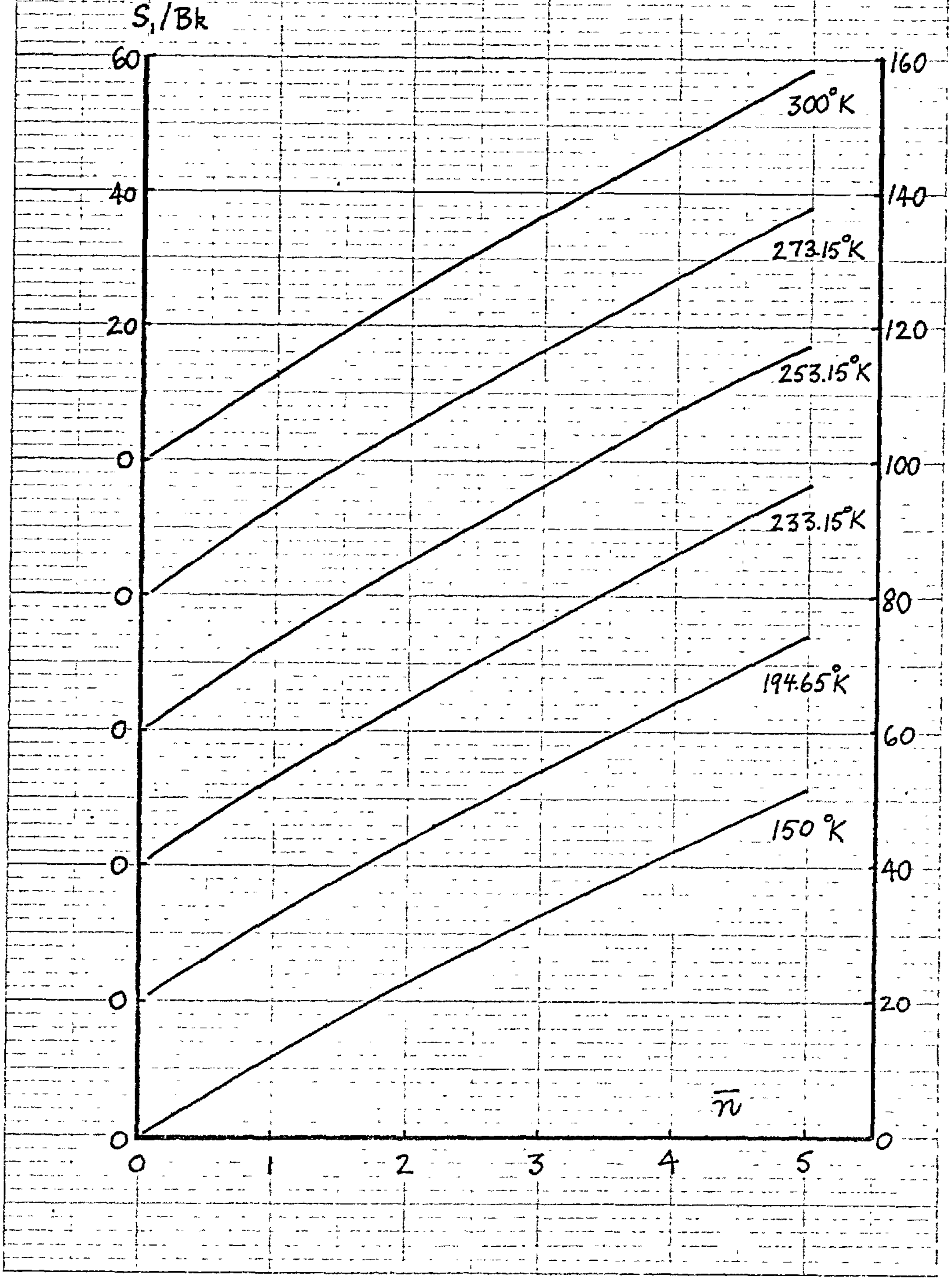


FIGURE 8.13 Entropy Contribution for Methane in Linde 5A

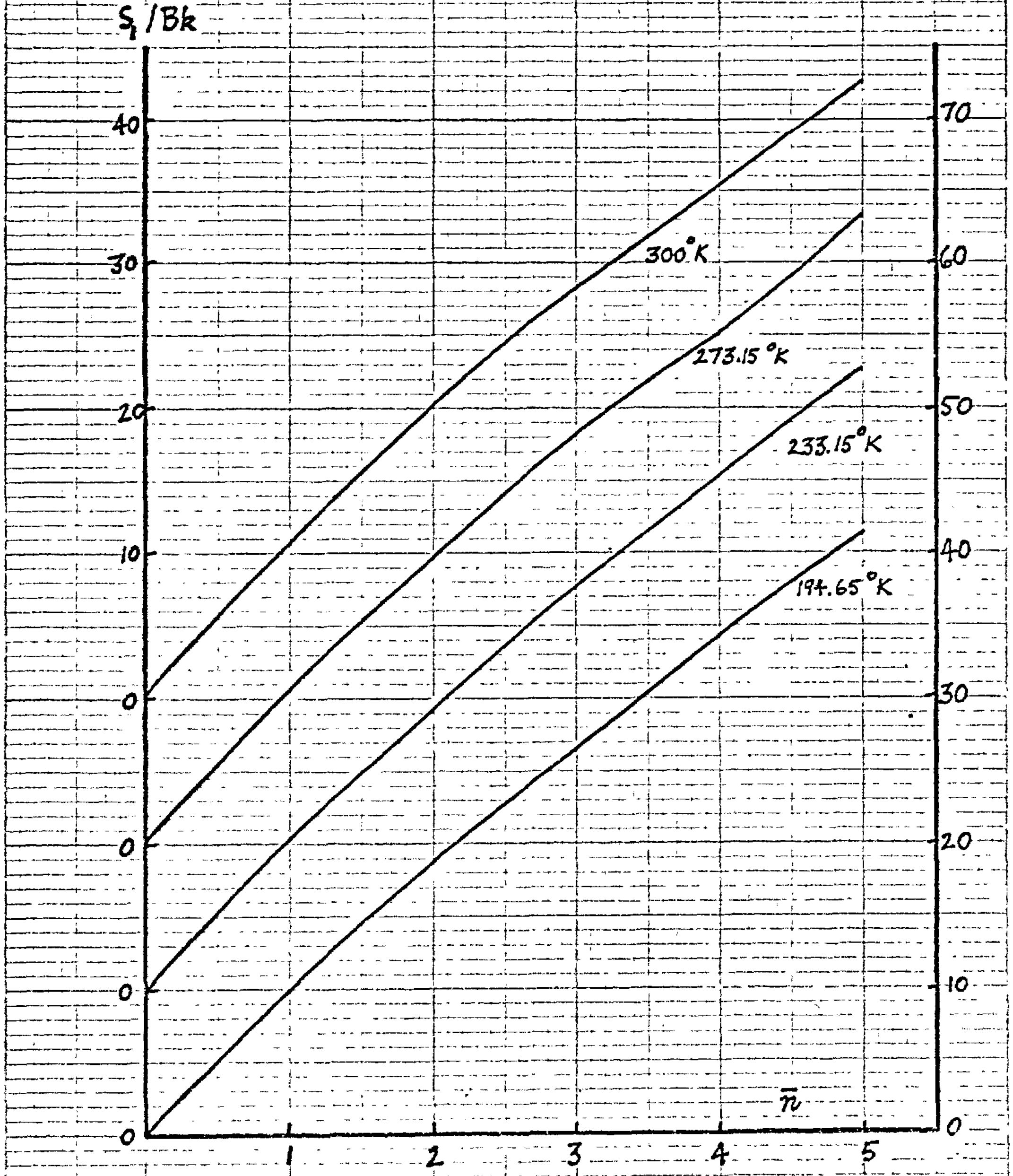


FIGURE 8.14 Entropy Contribution for Krypton in Linde 5A

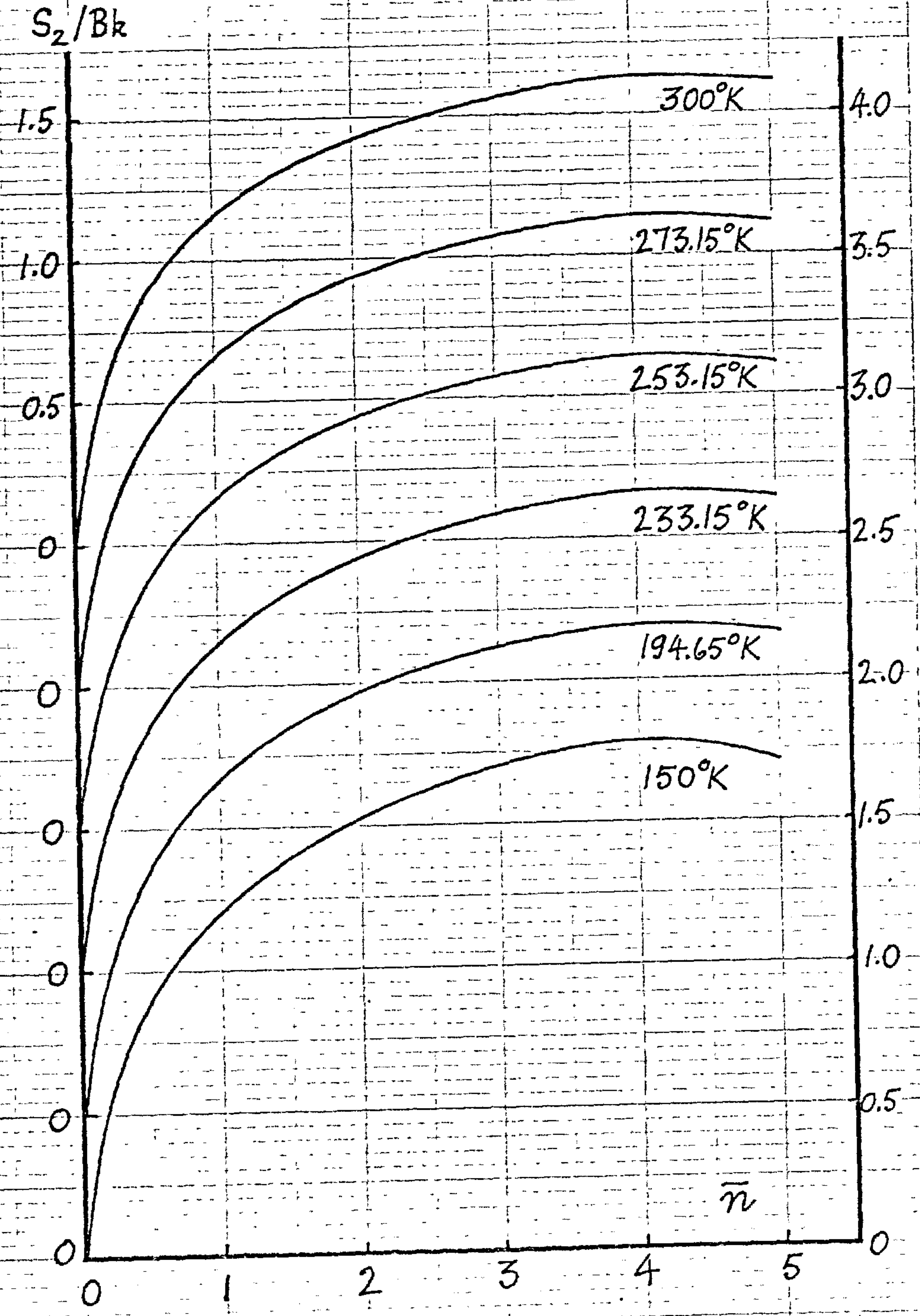


FIGURE 8.15 Entropy Contribution for Methane in Linde 5A

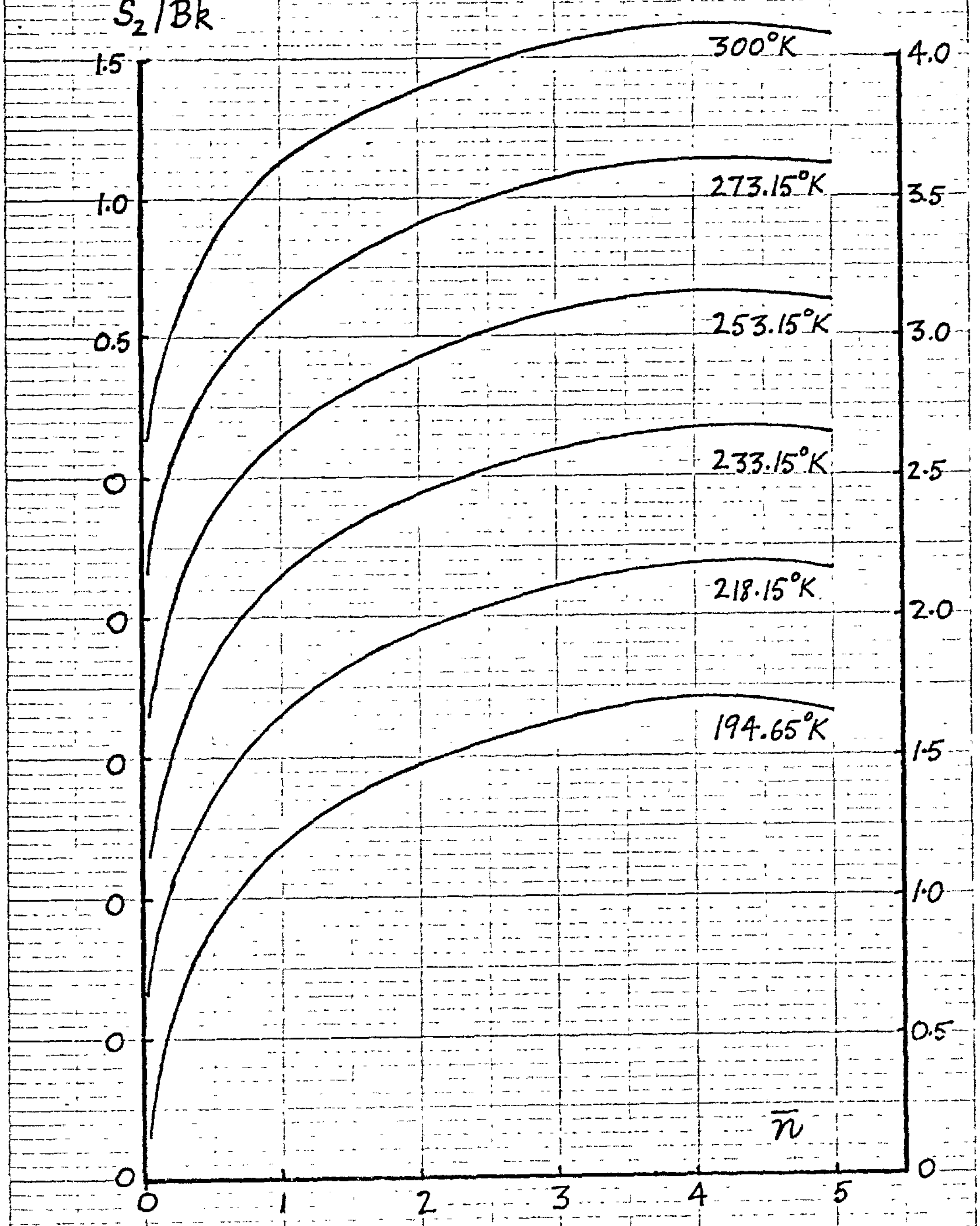


FIGURE 8.16 Entropy Contribution for Krypton in Linde 5A

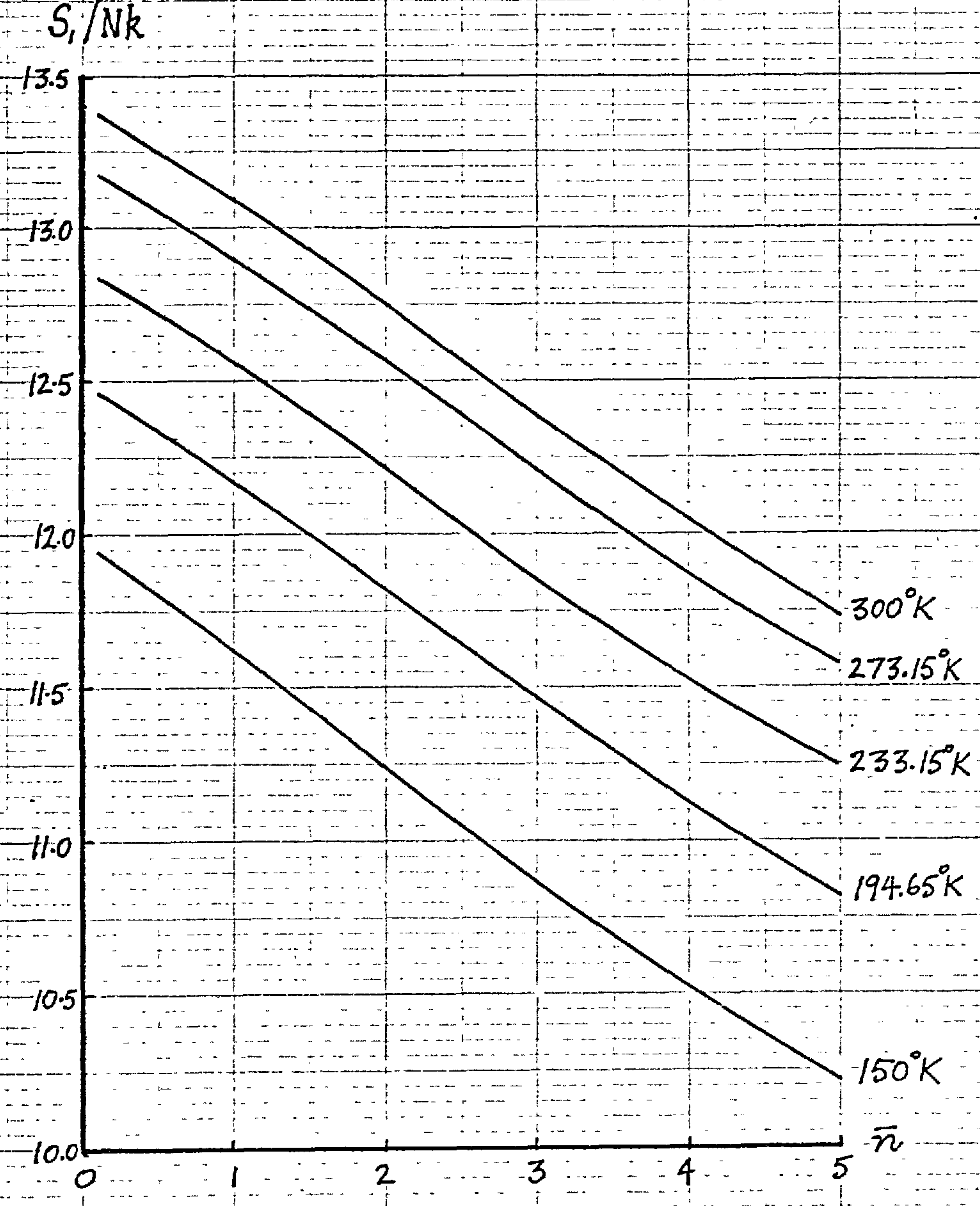


FIGURE 8.17 Entropy Contribution for Methane in Linde 5A

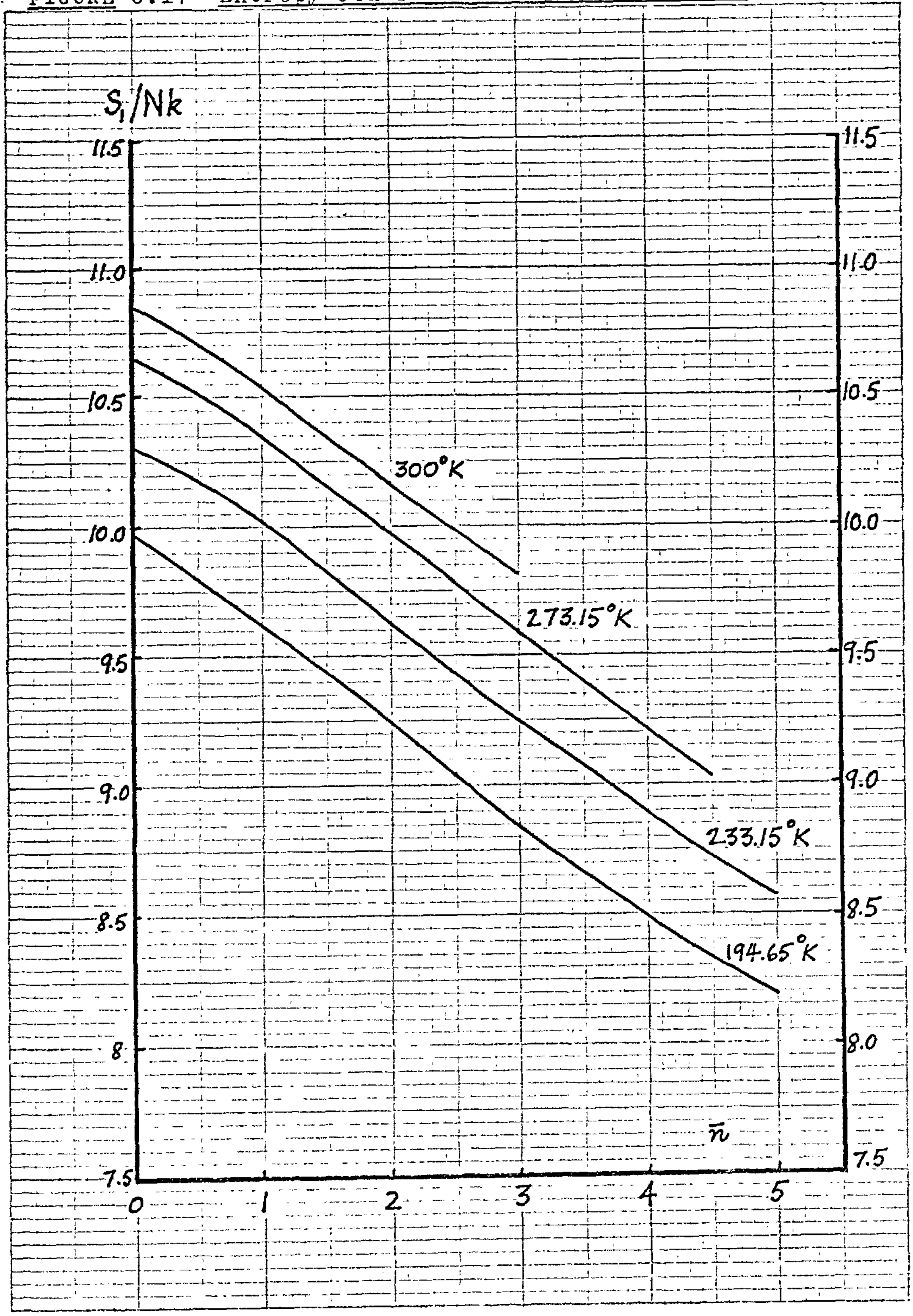


FIGURE 8.18 Entropy Contribution for Krypton in Linde 5A

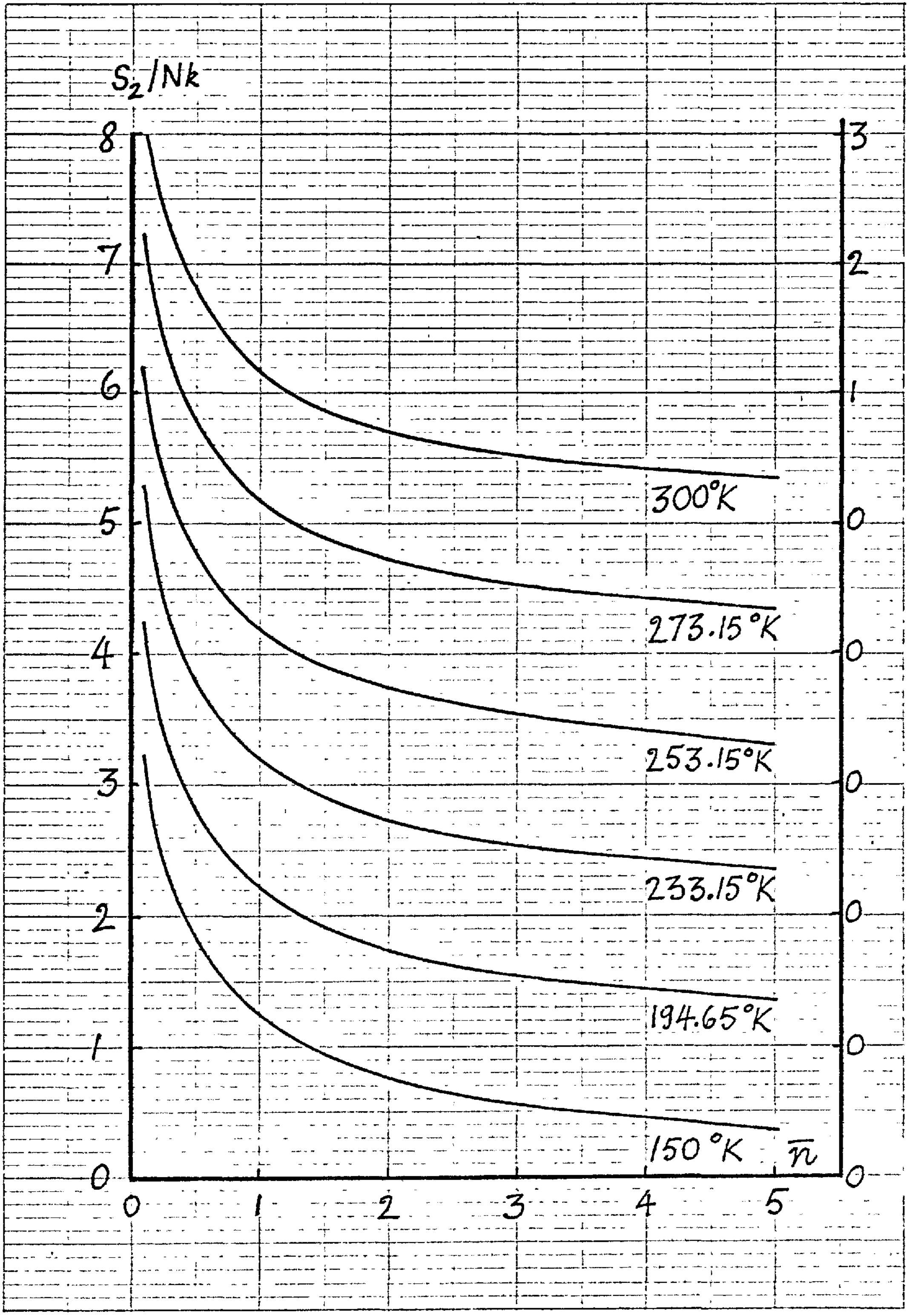


FIGURE 8.19 Entropy Contribution for Methane in Linde 5A

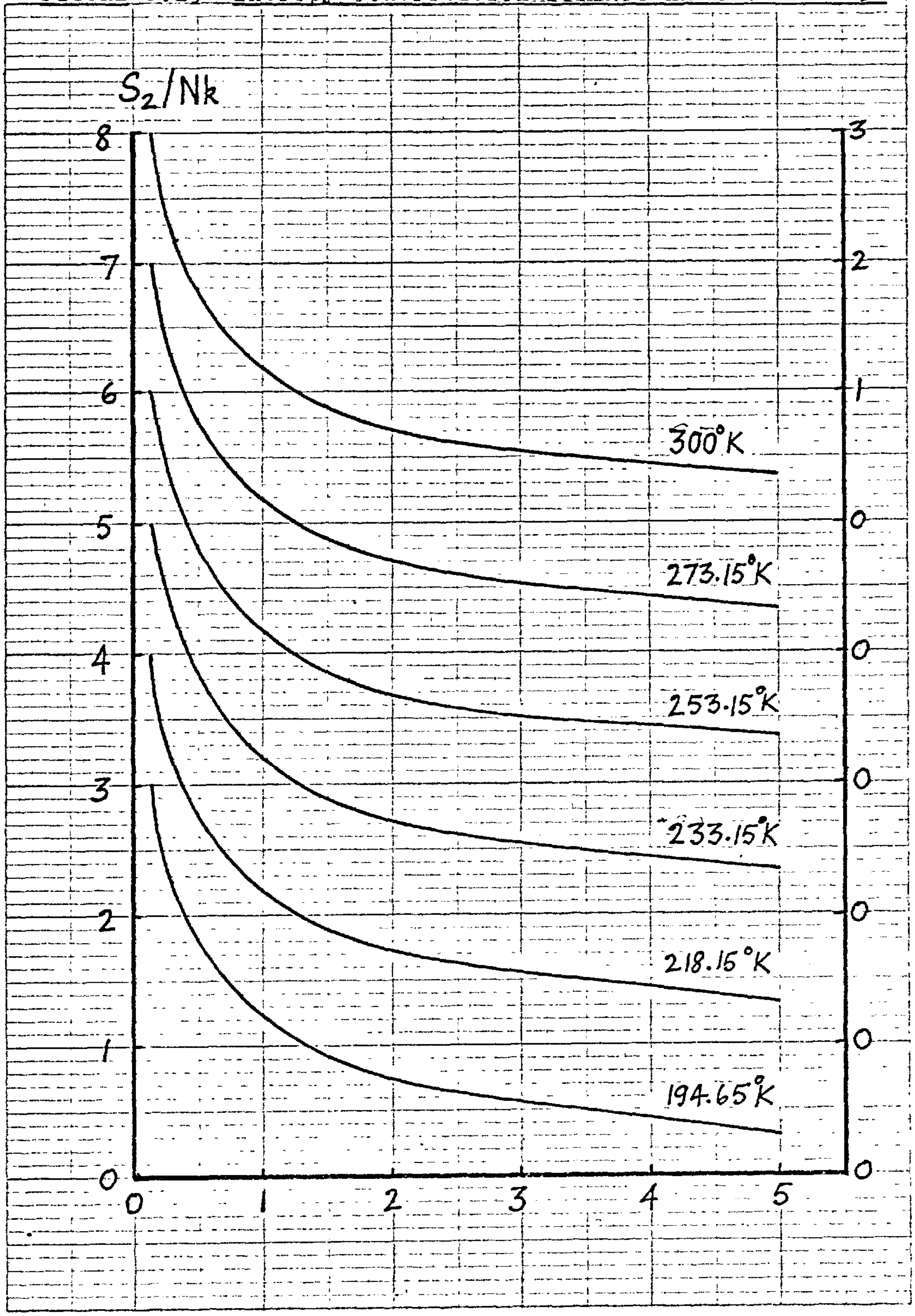


FIGURE 8.20 Entropy of Krypton in Linde 5A

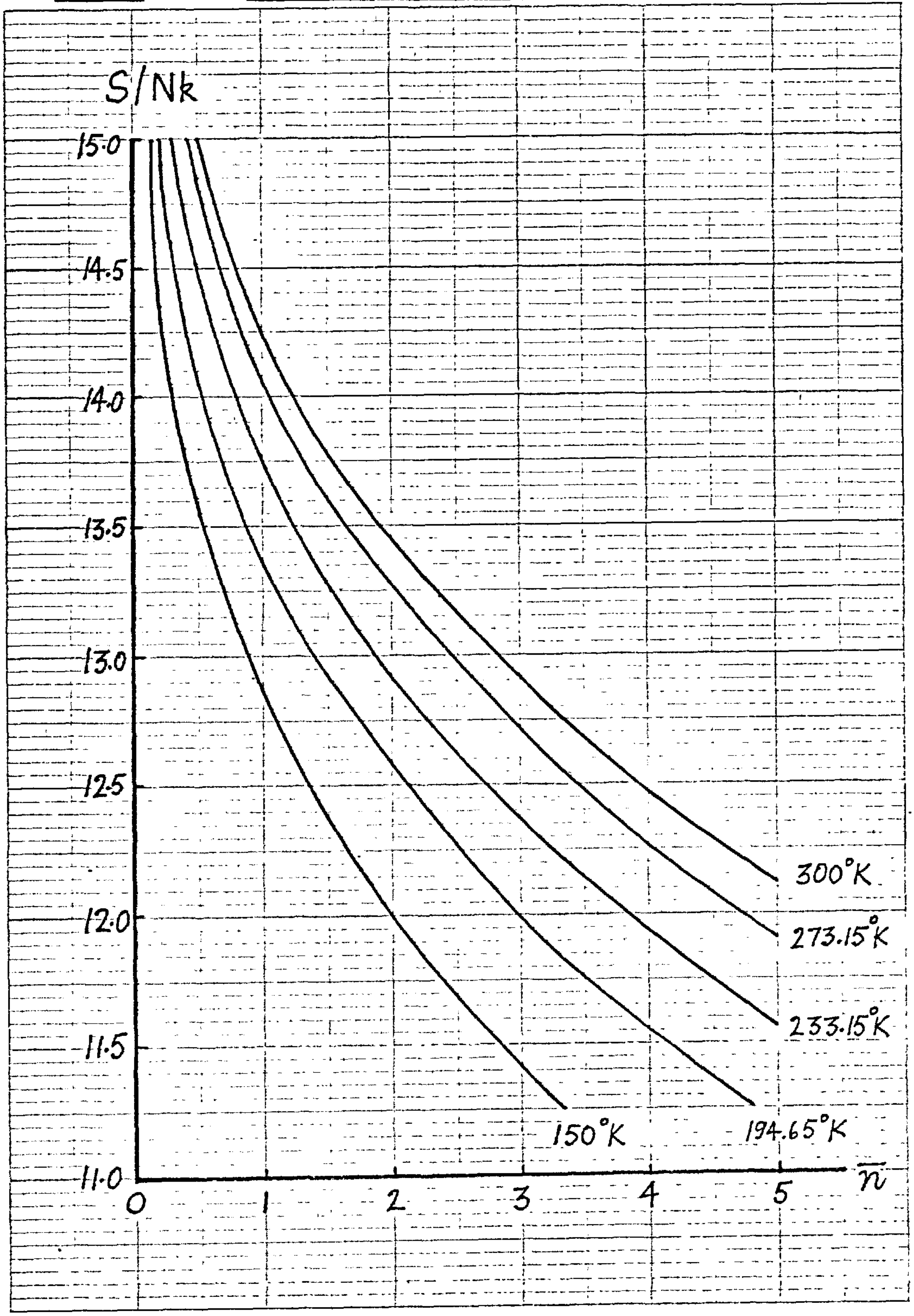
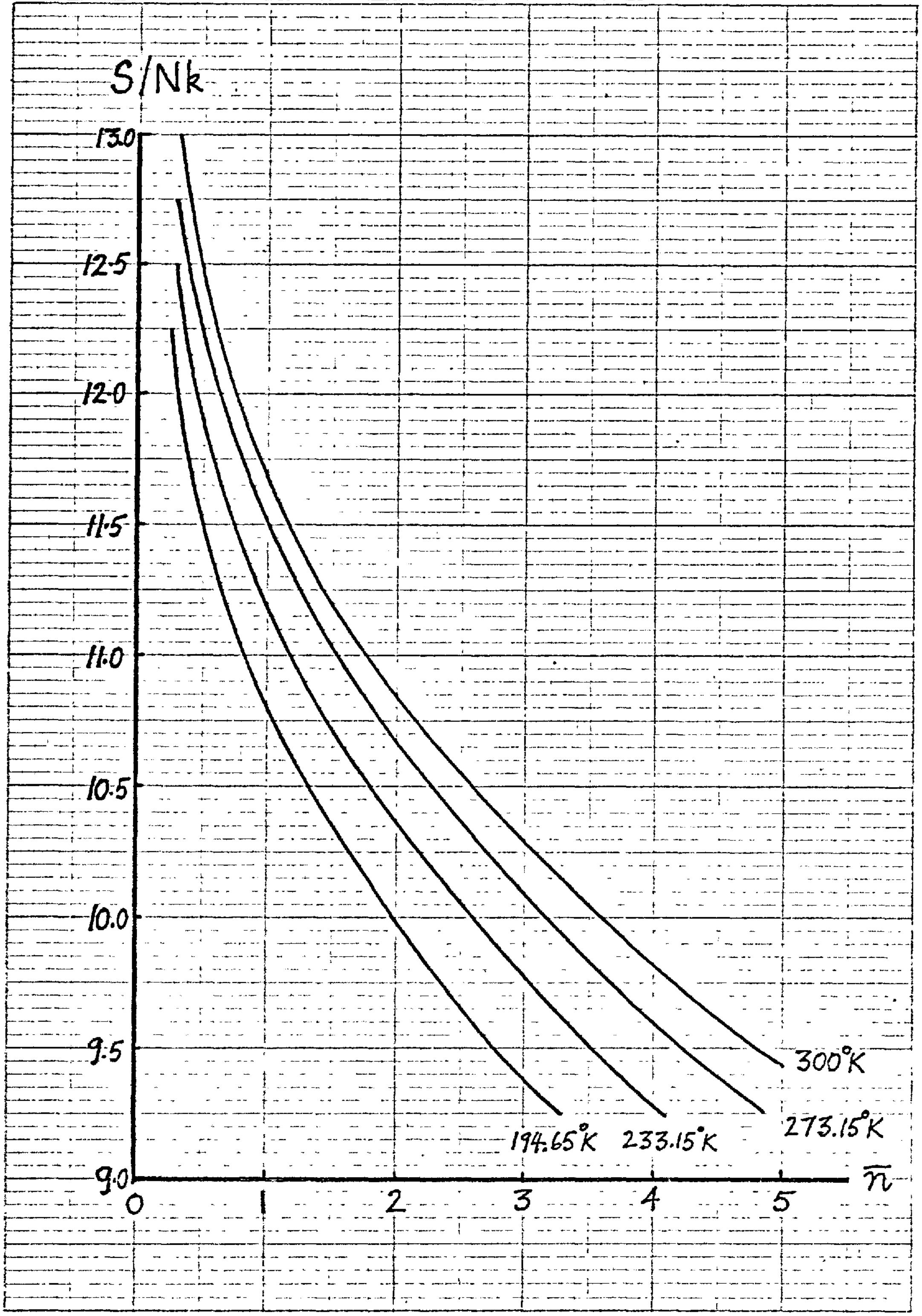


FIGURE 8.21 Entropy of Methane in Linde 5A



8.4 EXCESS FREE ENERGIES

The excess Gibbs free energies of the sorbate, ΔG, for the sorption of krypton and methane in Linde 5A, are defined by

$$\Delta G = H - TS - N\mu \qquad (8.4.1)$$

These were calculated from the exponential generating function E(T,z) by using the following direct result from (4.2.32) and (4.2.34) :

$$\Delta G = -BkT \ln E(T,z) \qquad (8.4.2)$$

All the series for E(T,z) as represented by (8.1.2) were summed on the computer up to $n = 7$. Results for $\Delta G/Bk$, $\Delta G/Nk$ and $\Delta G/NkT$ are presented in Figures 8.22-8.27.

As pointed out in Sections 4.7 and 4.8, in dealing with the microporous zeolite sorbents it is preferable not to give any direct mechanical interpretation to the excess free energy of the sorption system. Nevertheless the variation in the relative thermodynamic stability of this sorption system when $\overline{n}$ and T change can still be conveniently deduced from the behaviour of the $\Delta G/NkT$ curves.

FIGURE 8.22 Excess Free Energy of Krypton in Linde 5A

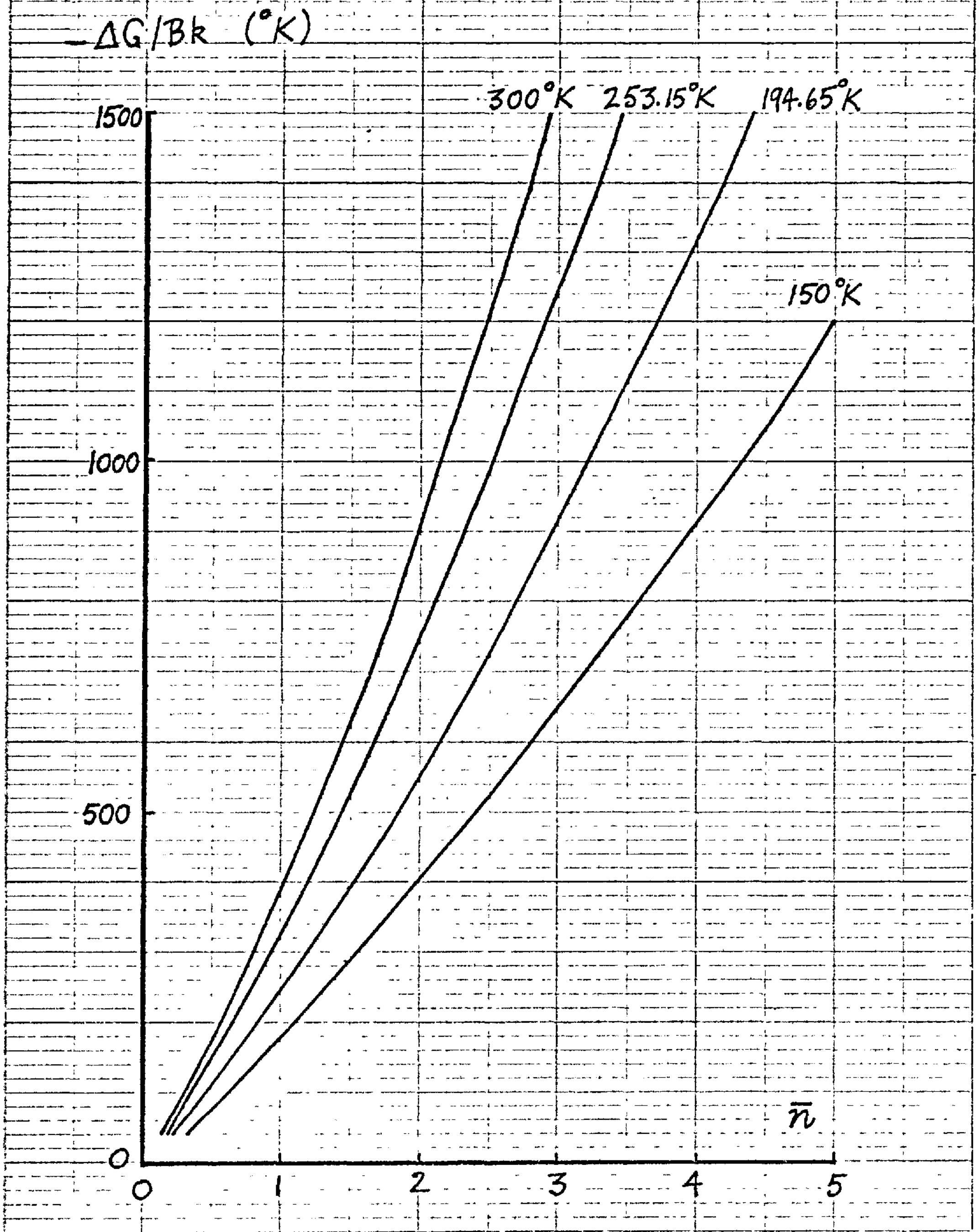


FIGURE 8.23 Excess Free Energy of Methane in Linde 5A

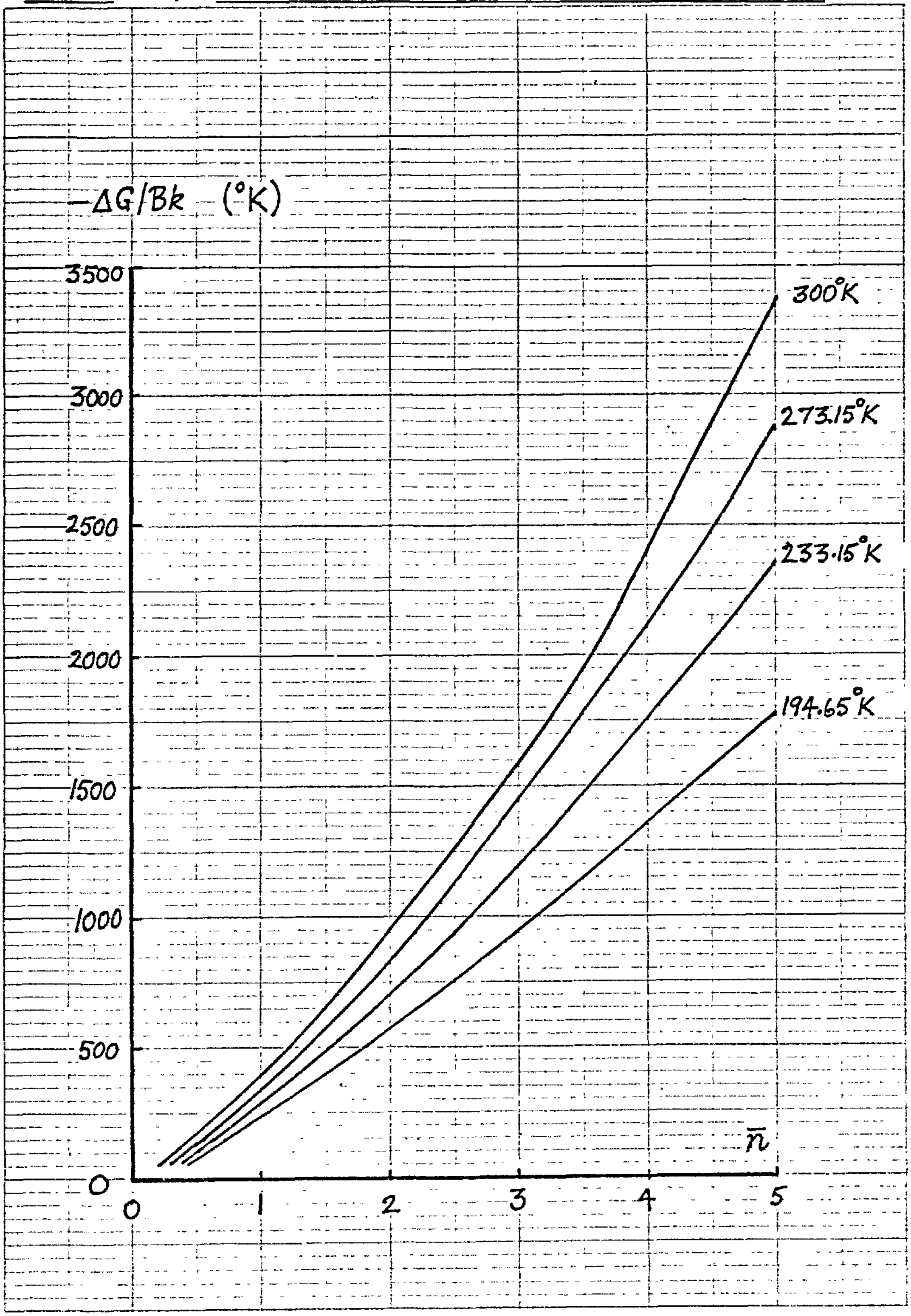


FIGURE 8.24 Excess Free Energy of Krypton in Linde 5A

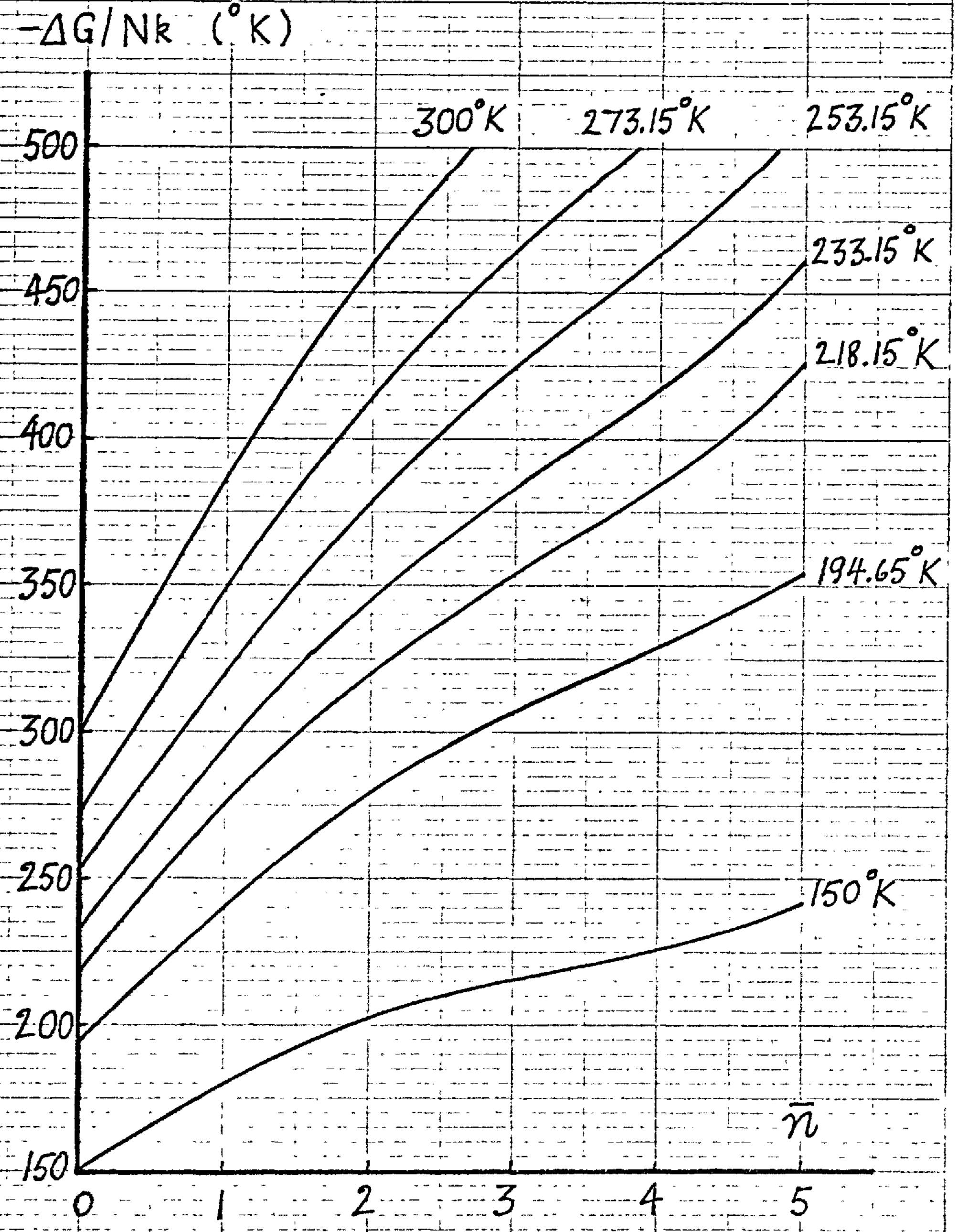


FIGURE 8.25 Excess Free Energy of Methane in Linde 5A

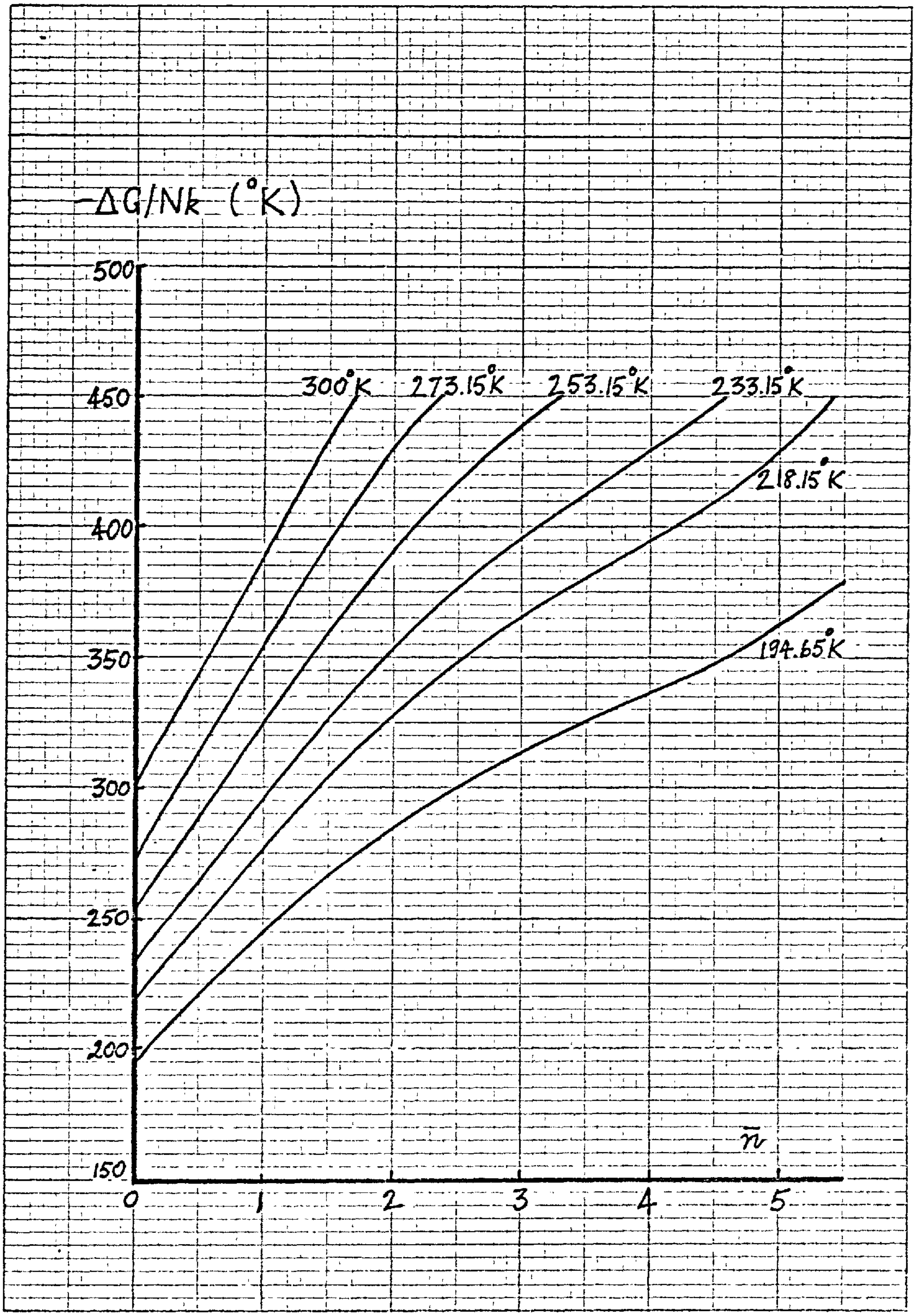


FIGURE 8.26 Excess Free Energy of Krypton in Linde 5A

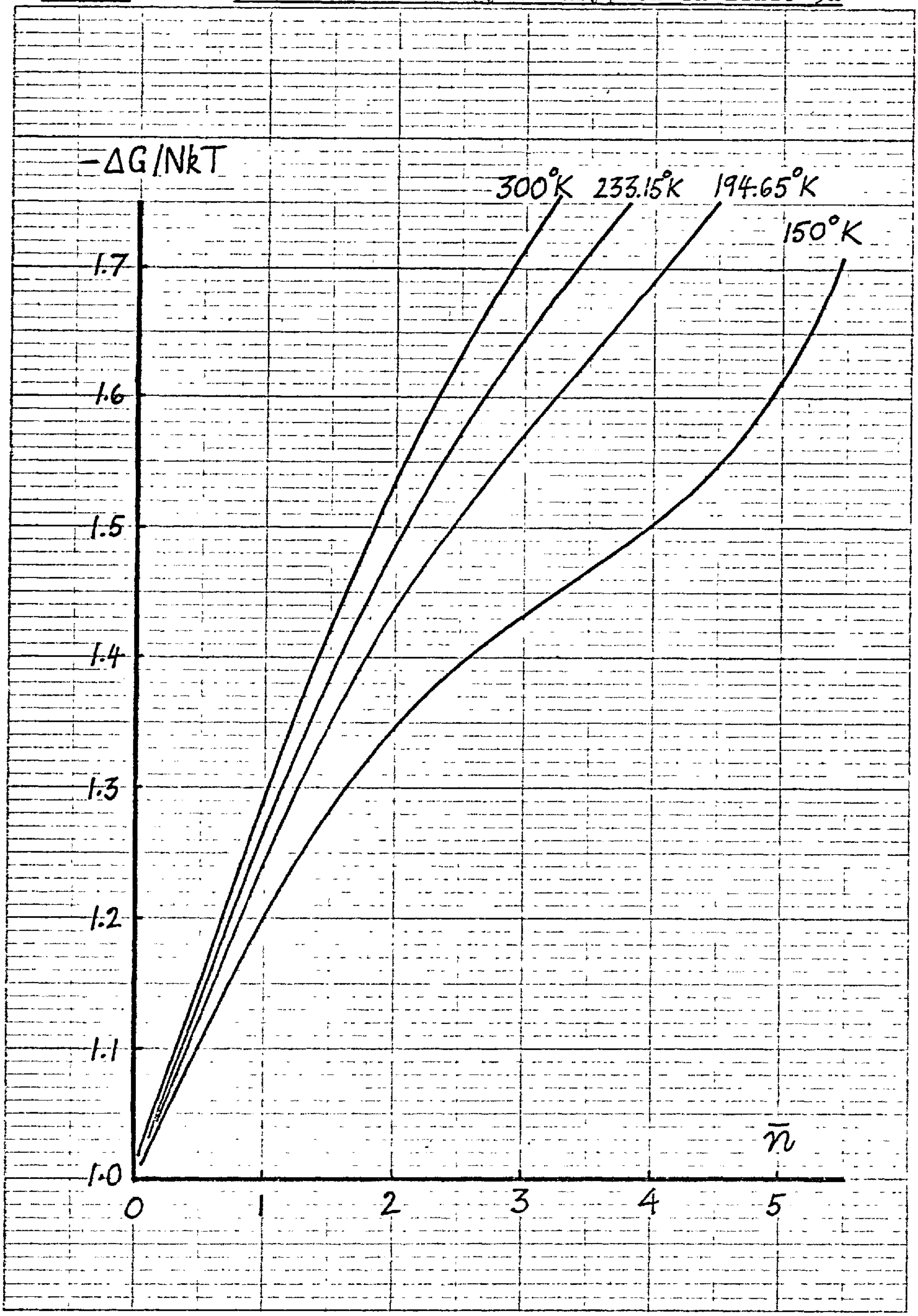
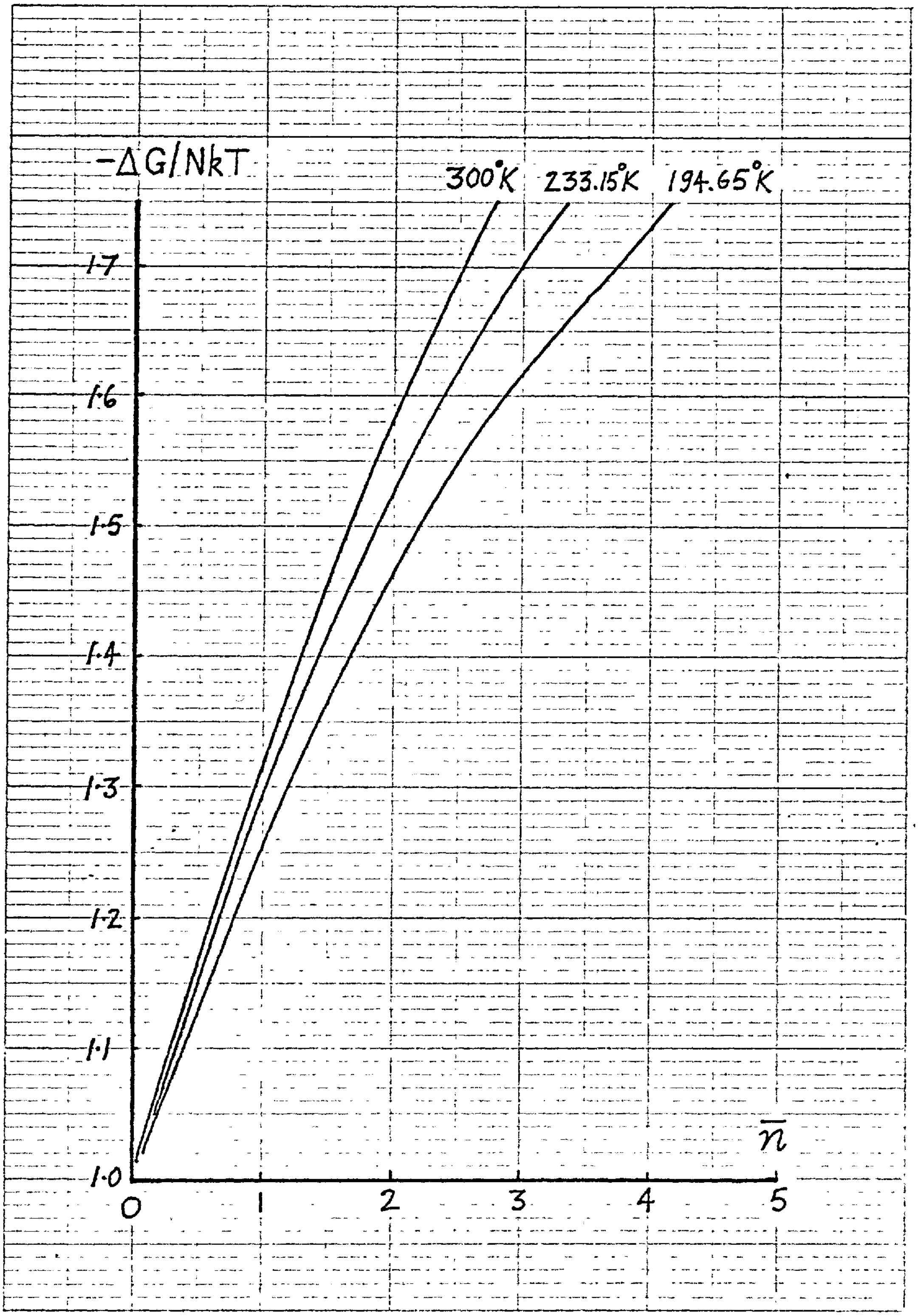


FIGURE 8.27 Excess Free Energy of Methane in Linde 5A



8.5 DIFFERENTIAL MOLAR QUANTITIES

The statistical thermodynamic formulae for the differential molar quantities in terms of the distribution function $g(n,T)$ and the variance $D(\bar{n},T)$ have already been derived in Section 4.5. The specialized forms of these for a single-component system were used to calculate the differential molar enthalpies and entropies for the sorption of krypton and methane in Linde 5A. All the summations concerned were performed on the computer up to $n = 7$. The relevant statistical thermodynamic parameters have been obtained in the previous sections. In Figures 8.28 - 8.35 results for $\frac{\partial H}{\partial N}$, $\frac{\partial S_1}{\partial N}$, $\frac{\partial S_2}{\partial N}$ and $\frac{\partial S}{\partial N}$ are presented.

The small differences between the integral and the differential molar quantities should be observed. Again, these results confirm the previous conclusions in Section 8.3 as regards the justification in using the integrated Clausius-Clapeyron equation and the entropy data for the purpose of interpreting physical behaviours of the sorbate molecules in zeolites.

FIGURE 8.28 Differential Molar Enthalpy of Krypton in Linde 5A

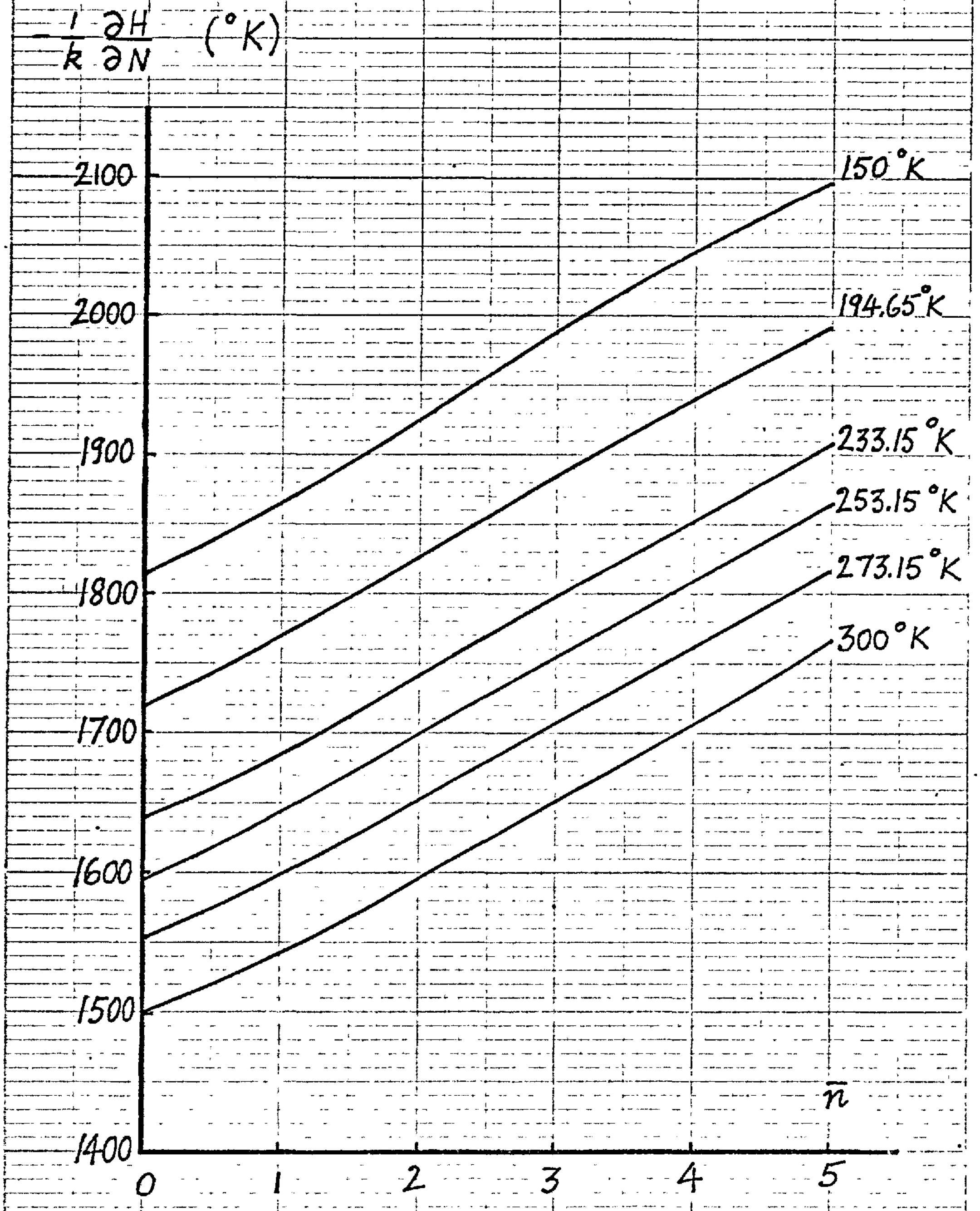


FIGURE 8.29 Differential Molar Enthalpy of Methane in Linde 5A

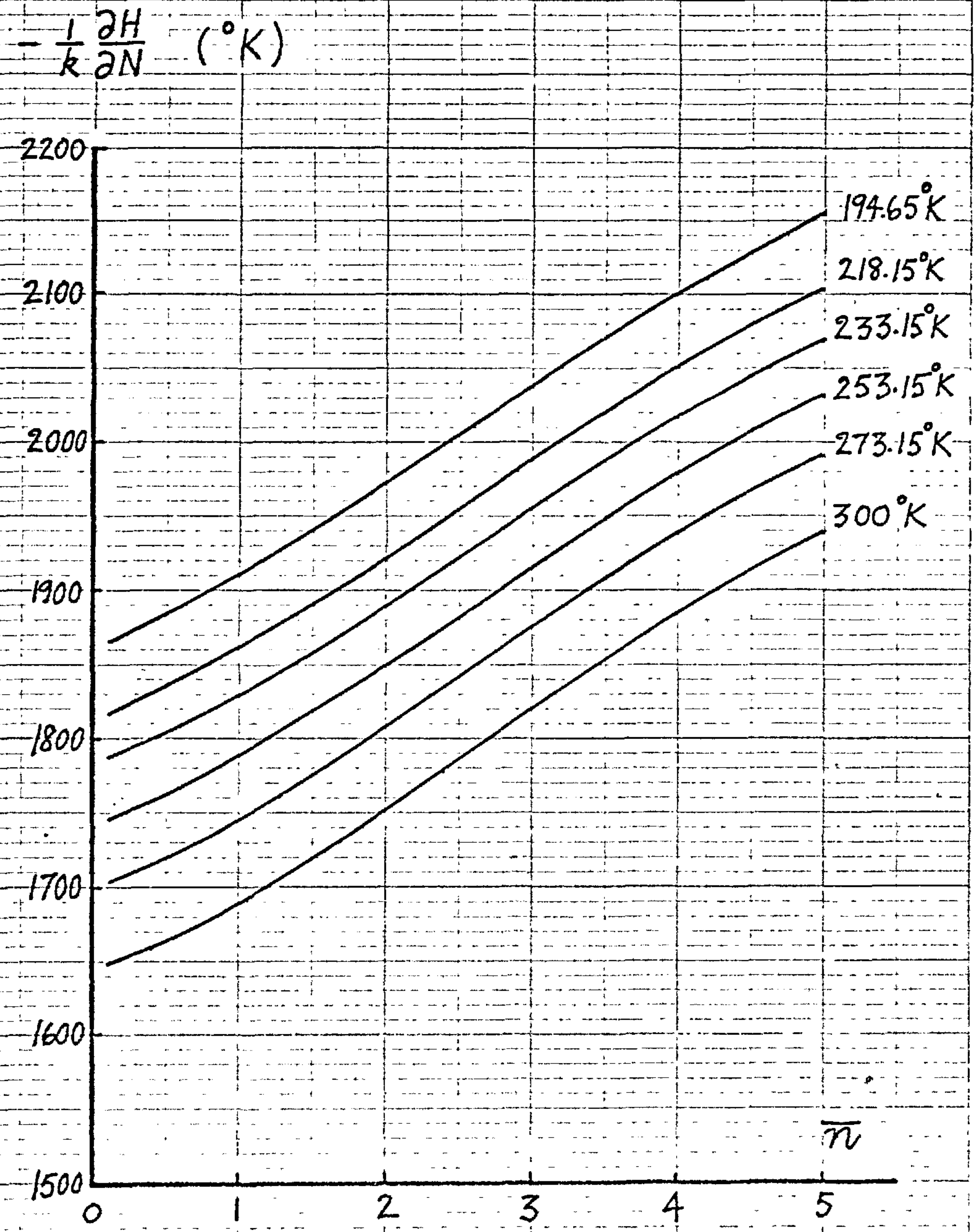


FIGURE 8.30 Differential Molar Entropy Contribution for Krypton in Linde 5A

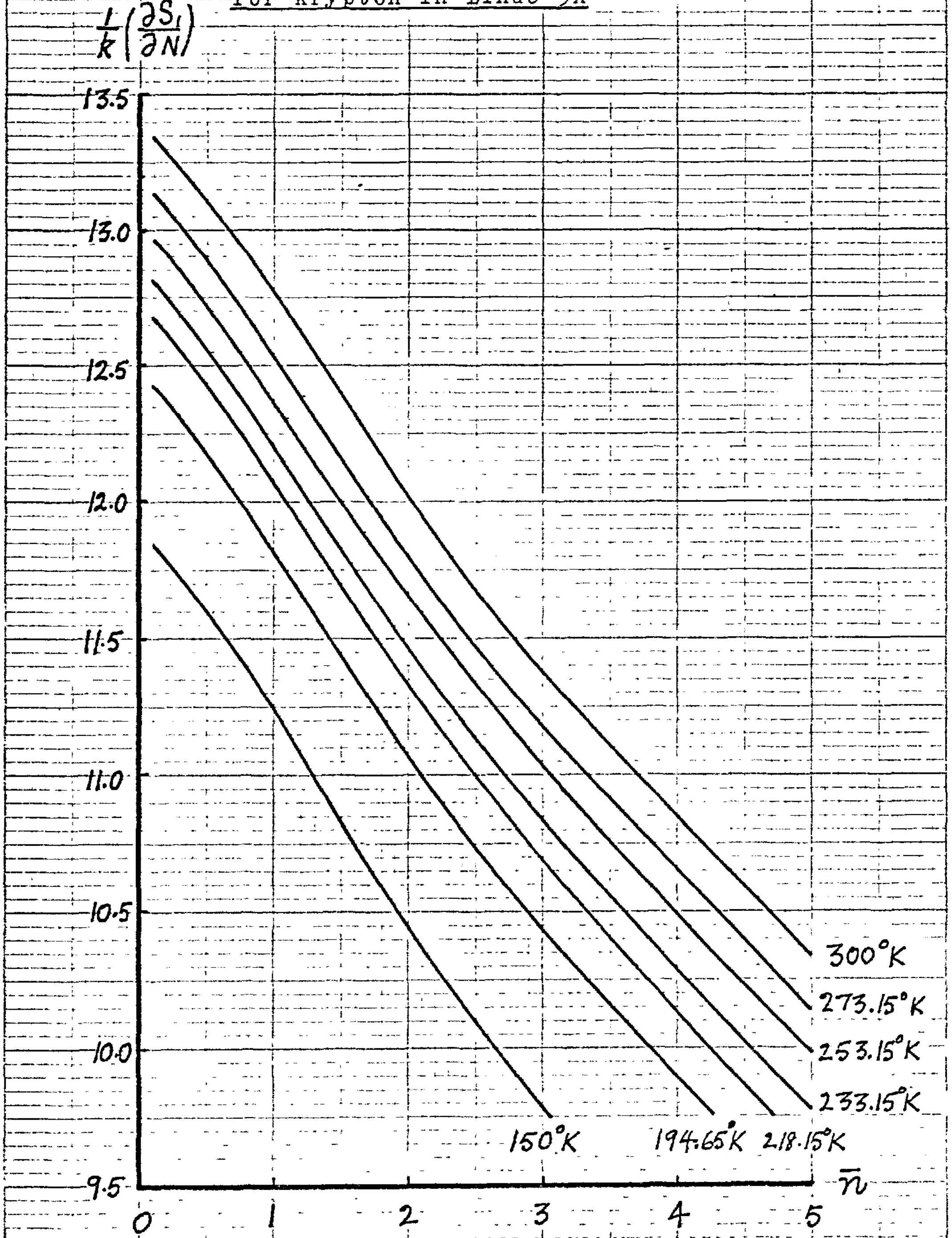


FIGURE 8.31 Differential Molar Entropy Contribution for Methane in Linde 5A

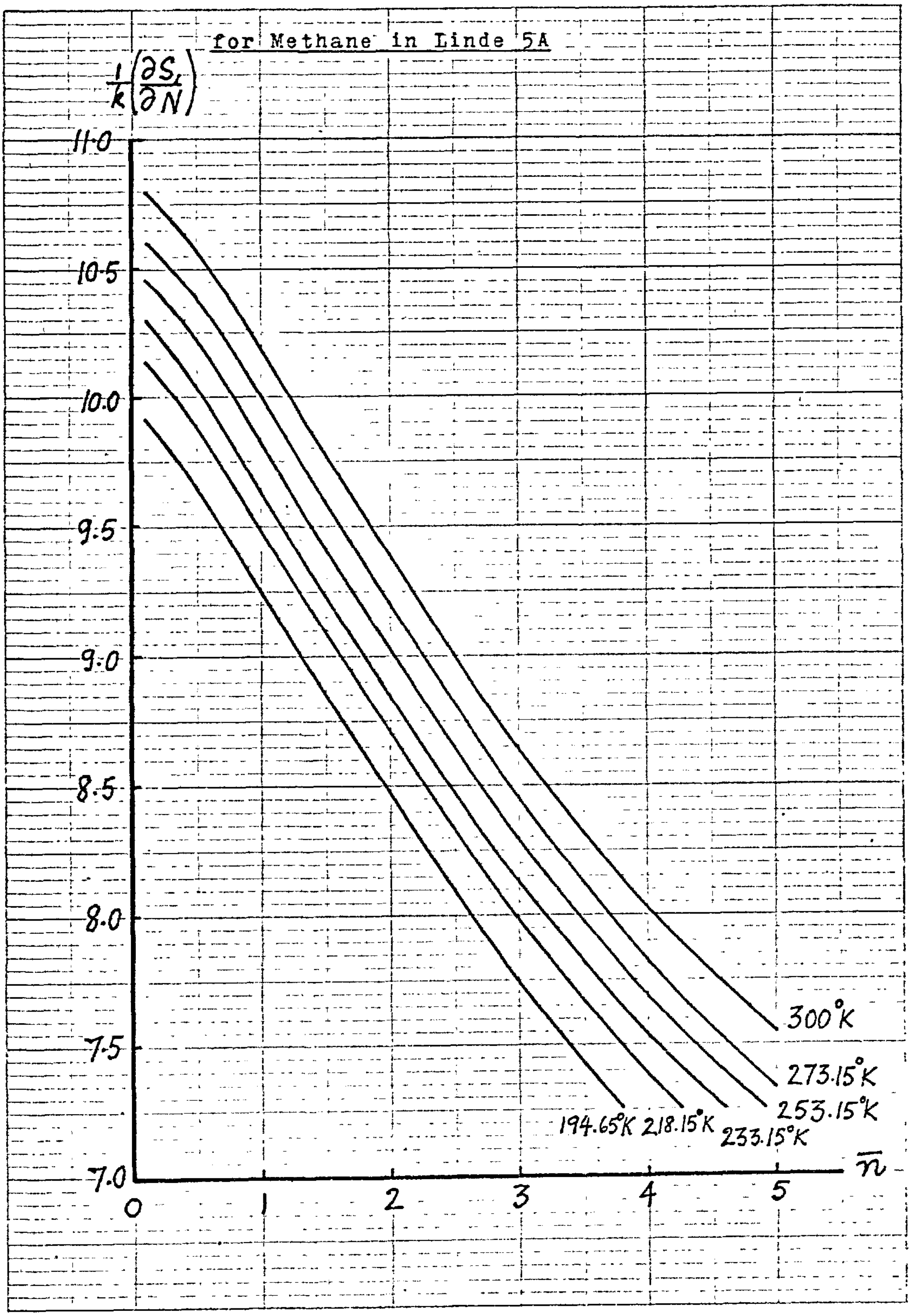


FIGURE 8.32 Differential Molar Entropy Contribution for Krypton in Linde 5A

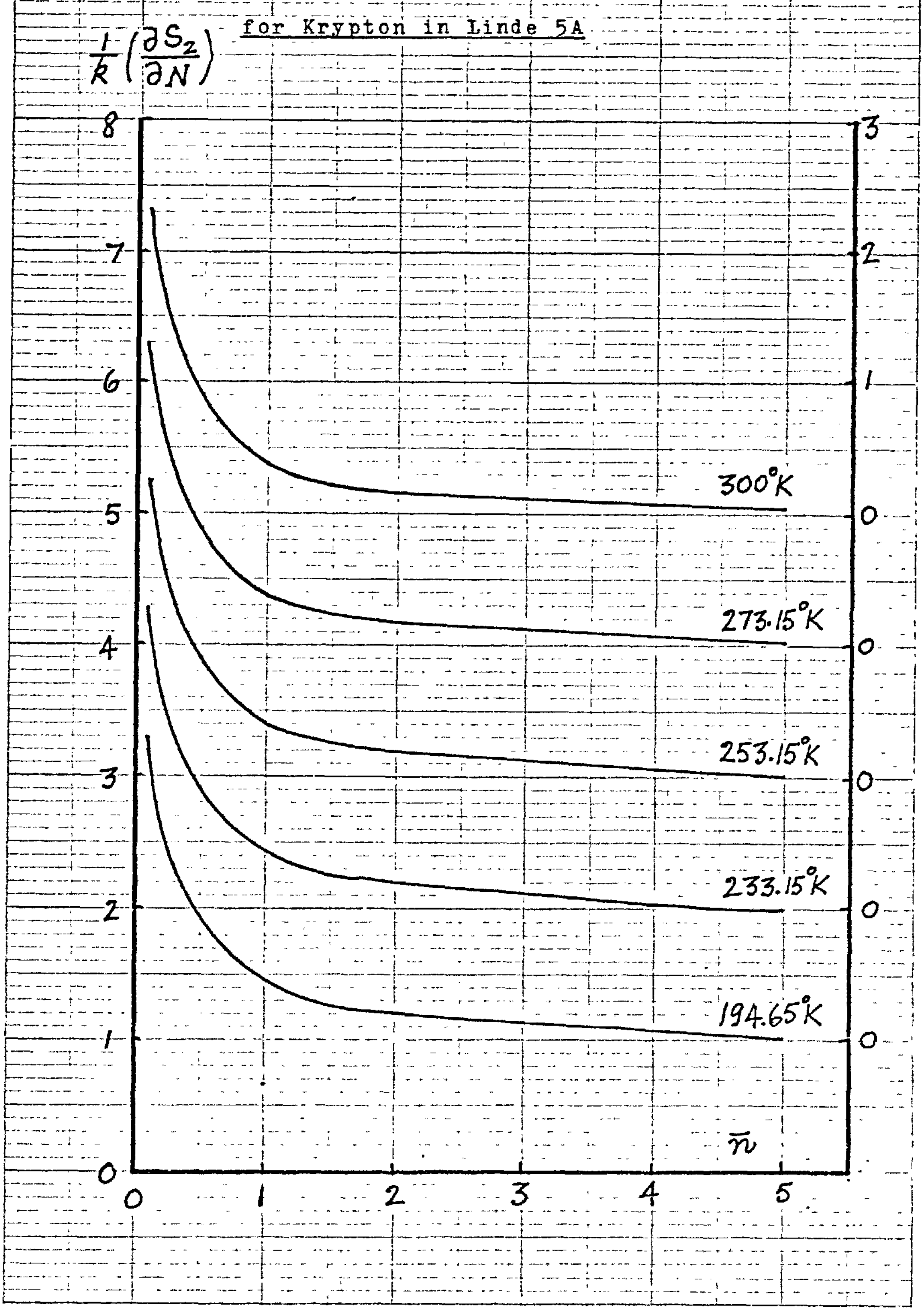


FIGURE 8.33 Differential Molar Entropy Contribution for Methane in Linde 5A

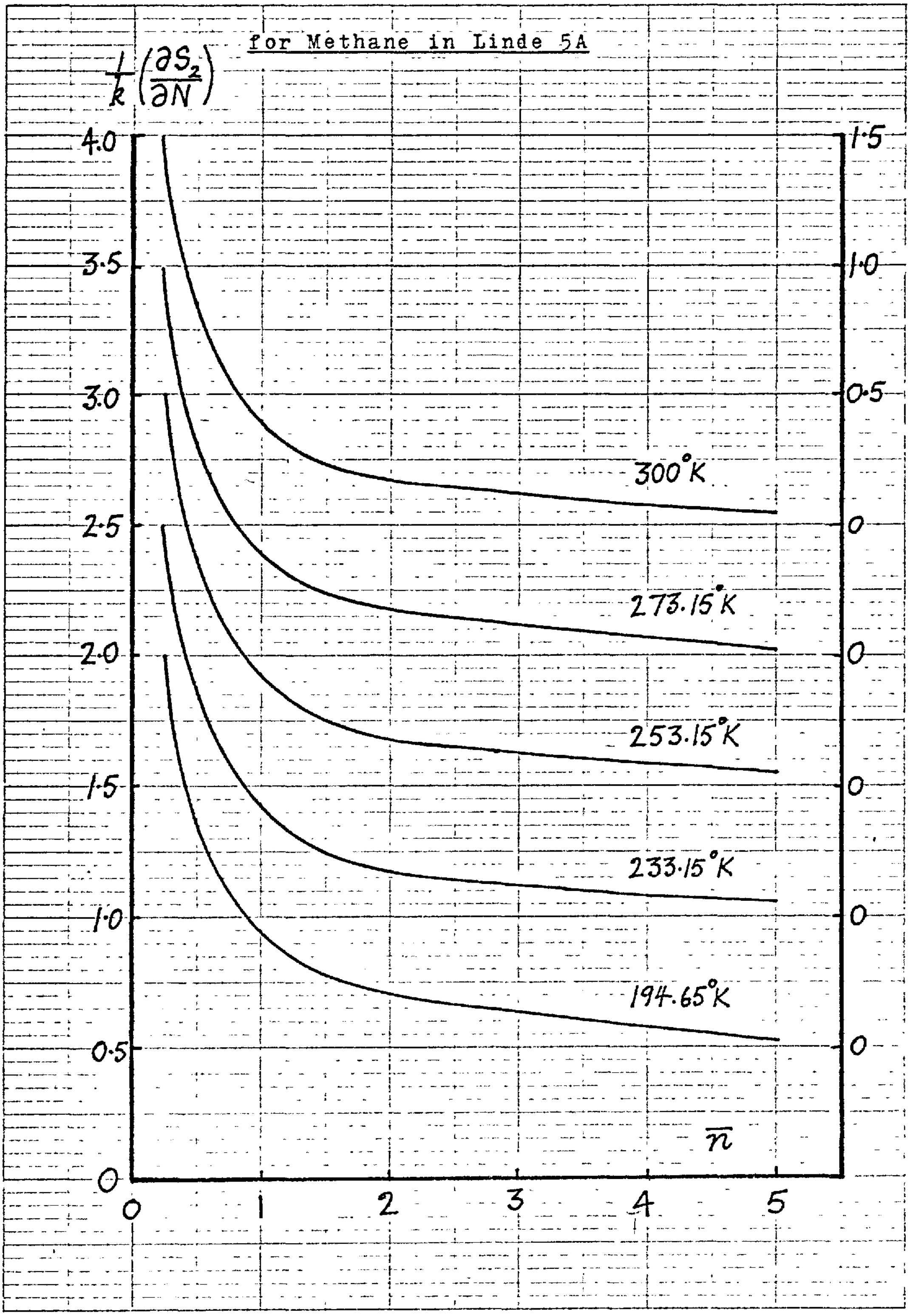


FIGURE 8.34 Differential Molar Entropy of Krypton in Linde 5A

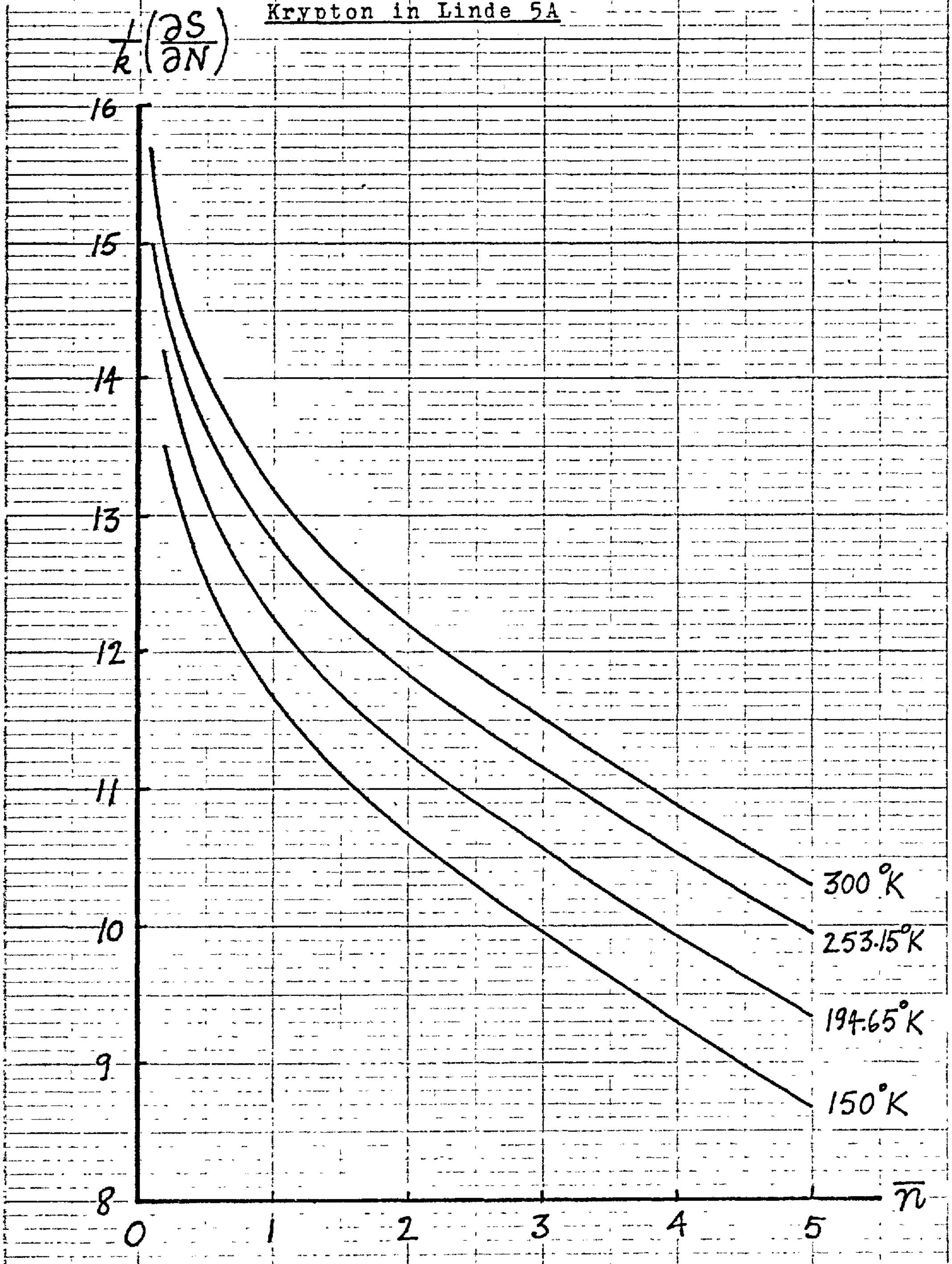
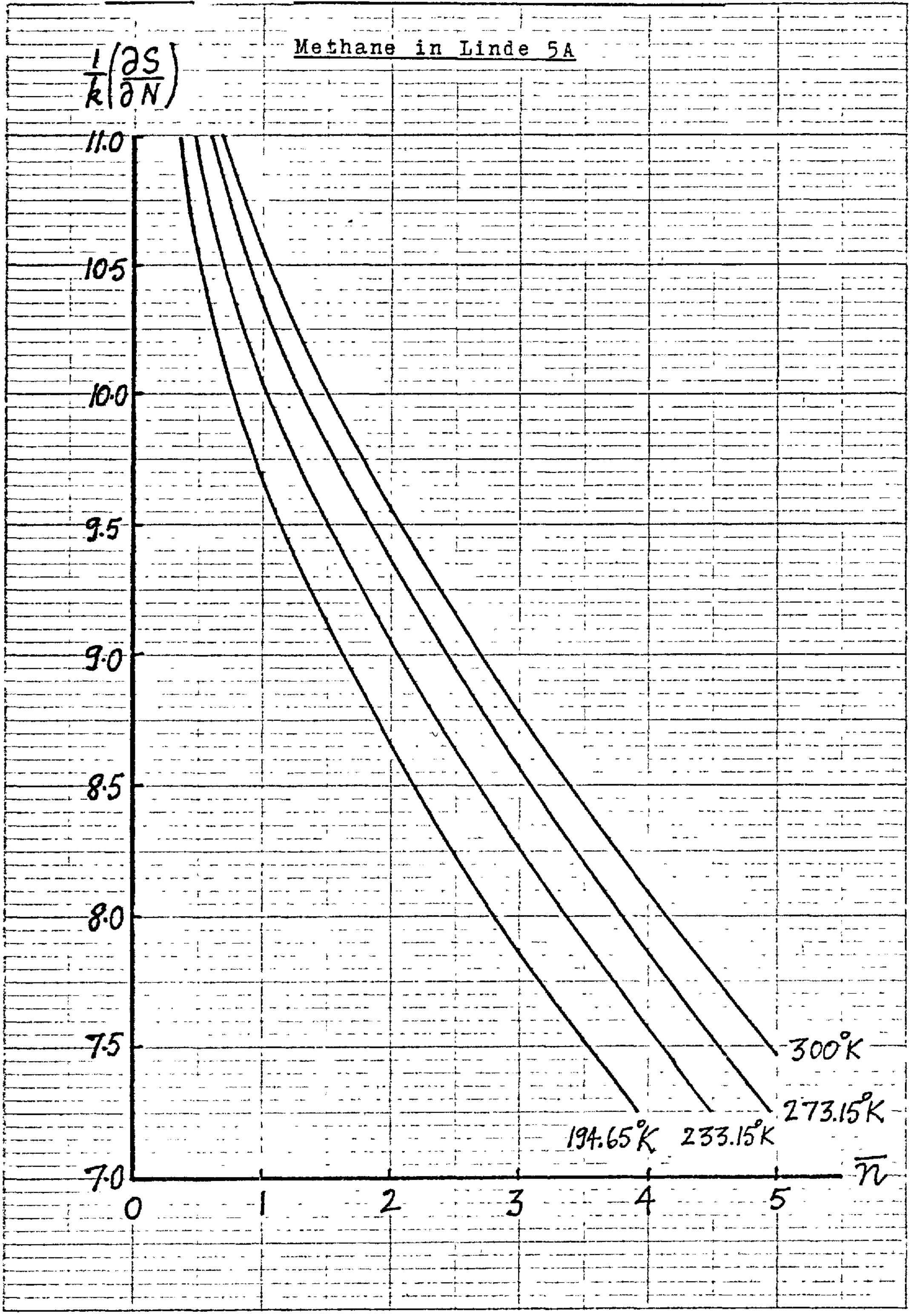


FIGURE 8.35 Differential Molar Entropy of Methane in Linde 5A



CHAPTER 9

GENERAL DISCUSSION

9.1 THE STATISTICAL THERMODYNAMIC ANALYSIS

Admittedly the complete statistical thermodynamic analysis in Chapters 2, 3 and 4 is rather formal and lengthy. Thus it seems desirable to outline the important steps of the derivations here in order to bring out the essential theory into a clearer physical perspective, especially as some familiarity with their results has already been made through a few specific applications. Again it should be emphasized that the thermodynamic system of interest consists of the sorbate in all the cavities of a macroscopic assembly, and not in just any one isolated cavity. Thermodynamic equilibrium is truly established between the sorbate system as a whole and the gas phase. Nevertheless the statistical thermodynamic properties of individual subsystems are allowed to fluctuate to any appreciable extent about their mean values. Between the subsystems in an assembly, thermal equilibrium is required; but, on the other hand, no further assumption has been made as regards material, mechanical, or any other type of equilibrium.

The canonical partition function $Z(\underset{\sim}{N},B,T)$ as given by (2.5.6) is a rigorous result for the theoretical model described. With this the statistical mechanical problem is in principle completely solved. The required thermodynamic association can subsequently be achieved by means of some standard relations, for instance (2.8.8) to (2.8.13). Mathematically, however, such an approach is not in reality very practicable, for (2.5.6) does involve complicated sums and products with awkward restrictive conditions. For this reason an attempt had to be made to find a more tractable way of effecting thermodynamic association.

First, $Z(\underset{\sim}{N},B,T)$ was re-expressed as a contour integral in (2.6.13); and expressions for the grand partition function $\Xi(B,T,\underset{\sim}{\lambda})$, and the microcanonical partition function $\Omega(B,T,U)$ were derived. However, it was then realized that none of these partition functions could be written in any form which may conveniently be differentiated or integrated with respect to the relevant thermodynamic parameters so as to give useful numerical results. More specifically, it did not appear that the exact result for $Z(\underset{\sim}{N},B,T)$ or for $\Xi(B,T,\underset{\sim}{\lambda})$ could be re-expressed as the B th power of some function that is not directly dependent on B. Empirically, of course, it is known that the asymptotic forms of both functions should behave thus for the macroscopic sorption system. A closer look at the form of (2.6.12) then immediately suggested that a physical interpretation of the exponential generating function $E(B,T,\underset{\sim}{\lambda})$ itself be made by means of a phenomenological consideration. Further analysis then reveals that $E(B,T,\underset{\sim}{\lambda})$

is in fact the quasi-grand partition function which can thermodynamically be associated with a system that is in complete thermal and material but only in partial mechanical equilibrium with its surroundings. Henceforth, the interpretation of statistical thermodynamic functions is on the whole quite straightforward.

A probability density function $g(\underset{\sim}{n},T)$ was then introduced in Section 4.3. This turns out to be of great help in the subsequent attempt to give a molecular statistical interpretation to the sorption phenomena. In Chapters 7 and 8 a quantitative study was made of certain specific sorption systems. Following these results, it is hoped that some basic questions concerning the nature and degree of localization of the sorbate in zeolite have been satisfactorily answered. Attention should again be drawn to the fact that the 'averaged' statistical thermodynamic quantities, such as $\bar{n}_s$, $\bar{u}$ and $\bar{s}$, are not just some inherent properties of any particular subsystem. The presence of such quasi-independent subsystems in a localized assembly necessarily implies an averaging over this assembly in a very specific manner.

As regards the true significance of the function $E(B,T,\underset{\sim}{\lambda})$, which appears to be an essential part of the present theoretical studies, some further remarks should now be made. In this thesis, $E(B,T,\underset{\sim}{\lambda})$ has been given a statistical thermodynamic interpretation. This was done essentially by identifying the environment of the molecular system and the relevant statistical mechanical ensemble for which it is the appropriate partition function. The role of $E(B,T,\underset{\sim}{\lambda})$ here can accordingly be compared with those of the grand partition function in its many applications to more familiar problems of statistical mechanics. The real reason for choosing a particular partition function to deal with is certainly one of mathematical convenience. So in this sense the use of $E(B,T,\underset{\sim}{\lambda})$ in the foregoing analysis should not cause any undue difficulty. As applied to the case of sorption in zeolites, the statistical thermodynamic interpretation of $E(B,T,\underset{\sim}{\lambda})$ can be seen to be physically very reasonable. This is particularly so in view of the fact that the incomplete mechanical equilibrium is also implied by this partition function. Thus, it is hoped that in the near future partition functions of the type $E(B,T,\underset{\sim}{\lambda})$ should find further useful applications in solving other statistical thermodynamic problems which similarly involve some localized assemblies of quasi-independent subsystems.

On the other hand, the exponential generating function $E(B,T,\underset{\sim}{\lambda})$ may also be regarded merely as a mathematical device. Any statistical thermodynamic interpretation is then effected through the canonical and the microcanonical partition functions. In this approach, the very specific way of coupling together a large number of quasi-independent subsystems of the assembly is simply reflected by the manner in which the canonical partition function of the assembly is related to the Blissard calculus of the exponential generating functions with the canonical partition functions of individual subsystems as appropriate coefficients.

It may be primarily a matter of taste which of the two points of view mentioned above is actually adopted. In principle, both are equally valid, provided of course that the various assumptions made and the true ranges of applicability to the particular system under study are fully understood. Again, this situation recalls a very similar problem concerning the use of the grand partition function for the purpose of analyzing any specific statistical model. It is well known that the introduction of a grand partition function into such a theory can normally be circumvented by applying the Darwin-Fowler method of steepest descents. Mathematically speaking, there is no real basic difference between these two approaches. Nevertheless, in practice, one method may appear to be aesthetically more satisfying than the other. In all cases the analyticity of the complex integrands concerned and the existence of the relevant grand partition functions are closely interrelated. Certainly the grand partition function is nothing more than an ordinary generating function of the sequence of individual canonical partition functions. The steepest descent also corresponds very well with the picking out of the largest term in the grand partition function.

Ideally, therefore, the appropriate choice between any such alternatives should always be based upon their relative merits, especially as regards simplicity and convenience. Physically, however, it may appear that one particular set of environmental variables associated with the theoretical model of interest is definitely more realistic than any other statistically equivalent set. Under such a circumstance the choice should not be made quite arbitrarily.

In the present work it has been found more reasonable, as well as more informative, to attach a physical meaning to $E(B,T,\underset{\sim}{\lambda})$. Mathematically, this is also the most convenient partition function to deal with in the subsequent analysis. In statistical mechanics, it can frequently be observed that the mathematically simplest and the most elegant description of a theoretical model is also a description that find the most direct physical interpretation. Thus, it is hoped that this remark has been illustrated by the present studies of the sorption in zeolites.

9.2 PHYSICAL ASSUMPTIONS

It is now appropriate to examine certain physical assumptions which have been made implicit in the foregoing theoretical studies.

(a) Mobility of the Sorbate Molecules

The assumption that the sorbate molecules can move about and be exchanged freely is certainly very reasonable as regards the sorption of non-polar molecules in zeolites, when the openings of the cavities concerned and their connecting channels are comparatively large. In these cases the sorbate molecules can travel to every part of the system without any need for large thermal excitations. The relevant potential barriers can be expected to affect various kinetic phenomena, such as the diffusion of molecules in and through the microporous crystals; but these should have no appreciable influence upon any equilibrium thermodynamic quantity that characterizes the assembly as a whole.

Sorption of large polar molecules at relatively low temperatures, on the other hand, may involve specific molecular interactions. (Smith 1967) This can indeed present a rather difficult problem. The polar molecules are firmly attached to the cations near the openings of zeolite cavities; and as a consequence some high energy barriers are introduced, which oppose the passage of additional sorbate molecules into these cavities. Under such circumstances some complication may arise from the metastable equilibrium. In particular it is known that the true equilibrium sorption of non-polar sorbate in certain zeolites can be markedly impeded by presorption of highly polar molecules, even when the concentration of the polar sorbate is well below saturation. (Barrer & Rees 1954a, 1954b, Rees & Berry 1967) In interpreting the sorption phenomena, equilibrium statistical thermodynamics can correctly be applied only when the time involved in attaining the true equilibrium is not too long in comparison with the time of physical measurements. So the above gives a natural limitation to the range of applicability of the present theoretical model.

(b) Quasi-independence of a Subsystem

At moderate temperature and sorbate concentration, any molecule sorbed in a specific cavity is expected to spend an appreciable length of time within that cavity before it eventually enters a neighbouring cavity or else goes into the gas phase. No doubt, this molecule, once it is sorbed, interacts with all the other molecules of the subsystem, with the cavity wall, and with the rest of the environment outside that cavity. The Boltzmann-averaged interaction energy of the subsystem can be calculated, and it is physically reasonable to suggest that this averaged energy should be almost independent of the location of the cavity concerned within the assembly. Consequently, as far as the interaction energy of a subsystem is concerned, the presence of a specific composition set in this subsystem at a given instant should have no appreciable influence on the probability for any other subsystem of the assembly to have any one of the possible composition sets in it. In other words, the occupancy numbers of different subsystems do not significantly correlate. Here it is recalled that in the case of sorption of krypton and methane in Linde 5A all contributions from the 'background' potentials actually amount to less than 10 % of the total potential of a subsystem. (Section 6.5)

It should be emphasized that the individual subsystems are considered as independent only in the very specific sense just mentioned. And for this reason it is preferable to use the term 'quasi-independence' to describe each subsystem. Indeed, when a large number of the subsystems are coupled together to form an assembly, they do influence each other, albeit in an indirect manner, through the statistical behaviour which necessarily results from the various physical boundary conditions that have been imposed on the whole assembly. The implication of combining completely independent subsystems in a localized assembly, on the other hand, has already been discussed in Section 4.4.

A notable consequence of the quasi-independence of each subsystem is that the detailed arrangement of such subsystems in the assembly does not enter into any subsequent statistical thermodynamic formulae. Whether the sorption cavities are actually arranged in a simple cubic array, as in the case of Linde 5A, or otherwise, is therefore immaterial. As regards the arrangement of the cavities within any assembly, the only fact that is directly relevant to the present theoretical model is that, in a macroscopic unit of the sorbent, all the cavities are fixed in space and are interconnected in such a way that every one of them is accessible to the sorbate molecules from all the other cavities. Certainly this requirement is satisfied by Linde 5A.

(c) Rigid Sorbent Structure

In the foregoing the sorbent has been considered as an inert solid, such that there is no dimensional change accompanying any variation in the sorbate concentration. As far as the sorption of non-polar molecules in Linde 5A is concerned this is certainly a very reasonable assumption. It is known that the dimensions of Linde 5A framework are almost independent of the concentration of a wide variety of sorbates, such as SO_2, Kr, Xe, Br_2 and I_2. X-ray diffraction studies have shown that the movements of the O anions in this zeolite are not greater than 0.1 Å. (Smith 1967) In general, however, the aluminosilicate frameworks of different zeolites have widely varying geometrical stabilities, and the extents of their reversible distortion can also vary considerably. For example, the O anions of the 8-membered rings in chabazite can move as much as 0.5 Å. (Fang & Smith 1964) Some zeolites may even collapse irreversibly on dehydration.

Of even more significance is the fact that the exchangeable cations can move in response to the sorbate molecules. This effect is expected to be negligible in the case of sorption of krypton and methane in Linde 5A; but in the cases of sorption of highly polar molecules it can be quite important. As the polar molecules enter a sorption cavity the cations tend to move away from the framework O anions to some positions permitting the most favourable contact with the sorbate molecules.

(d) Internal States of Sorbate Molecules

In the present study the internal states of sorbate molecules have not been considered explicitly. It is assumed that the rotational, vibrational and electronic states of these molecules do not change on sorption. As regards krypton and methane this assumption appears to be reasonable. However, the same cannot be expected to apply in other cases where there exist specific molecular interactions with the sorbent. More specifically, it is clear that the relatively simple potential functions which have been chosen to represent the sorbate-sorbate and sorbate-sorbent interactions in Chapter 6 are quite inadequate for the purpose of a detailed statistical mechanical study in such cases.

9.3 PHENOMENOLOGICAL APPROACHES

Thermodynamic measurements have already been made on sorption systems of a wide variety of sorbates in zeolites. (Kiselev & Lopatkin 1967) Equilibrium thermodynamic properties which have been extensively studied include sorption isotherms and heats of sorption. The interpretation of these experimental data is normally based on the choice of a theoretical equation of state that truly describes the sorbate in the system under study. (Steele 1966) Of course, many equations of state are available, each of which describes a particular molecular statistical model. The choice can thus be difficult, especially when quite different models can lead to rather similar theoretical isotherms. Fortunately, in the case of sorption in zeolites the crystal structures of these sorbents are known with accuracy. As a result the reasonable choice of a molecular model for statistical mechanical studies is conveniently restricted.

It is well known that accurate measurements of the heats of sorption are difficult. So the test of a specific theoretical model depends largely on isothermal data alone. However, the quality of fit between an experimental and a theoretical isotherm is not in itself always an adequate proof of the applicability of the chosen molecular statistical model. Nor is it any guarantee that the physical interpretation of the parameters obtained from the curve-fitting process is necessarily meaningful. Thus, in practice, a detailed interpretation of a set of sorption data is convincing only after quite extensive testing of experiment against theory, over a wide range of temperature and sorbate concentration. Indeed the theoretical model that has been chosen here appears to be very appropriate for the sorption systems studied. But, strictly speaking, any satisfactory conclusion concerning its validity could not be drawn until after more detailed analyses and comparisons of theoretical results and experimental data in the future.

In studying the sorption in zeolites the nature of localization of the sorbate should be of particular interest. In this work the molecular distribution functions of specific subsystems and their distribution densities within the assembly could be conveniently deduced from the knowledge of relevant molecular and atomic parameters. As regards the sorption of krypton and methane in Linde 5A these theoretical results seem to give very reasonable physical pictures. However, as no experimentally determined data are available for direct comparison, the validity of the molecular statistical model concerned has not yet been subjected to a critical test. Quantitative studies of the localization cannot in such cases depend entirely on equilibrium thermodynamic data, for as a rule thermodynamic properties are not very sensitive to the detailed molecular arrangements.

Thus it is clear that more direct data concerning the localization of sorbate molecules within the zeolite sorbents are at present needed. In this connection it should be mentioned that the following techniques are likely to give valuable quantitative results in the future: X-ray and neutron diffractions, thermal neutron scatterings, dielectric measurements, and various spectroscopic methods. Moreover, since the present equilibrium statistical thermodynamic analyses give no indication of the time-scales involved in the sorption phenomena, some of the above techniques should at least be useful as supplementary studies.

9.4 CONCLUDING REMARKS

The most remarkable results which have emerged from the foregoing theoretical studies are those concerned with interpreting the nature of localization of the sorbate molecules within the zeolite sorbent. The manner and extent of such localization was studied quantitatively, and for this purpose some useful concepts such as the molecular distribution functions and the distribution densities were introduced. In sorption studies it is normal to speak of a sorbate system that is completely localized, or of a two-dimensional sorbate fluid, with or without significant sorbate-sorbate interactions. However, the foregoing results have shown how such qualitative pictures may not always be adequate for the true understanding of the sorption phenomena. In particular one should have in mind the gradual changes of behaviour of the sorbate following some slight variations of temperature and sorbate concentration.

In principle, the essential statistical mechanical problem associated with the molecular statistical model chosen for the multicomponent sorbate in zeolite has been completely solved. On the other hand, in applying these theoretical results to any specific sorption system, there remain some major difficulties. First, the required knowledge of suitable parameters for the atomic and molecular interactions is still largely inadequate. Then, the computation for any specific subsystem is extremely time-consuming. Even with many simplifying assumptions for the case of a one-component system in an assembly of identical Linde 5A cavities, the theoretical investigation of statistical thermodynamic properties was in practice limited by the present computing capacity to the cases of fairly low sorbate concentrations, except as regards the internal energy of a subsystem. When some detailed information concerning the localization of sorbate molecules was needed, the mathematical difficulty was even more serious. However, as the computing facilities are likely to be much improved in the future, it is hoped that further theoretical studies of more complicated cases of the sorption in a wide variety of zeolites will be attempted following the techniques of the present studies.

APPENDIX 1 THE CONFIGURATION INTEGRAL Q_2^o

Consider the subsystem shown in Figure A1 of two identical hard-sphere molecules of collision diameter σ in a spherical cavity of radius a and of effective wall thickness σ'. The free radius of this cavity is $R = a-\sigma'$. Let $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ be the position vectors of the two molecules from cavity centre. The configuration integral for this subsystem is

$$Q_2^o = \int d\underset{\sim}{r}_1 \int d\underset{\sim}{r}_2 \exp\left[-U(\underset{\sim}{r}_1,\underset{\sim}{r}_2)/kT\right] \qquad (A.1.1)$$

where each integration is carried out over the entire cavity volume.

In view of the hard-core cut-off potentials, the interaction energy $U(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$ concerned vanishes for all configuration sets without molecule-molecule or molecule-wall overlap, but is infinite otherwise. Thus for all positive definite temperatures the integrand in (A.1.1) can only take a value of either 1 or 0. Now take molecule 1 as the reference molecule which can be in any general position within the spherical space of radius R. Consider all configurations of molecule 2 for which there is no overlap.

When $R \geq \sigma$, it is clear from Figure A1 that Q_2^o can be written as a sum of two integrals with respect to the variable r (the magnitude of $\underset{\sim}{r}_1$), the integrations with respect to the other five coordinates having been carried out explicitly,

$$Q_2^o = \int_0^{R-\sigma} \left[\frac{4}{3}\pi R^3 - \frac{4}{3}\pi\sigma^3\right] 4\pi r^2 dr \quad + \int_{R-\sigma}^{R} \left[\frac{4}{3}\pi R^3 - \frac{4}{3}\pi\sigma^3 + \Delta\right] 4\pi r^2 dr \tag{A.1.2}$$

where Δ is the excluded volume of molecule 2.

Now Δ is given by the volume difference of two segments of the spheres of radii R and σ made by the common plane at distances x and x+r respectively from the centres of these spheres, where $x = (R^2 - \sigma^2 - r^2)/2r$. Thus

$$\begin{aligned}\Delta &= \frac{\pi}{3}\left[2\sigma^3 - 3\sigma^2 x + x^3\right] - \frac{\pi}{3}\left[2R^2 - 3R^2(x+r) + (x+r)^3\right] \\ &= \frac{\pi}{4r}(R^2-\sigma^2)^2 - \frac{2\pi}{3}(R^3-\sigma^3) + \frac{\pi r}{2}(R^2+\sigma^2) - \frac{\pi}{12} r^3 \qquad \text{(A.1.3)}\end{aligned}$$

for $R-\sigma \leq r \leq R$.

The first integral in (A.1.2) can be directly integrated. Substitution of (A.1.3) in the second integral followed by an integration and some simple algebraic manipulation then lead to the desired result :

$$\begin{aligned}Q_2^o &= \frac{16}{9}\pi^2(R^3-\sigma^3)(R-\sigma)^3 + 4\int_{R-}^{R} \left[\frac{2}{3}\pi(R^2-\sigma^3)r^2 + \frac{\pi r}{4}(R^2-\sigma^2)^2 \right. \\ &\qquad \left. + \frac{\pi}{2}r^3(R^2+\sigma^2) - \frac{\pi}{12}r^5\right] dr \\ &= \pi^2\left[\frac{16}{9}R^6 - \frac{16}{9}R^3\sigma^3 + R^2\sigma^4 - \frac{1}{18}\sigma^6\right] \qquad \text{(A.1.4)}\end{aligned}$$

It can be shown by a slightly variant geometrical consideration that this result is also valid when $\frac{1}{2}\sigma \leq R \leq \sigma$.

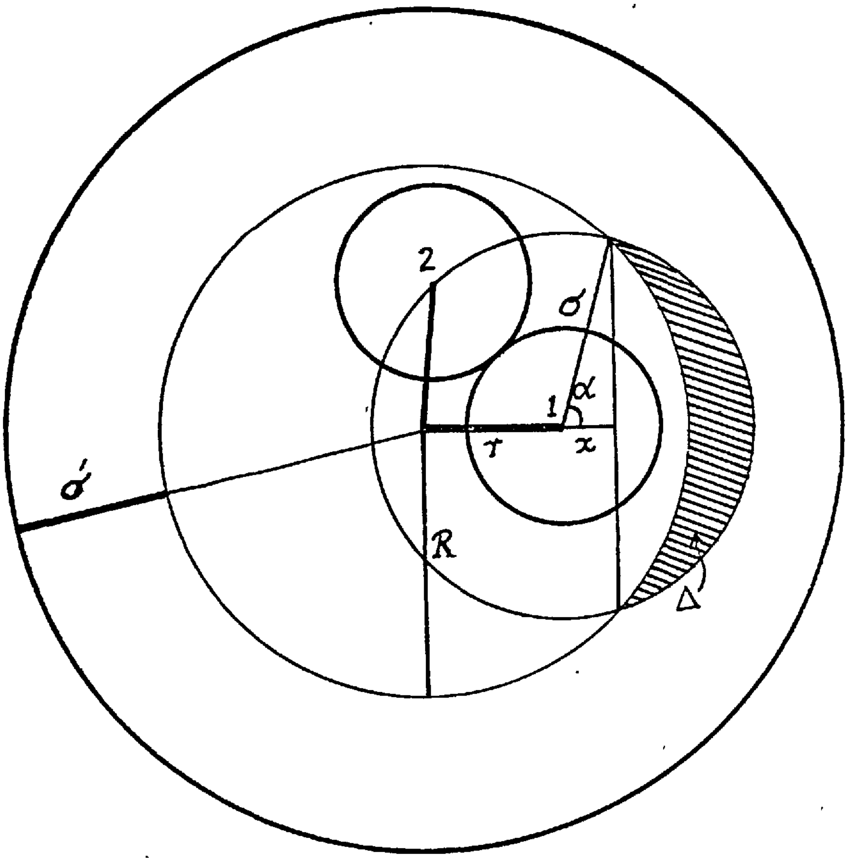


FIGURE A1 Cross Section of the Subsystem of Two Hard-sphere Molecules in a Spherical Cavity

$$\cos\alpha = (R^2-\sigma^2-r^2)/2r\sigma$$

$$x = (R^2-\sigma^2-r^2)/2r$$

$$r + x = (R^2-\sigma^2+r^2)/2r$$

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