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APPLICATION OF THE VAN'T HOFF EQUATION TO ADSORPTION EQUILIBRIA¹

H. H. ROWLEY AND W. B. INNES

Isothermal adsorption data for many gases and vapors on charcoal and other adsorbents have been shown by various investigators (1), (2), (3), (4), to agree satisfactorily with the Langmuir adsorption isotherm, except for deviations, possibly due to multi-layer adsorption, as the pressure of the saturated vapor is approached.

The Langmuir equation is derived on the hypothesis of a unimolecular adsorbed layer. The rate of adsorption, assumed proportional to the pressure p and the fraction of the surface unoccupied, $(1 - \theta)$, is equated to the rate of desorption which is assumed proportional to the fraction of the surface covered, θ , giving the equation below:

$$C_1 p(1 - \theta) = C_2 \theta \quad (1)$$

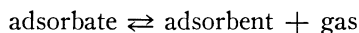
This can be rearranged to give:

$$\frac{C_2}{C_1} = \frac{p(1 - \theta)}{\theta} = k \quad (2)$$

Plots of this equation for different values of k are given in Fig. 1. If the amount adsorbed at equilibrium per gram of adsorbent is v and the amount adsorbed per gram of adsorbent when the surface is completely covered is φ ;

$$\theta = \frac{v}{\varphi} \quad \text{and} \quad k = \frac{p(\varphi - v)}{v} \quad (3)$$

The reaction of desorption can be represented by the equation below:



According to the Langmuir conception, $(1 - \theta)$ can be interpreted as a measure of the concentration of the adsorbent at the surface, θ as a measure of the concentration of the adsorbate, and the pressure as a measure of the concentration of the gas. The constant k thus identifies itself as the mass law equilibrium constant for this reaction. From another viewpoint, k can be considered as the vapor pressure of the adsorbate when the fraction of the surface

¹ For a more nearly complete work on the subject see Master's Thesis of W. B. Innes, State University of Iowa, 1939.

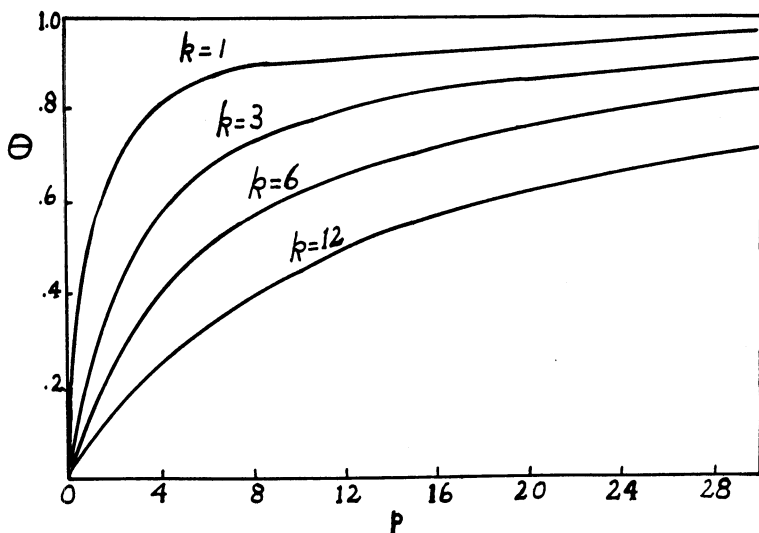


Fig. 1. Langmuir isotherms for different values of the adsorption equilibrium constant.

covered influences equally the rate at which molecules leave the surface and the rate at which molecules go on the surface, i.e. when the fraction of the surface covered, ϑ , is one-half. The variation of an equilibrium constant with temperature can be represented by the van't Hoff equation.

$$\frac{d \ln k}{dT} = + \frac{\Delta H^\circ}{RT^2} \tag{4}$$

k = equilibrium constant.

ΔH° = The heat content of the products minus the heat content of the reactant, all in standard states.

Integrating and assuming ΔH° constant with temperature:

$$\ln k = - \frac{\Delta H^\circ}{RT} + C \tag{5}$$

Substituting the value of k from equation (2) in this expression and choosing the standard state for the gas as 1 mm. Hg., for the adsorbate $\vartheta = 1$, for the adsorbent $(1 - \vartheta) = 1$, a general equation relating the fraction of the surface covered, the temperature, and the pressure of the gas in equilibrium with the surface is obtained:

$$\ln \frac{P(1 - \vartheta)}{\vartheta} = - \frac{\Delta H^\circ}{RT} + C \tag{6}$$

Using the data of Pearce and associates (5-13) this equation has been tested and the constants ΔH° , k at 25°C., and C have been

evaluated and are given in Table I. Typical plots for the change of k with temperature are given in Fig. 2. Agreement was found to be satisfactory in most cases except for deviations as the pressure of the saturated vapor was approached. To evaluate k , it is

Table I

	ΔH Cal. Exptl.	$+\Delta H^\circ$ Cal.	C	Φ CC. (n. t. p.)	Temp. Range in $^\circ\text{C}$.	k in mm. Hg 25°
Methyl chloride	9200	7700	17.0	159-.22t	$-30^\circ - 180^\circ$	56.4
Ethyl chloride	11600	8800	16.3	115-.14t	$0^\circ - 180^\circ$	5.0
Propyl chloride	15000	10000	15.9	98-.14t	$0^\circ - 130^\circ$	0.5
Methylene chloride		8550	15.3	126-.29t	$-30^\circ - 100^\circ$	2.2
Chloroform	14900	9200	14.1	104-.17t	$0^\circ - 100^\circ$	0.5
Acetone	13400	10500	15.1	127-.28t	$40^\circ - 130^\circ$	
Methyl acetate	10500	6600	10.5	110-.46t	$0^\circ - 100^\circ$	0.5
Dimethyl ether		6000	13.3	124-.24t	$0^\circ - 180^\circ$	0.3
Diethyl ether		8500	13.1	89-.19t	$40^\circ - 180^\circ$	
Ethylene chloride		9800	14.7	119-.33t	$40^\circ - 140^\circ$	
Ethylidene chloride		8600	13.7	107-.26t	$40^\circ - 140^\circ$	
Methyl alcohol	13700	8000	15.1	225-.48t	$60^\circ - 100^\circ$	
Ethyl alcohol		8000	14.6	175-.40t	$60^\circ - 100^\circ$	
Methylamine		5500	13.6	187-.54t	$0^\circ - 80^\circ$	128

necessary to know the value of φ , the amount adsorbed when the surface is completely covered. This quantity φ can be evaluated from the slope of the straight line obtained, if the data fits the Langmuir equation, when $\frac{p}{v}$ is plotted against p . Also the value

can be obtained by inspection of the adsorption isotherm if data on the flat portion of the curve are available. The magnitude of φ was found to decrease linearly with the temperature in all cases ex-

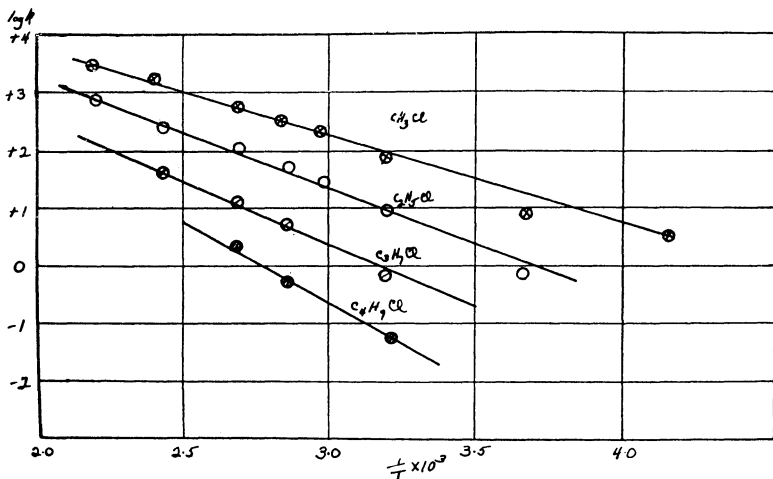


Fig. 2. Plots of the log of the adsorption equilibrium constant as a function of the reciprocal of the absolute temperature, using the data of Pearce and Taylor.

amined as shown in Fig. 3. The quantity k was evaluated as the equilibrium pressure when the surface was half covered.

The general equation (6) yields three special cases: the isothermal case when the temperature is constant, the isobaric case when

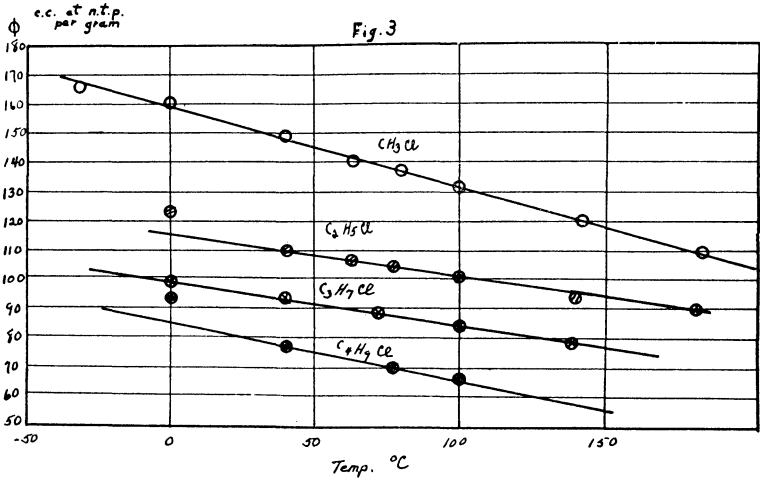


Fig. 3. Variation with the temperature of the amount adsorbed per gram of adsorbent when the surface is completely covered.

the pressure is constant, and a third case where the fraction of the surface covered is constant. The isothermal case relates the fraction of the surface covered to the equilibrium pressure:

$$\vartheta = \frac{p}{k + p}; \quad k = e^{(C - \Delta H^\circ / RT)} \quad (7)$$

When the fraction of the surface covered remains constant an equation relating the equilibrium pressure with the temperature is obtained:

$$\ln p = -\frac{\Delta H^\circ}{RT} + b \text{ where } b = \ln \frac{\vartheta}{1 - \vartheta} + C \quad (8)$$

In the isobaric case the fraction of the surface covered is related to the temperature:

$$\ln \frac{\vartheta}{1 - \vartheta} = \frac{\Delta H^\circ}{RT} - d \text{ where } d = C - \ln p \quad (9)$$

The case when the fraction of the surface covered is constant has the form of the Clapeyron equation. The isobaric equation is a new expression which is compared with the adsorption data for ethyl chloride in Fig. 4. The shape of these plots appear characteristic for all isobaric adsorption data examined.

As shown by the work of Pearce and associates (5-13), applica-

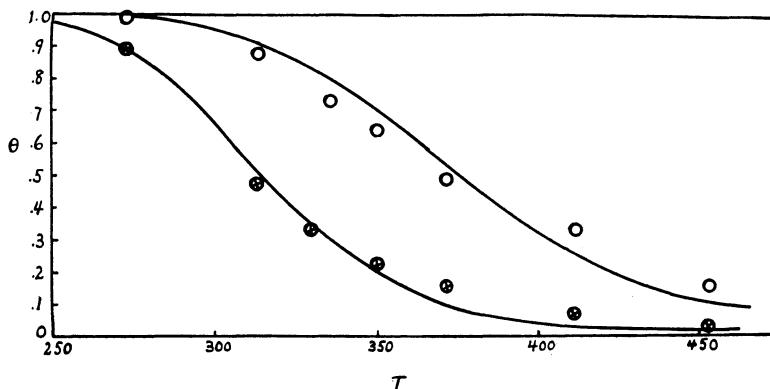


Fig. 4. Isobaric adsorption of ethyl chloride on charcoal. Theoretical curves using equation 9, and experimental points. Upper curve calculated for a pressure of 100 mm. Hg. and lower curve for 10 mm. Hg. O adsorption data at 100 mm. Hg. ⊕ adsorption data at 10 mm. Hg.

tion of the Clapeyron equation to the isosteric data when the amount adsorbed remains constant gives lower values for the heat of adsorption than does direct measurement. The ΔH° values obtained by applying the van't Hoff equation to these data are even lower. The explanation of this discrepancy perhaps lies in the fact that the calculated ΔH° values correspond to the heat effect if the adsorption took place at a constant value of ϑ , whereas ϑ actually increases in the course of an experimental measurement. The discrepancy would then be due to the heat effect involved in the increase of ϑ . The calculated heat effect, ΔH° obtained from equation (4) would appear to be due wholly to interaction of the adsorbent with the adsorbate if k is governed only by the reaction of the gas with the adsorbent. The second heat effect could be explained as being due to interaction between the adsorbed molecules, i.e. the heat effect due to crowding adsorbate molecules together as ϑ is increased. The decrease of Φ with temperature is a manifestation of this heat effect. Measured values of heat of adsorption are included with calculated values in Table I. These data were obtained by Pearce and associates on the same charcoal on which adsorption measurements were made.

Values of $\frac{P_0}{k}$ (P_0 = saturated vapor pressure of the liquid) and φ have been used (14) in qualitatively predicting which components will be selectively adsorbed from a solution. Large values of $\frac{P_0}{k}$ and of φ in comparison with the values for other components would favor the selective adsorption of this component.

Plots of isobaric equation 9 for each gas should be useful in qualitatively determining the best temperature and pressure to effect separation of gases or vapors by adsorption.

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