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DIFFUSION WITH CHEMICAL REACTION: AN ATTEMPT TO EXPLAIN NUMBER DENSITY ANOMALIES IN EXPERIMENTS INVOLVING ALKALI VAPOR

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16. Abstract

This report theoretically examines the mutual diffusion of two reacting gases which takes place in a bath of inert gas atoms. Solutions are obtained between concentric spheres, each sphere acting as a source for one of the reactants. The calculational model is used to illustrate severe number density gradients observed in absorption experiments with alkali vapor. Severe gradients result when $\sqrt{\kappa/D}\ R \approx 5$ where κ, D, and R are respectively the second order rate constant, the multicomponent diffusion constant, and the geometrical dimension of the experiment.

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DIFFUSION WITH CHEMICAL REACTION: AN ATTEMPT TO EXPLAIN NUMBER DENSITY ANOMALIES IN EXPERIMENTS INVOLVING ALKALI VAPOR

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SUMMARY

This report theoretically examines the mutual diffusion of two reacting gases which takes place in a bath of inert gas atoms. Solutions are obtained between concentric spheres, each sphere acting as a source for one of the reactants.

The model is an attempt to explain recent anomalies in alkali densities which have been observed in optical absorption experiments. Severe spatial gradients of alkali density were noted when uniform distributions were expected. This paper suggests that the observations might be explained in terms of the alkali reacting with outgassing and desorption products from the walls of the vessel.

Coupled equations for spatial density distributions of the reacting components are provided; the coupled equations can be solved by iteration and depend only on diffusion coefficients, second-order rate constants for the reaction, and geometric dimensions of the apparatus. Formulas are provided to estimate the rate constant when it is otherwise unavailable. Results should be applicable to the treatment of other chemically reacting species.

INTRODUCTION

Recent measurements (ref. 1) of the alkali number density distribution over reservoirs of the molten metal have uncovered very severe spatial gradients when uniform distribution is expected from cursory kinetic theory considerations. Typically, the reservoir of alkali is placed in an isothermal vessel containing several hundred torr (1 torr = 133 N/m^2) of inert gas. Mean free paths and times for alkali-inert gas encounters are, respectively, on the order of 10^{-5} cm and 10^{-9} sec at the temperatures considered. In seconds the alkali density is expected to be uniform throughout the container and to have a value comparable with that predicted by using vapor pressure data. Observed variations of over a decade change per cm are not uncommon. Figure 1 describes typical experimentally observed alkali number density distributions.

The vessels used in the experimental measurements of reference 1 were prepared with moderate care. Typically, after rough pumping for several hours with mild heating to accelerate outgassing, the alkali was added in a nitorgen-flushed glove box. The vessels were flushed with dry inert gas and subsequently closed, pumped, and backfilled to several hundred torr of inert gas. However, some residual desorption and outgassing is still to be expected under these conditions.

This paper theoretically investigates whether residual desorption and outgassing levels in the early phases of experimentation (usually several days) could account for the observed spatial gradients. The calculational model is used to illustrate the types of effects observed in reference 1.

The geometry of the experimental setup is dictated by considerations for measuring optical transmission. The source of alkali is preferably kept on the periphery of the container and outside the light path. In the present study the theoretical model is treated in a simpler, symmetric configuration to facilitate solving the related partial differential equations with boundary conditions. It is felt that the similarities will overshadow the geometric differences enough to make the description applicable to experiments in reference 1.

The idea for treating this problem as diffusion with absorption (through reaction), was considered as an analog to the thermal diffusion of neutrons in a reactor with moderator. (See ref. 2.) Girifalco and Behrendt (ref. 3) also treat the diffusion equation with source and sink terms in spherical coordinates. They employ eigenfunction expansion techniques and have source terms distributed throughout, rather than being localized on the boundaries as in this case; therefore, their results are not applicable here.

The consequences of the effect described in this paper can be drastic in those situations where the gas phase is calculated from vapor pressure data on the liquid or solid phase of a reservoir whenever a reactive constituent is present even in trace amounts. In closed systems where there is no liquid reservoir of material present, the reaction would, of course, quickly deplete the reacting gas phase constituent. In other situations when gradients exist and average densities are calculated on the premise of constant density, measured density values would appear to be lower than those predicted from vapor pressure equations. Reference to both of these effects (sometimes under the guise of nonrepeatability) is frequent in experimental papers concerned with absorption vessels and discharge tubes. The high reactivity of alkali makes the effect easier to observe than usual.

SYMBOLS

A	species type, mnemonic for alkali
B	species type, mnemonic for buffer or bath
C	species type, mnemonic for contaminant
C_i	constant ($i = 1, 2, \ldots, 6$, cm^{-2}
D	diffusion constant, $\mathrm{cm}^2\text{-}\mathrm{sec}^{-1}$
D_{ij}	generalized diffusion coefficient, $\mathrm{cm}^2\text{-}\mathrm{sec}^{-1}$
$\mathcal{D}_{ij}$	binary diffusion coefficient, $\mathrm{cm}^2\text{-}\mathrm{sec}^{-1}$
ΔE	activation energy, erg
f( )	auxiliary function defined prior to equation (9), cm^{-2}
G	Laplace transform of g, $\mathrm{cm}^{-2}\text{-sec}$
g( )	auxiliary function, $\equiv r\eta$, cm^{-2}
$\bar{g}$	parameter modifying annihilation constant, dimensionless
h	Planck constant, 6.63×10^{-27} erg-sec
h(r)	auxiliary function defined prior to equation (12), cm^{-2}
I	moment of inertia, $\mathrm{g}\text{-}\mathrm{cm}^2$
$\vec{J}$	flux, number of particles per unit area per unit time across a surface whose normal is specified by the vector, $\mathrm{cm}^{-2}\text{-}\mathrm{sec}^{-1}$
k	Boltzmann constant, 1.38×10^{-23} $\mathrm{J}\text{-}\mathrm{K}^{-1}$ $\left(1.38 \times 10^{-16}\ \mathrm{erg}\text{-}\mathrm{K}^{-1}\right)$
$\mathcal{L}\{\}$	Laplace transform operator

$\mathcal{L}^{-1}\{\,\}$	inverse Laplace transform operator
m_i	mass of species i, g
m_{ij}	reduced mass of species i and j, $m_i m_j / (m_i + m_j)$, grams
N(T)	number density obtained from vapor pressure (or outgassing) for temperature T, cm^{-3}
n	number density, cm^{-3}
$\mathcal{O}$	order of magnitude
p	pressure, torr (1 torr = 133 N/m^2)
Q	collision cross section, cm^2
q	time constant for outgassing rate, sec
R	radius of container, cm
r	radius coordinate, cm
r_o	radius of source bead, cm
s	Laplace transform partner for t, sec^{-1}
T	temperature, K
t	time, sec
t_o	time of impulse perturbation in source strength, sec
X^*	activated complex concentration, cm^{-3}
Z^*	partition function for activated complex, cm^{-3}
z	partition function for single mode, dimensionless or cm^{-1}

β	attenuation parameter, cm^{-1}
γ	attenuation parameter, cm^{-1}
Δ	perturbation strength parameter, dimensionless
$\delta(\ )$	Dirac delta function
ϵ	ratio of vibrational to rotational partition functions per mode, dimensionless
ζ	attenuation parameter, cm^{-1}
η	number density excess, cm^{-3}
κ	annihilation constant, sec^{-1}
ν	frequency, sec^{-1}

$\tau = t - t_0$, sec

Superscripts:

d	dissociation
e	electronic
r	rotational
t	translational
v	vibrational
∞	steady state

Subscripts:

a	alkali
b	buffer

c	contaminant
i,j,k	labels for arbitrary species or constants
*	activated complex less one degree of vibrational freedom

THEORY

The model for this problem is sketched in figure 2. A small bead of alkali metal having radius r_0 is situated in the center of a spherical cavity whose radius R is usually much greater than r_0. The concentration of gas phase alkali is of interest and is designated $n_a(r,t)$. Instead of treating the heterogeneous phase problem from first principles, it will be assumed that the liquid phase (temperatures of interest are above the melting point of the alkali) is in equilibrium with its vapor in a thin shell surrounding the bead. The concentration of gas phase atoms at r_0 is taken from equilibrium vapor pressure data; thus, the difficult interface problem is avoided.

Atoms of type A (alkali) diffuse outward into a bath containing predominantly species B (buffer gas). Also present are contaminant atoms designated C which desorb and outgas from the walls at R. Atoms B are inert and react with neither A nor C, but encounters of A and C can result in the formation of AC, which effectively removes A (alkali) as an atomic constituent.

An alkali atom leaves the vicinity of the bead and moves at several thousand meters per second. The alkali atom is constantly battered by B atoms; this condition makes A atom's path very tortuous and improves its chances for an encounter with C before it can reach the outer wall. If only A and C were present at their low partial pressures, encounters would be very unlikely and, in fact, the mean free paths would be governed more by the container dimensions than by atomic encounters (Knudsen regime). The mutual diffusion of A and C will result in gradients of n_a because of chemical reaction. The presence of B is acknowledged through use of a generalized diffusion coefficient to be defined later.

A comprehensive and readable discussion of diffusion is to be found in reference 4. For the homogeneous phase problem the net flux of particles is governed by Fick's empirical law

$$\vec{J} = -D(\vec{r})\vec{\nabla}n(\vec{r},t) \tag{1}$$

where $\vec{J}$ is the net number of molecules crossing unit area per unit time in the direction specified by $\vec{J}$, n is the number density, and D is the diffusion coefficient. In a given volume element the only mechanism for n to change is by chemical reaction; the reaction rate is denoted by an annihilation constant κ, which usually is expected to depend on the concentration of reactant present. (See the following equations and the appendix.) Mathematically,

$$\frac{dn(\vec{r},t)}{dt} = -\kappa n(\vec{r},t) \tag{2}$$

or

$$\frac{\partial n(r,t)}{\partial t} + \vec{\nabla} \cdot \vec{J} = -\kappa n(\vec{r},t) \tag{3}$$

By using Fick's law,

$$\frac{\partial n(\vec{r},t)}{\partial t} - \overrightarrow{\nabla D(\vec{r})} \cdot \overrightarrow{\nabla n(\vec{r},t)} - D(\vec{r})\nabla^2 n(\vec{r},t) = -\kappa n(\vec{r},t)$$

Rearranging this equation yields

$$\frac{\partial n(\vec{r},t)}{\partial t} = D(\vec{r})\nabla^2 n(\vec{r},t) + \overrightarrow{\nabla D(\vec{r})} \cdot \overrightarrow{\nabla n(\vec{r},t)} - \kappa n(\vec{r},t) \tag{4}$$

In practice, the diffusion coefficient is governed by the bath atoms and its gradient is negligible. Henceforth $\overrightarrow{\nabla D}(\vec{r})$ is assumed to be zero. An explicit expression for the annihilation constant is derived in the appendix. It is reasonable to suppose that it will depend functionally on the concentration of reacting species. Solutions to the following coupled equations are sought:

$$\frac{\partial n_a(\vec{r},t)}{\partial t} \approx D_{ac}(\vec{r})\nabla^2 n_a(\vec{r},t) - \kappa_a(n_c)n_a(\vec{r},t) \tag{5a}$$

$$\frac{\partial n_c(\vec{r},t)}{\partial t} \approx D_{ac}(\vec{r})\nabla^2 n_c(\vec{r},t) - \kappa_c(n_a)n_c(\vec{r},t) \tag{5b}$$

The experiments in reference 1 took place over several hours or days. Mostly, it is the steady-state solution which is sought, and these concentrations are identified with a superscript $n(\vec{r},t=\infty) \equiv n^{\infty}(\vec{r})$. An approximate method of studying the damping of perturbations to the steady-state values is discussed subsequently with possible application to empirically estimating κ.

Steady-State Solutions

Possible anisotropy in the problem (for example, gravitational effects) is neglected and spherical symmetry in alkali-inert atom collisions is assumed. Then, $n(\vec{r},t) = n(|\vec{r}|,t) = n(r,t)$ and the Laplacian operator simplifies to

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} \tag{6}$$

Expression for $n_a^{\infty}(r)$.- The boundary conditions for the problem will be

$$n_a^{\infty}(r_o) = N_a(T) \tag{7a}$$

and

$$\overrightarrow{\nabla n_a}(R) = 0 \tag{7b}$$

The first equation follows from restricting the number density to be the equilibrium value at the interface to sidestep the multiphase aspects. The second equation follows from Fick's law and the requirement that there be no net flow of alkali across the container boundary. Equation (5a) reduces to

$$D_{ac}\frac{1d}{r^2dr}r^2\frac{d}{dr}n_a^{\infty}(r) - \kappa_a(n_c)n_a^{\infty}(r) = 0 \tag{8}$$

The equation for the related function $f = rn_a^{\infty}(r)$ is even simpler, for example,

$$\frac{d^2f}{dr^2} - \gamma^2 f = 0 \tag{9}$$

with $\gamma^2 = \kappa_a(n_c)/D_{ac}$.

Equation (9) is nonlinear and is coupled to equation (5b) through the dependence of γ on n_c. The slight dependence of D_{ac} on n_c has already been neglected on deriving equation (5a) from equation (4). Instead of solving equation (9) and its coupled partner equation (12) by a direct numerical approach, an iteration process is used. This method allows γ to be treated as a known "constant" at any iteration, since its value is available from the previous iteration. This procedure is not unlike the procedure used to treat nonlocal terms in the self-consistent field calculations in atomic physics. If γ is "constant," then

$$f(r) = C_1 \cosh \gamma r + C_2 \sinh \gamma r$$

Boundary condition (7b) relates C_1 to C_2 as

$$C_2 = C_1 \frac{\gamma R \tanh \gamma R - 1}{\tanh \gamma R - \gamma R}$$

Applying equation (7a) fixes C_1 as

$$C_1 = \frac{r_o N_a(T)}{\cosh \gamma r_o + \dfrac{\gamma R \tanh \gamma R - 1}{\tanh \gamma R - \gamma R} \sinh \gamma r_o}$$

With C_1 so defined, the steady-state solution may be expressed as

$$n_a{}^{\infty}(r) = \frac{C_1}{r}\left(\cosh \gamma r + \frac{\gamma R \tanh \gamma R - 1}{\tanh \gamma R - \gamma R} \sinh \gamma r\right) \tag{10}$$

Equation (10) simplifies whenever γR is either very large or very small. The magnitude of γ is governed primarily by the local concentration of n_c. To be specific, if $\gamma R \geqq 5$ then $\tanh \gamma R \approx 1$, $C_2 \approx -C_1$, and $C_1 \approx r_o N_a(T) e^{\gamma r_o}$. Then equation (10) is approximately

$$n_a{}^{\infty}(r) \approx \frac{r_o}{r} N_a(T) e^{-\gamma(r-r_o)} \qquad (\gamma R \text{ large})$$

As a corollary large gradients in the n_a distribution are to be expected whenever $\sqrt{\kappa_a / D_{ac}}\, R \approx 5$.

To examine the limit as $\gamma \to 0$, rewrite equation (10) as

$$n_a{}^{\infty}(r) = \frac{r_o N_a(T)}{r} \, \frac{(\tanh \gamma R - \gamma R)\cosh \gamma r + (\gamma R \tanh \gamma R - 1)\sinh \gamma r}{(\tanh \gamma R - \gamma R)\cosh \gamma r_o + (\gamma R \tanh \gamma R - 1)\sinh \gamma r_o} \tag{10a}$$

Then since for γR small $\sinh(\gamma R) \approx \gamma R + (\gamma R)^3/6$, $\cosh(\gamma R) \approx 1 + (\gamma R)^2/2$, and $\tanh(\gamma R) \approx \gamma R - (\gamma R)^3/3$ to order 3, equation (10a) becomes

$$n_a^{\infty} \approx \frac{r_o N_a(T)}{r} \, \frac{-\gamma^3 R^3/3 + \left(\gamma^2 R^2 - 1\right)\left(\gamma r - \gamma^3 r^3/6\right)}{-\gamma^3 R^3/3 + \left(\gamma^2 R^2 - 1\right)\left(\gamma r_o - \gamma^3 r_o^{\,3}/6\right)}$$

$$= \frac{r_o N_a(T)}{r} \cdot \frac{-r + \gamma^2\left(r^3/6 + rR^2 - R^3/3\right) + \mathcal{O}\left(\gamma^4\right)}{-r_o + \gamma^2\left(r_o^{\,3}/6 + r_o R^2 - R^3/3\right) + \mathcal{O}\left(\gamma^4\right)}$$

then

$$\lim_{\gamma \to 0} n_a^{\infty}(r) = N_a(T) \qquad (\gamma R \to 0)$$

Expression for $n_c^{\infty}(r)$.- The n_a and n_c solutions are coupled through the annihilation constant and may be solved by iteration. An explicit expression for the C concentration is needed:

$$D_{ac} \nabla^2 n_c^{\infty}(r) - \kappa_c\left(n_a\right) n_c^{\infty}(r) = 0 \tag{11}$$

By using the angle independent Laplacian and letting $h(r) = r n_c^{\infty}$, equation (11) can be reduced to

$$\frac{d^2 h(r)}{dr^2} - \beta^2 h(r) = 0 \tag{12}$$

where $\beta^2 = \kappa_c\left(n_a\right) / D_{ac}$.

The boundary conditions analogous to equations (7a) and (7b) are

$$n_c^{\infty}(R) = N_c(T) \tag{13a}$$

$$\overrightarrow{\nabla} n_c^{\infty}\left(r_o\right) = 0 \tag{13b}$$

where $N_c(T)$ is the number density estimated from measurements of outgassing pressure. Empirically, outgassing depends on time, temperature, and construction material. Equation (13b) implies that there is no net flux of C across the surface of the bead. With the same stipulations as applied to n_a^{∞}, the solution is

$$h(r) = C_3 \cosh \beta r + C_4 \sinh \beta r$$

where the boundary conditions require that

$$C_3 = C_4 \frac{\tanh \beta r_o - \beta r_o}{\beta r_o \tanh \beta r_o - 1}$$

and

$$C_4 = RN_c(T) \frac{\beta r_o \tanh \beta r_o - 1}{\left(\tanh \beta r_o - \beta r_o\right)\cosh \beta R + \left(\beta r_o \tanh \beta r_o - 1\right)\sinh \beta R}$$

Therefore,

$$n_c^{\infty} = \frac{RN_c}{r}\left[\frac{\left(\tanh \beta r_o - \beta r_o\right)\cosh \beta r + \left(\beta r_o \tanh \beta r_o - 1\right)\sinh \beta r}{\left(\tanh \beta r_o - \beta r_o\right)\cosh \beta R + \left(\beta r_o \tanh \beta r_o - 1\right)\sinh \beta R}\right] \tag{14}$$

Expressions for κ_a, κ_c, and D_{ac}.- Only binary diffusion is considered. Let $\mathcal{D}_{ij}$ represent the binary diffusion coefficient of species i and j. Then the lowest order approximation to the exact theory using hard sphere approximations for the collision integrals gives (for example, see ref. 5, eqs. 7.4-38 and 8.2-5)

$$\mathcal{D}_{ij} = \frac{3}{8}\left(\frac{\pi kT}{2m_{ij}}\right)^{1/2} \frac{1}{\left(n_i + n_j\right)Q_{ij}} \tag{15}$$

where m_{ij} is the reduced mass and Q_{ij} is the kinetic cross section for i - j collisions.

Using perturbation expansions to solve the transport equations for multicomponent systems, the generalized diffusion coefficient D_{ij} may be written in terms of the binary counterparts. For example, if a third component k is present (eq. 11.2-41 of ref. 5), then

$$D_{ij} = \mathcal{D}_{ij}\left[1 + \frac{n_k\left(m_k\mathcal{D}_{ik}/m_j - \mathcal{D}_{ij}\right)}{n_i\mathcal{D}_{jk} + n_j\mathcal{D}_{ik} + n_k\mathcal{D}_{ij}}\right]$$

In particular, for the problem treated in this paper,

$$D_{ac} = \mathcal{D}_{ac}\left[1 + \frac{n_b\left(m_b\mathcal{D}_{ab}/m_c - \mathcal{D}_{ac}\right)}{n_a\mathcal{D}_{bc} + n_c\mathcal{D}_{ab} + n_b\mathcal{D}_{ac}}\right] \tag{16}$$

Note that when the concentration of n_b dominates, $n_a\mathcal{D}_{bc}$ and $n_c\mathcal{D}_{ab}$ are negligible in the denominator and

$$D_{ac} \approx \mathcal{D}_{ac}\left(1 + \frac{m_b\mathcal{D}_{ab}}{m_c\mathcal{D}_{ac}} - 1\right) = \frac{m_b\mathcal{D}_{ab}}{m_c}$$

so that it is really the dominant species which hinders the flow of A as expected.

As defined in the diffusion equations, the annihilation constant κ is identified with the rate constant for a second-order chemical reaction. Kinetic theory considerations show κ to be proportional to the cross section for encounter Q_{ac}, the relative velocity of approach $\propto\left(T/m_{ac}\right)^{1/2}$, and the number density of the reacting partner. More detailed consideration introduces an activation energy ΔE representing an energy barrier which the reactants must surmount before a reaction can occur. Finally, an additional proportionality constant $\bar{g}$ accounts for the internal complexity of reactants in energy allocation. In the appendix an expression for κ is derived on the basis of Eyring's theory, where it is shown that

$$\kappa_{a,c} = \bar{g}Q_{ac}\left(8kT/\pi m_{ac}\right)^{1/2} n_{c,a} e^{-\Delta E/kT} \tag{17}$$

where A is atomic and

$\bar{g} \approx 1$ (C is atomic)

$0.01 \leqq \bar{g} \leqq 0.1$ (C is diatomic)

$0.0001 \leqq \bar{g} \leqq 0.01$ (C is polyatomic)

Time-Dependent Solution

Assume that conditions are such that equation (10) reduces to a decaying exponential at some intermediate radius r where $r_o < r < R$ and that at time $t = t_o$, the source strength is instantaneously increased by a dimensionless factor Δ to the value

$(1 + \Delta)N_a(T)$. Mathematically, this condition amounts to a source perturbation representable as $\Delta N_a(T)\ \delta(r - r_o)\ \delta(t - t_o)$. In practice the surface of the alkali is dirty or contains an oxide coating so that the observed vapor pressure value is reduced to some fraction of the value (at temperature T) listed in the handbooks. If the surface is mechanically disturbed in some way, then some "clean metal" is momentarily exposed, and the vapor pressure is expected to jump discontinuously for a short time as described above.

The time dependence is carried in a function $\eta_a(r,t)$ so that $n_a(r,t) = n_a^\infty + \eta_a(r,t)$. Then for $t > t_o$,

$$\dot{n}_a = \dot{n}_a^\infty + \dot{\eta}_a(r,t) = \left(D_{ac}\nabla^2 - \kappa_a\right)n_a^\infty + \left(D_{ac}\nabla^2 - \kappa_a\right)\eta_a(r,t)$$

In the preceding expression steady-state values of $\dot{n}_a^\infty$ and $\left(D_{ac}\nabla^2 - \kappa_a\right)n_a^\infty$ are zero. The function η must satisfy

$$\dot{\eta}_a(r,t) = \left(D_{ac}\nabla^2 - \kappa_a\right)\eta_a(r,t)$$

with

$$\eta_a(r,t) = 0 \qquad \left(t \leqq t_o\right)$$

Let $r\eta_a = g_a$ and measure time from t_o by using time variable $\tau = t - t_o$. The function g_a must satisfy

$$\dot{g}_a(r,\tau) = D_{ac}\frac{d^2 g_a}{dr^2} - \kappa_a g_a(r,\tau)$$

This equation may be solved with Laplace transforms. The transform partners will be $g_a \longrightarrow G_a$ and $\tau \longrightarrow s$. Denoting the transform operator as $\mathcal{L}$ then

$$\mathcal{L}\left\{\dot{g}_a(r,\tau)\right\} = D_{ac}\frac{d^2}{dr^2}\mathcal{L}\left\{g_a\right\} - \kappa_a\mathcal{L}\left\{g_a(r,\tau)\right\}$$

where the commutability of $\mathcal{L}$ and d^2/dr^2 has been used. From the properties of Laplace transforms (ref. 6, p. 4) and the initial condition,

$$sG_a(r,s) - g_a(r,0) = D_{ac}\frac{d^2}{dr^2}G_a(r,s) - \kappa_a G_a(r,s)$$

where the steady-state value of $g_a(r,0)$ is zero. The solution is $G_a(r,s) = C_5e^{\zeta r} + C_6e^{-\zeta r}$ with $\zeta = \left[(\kappa_a + s)/D_{ac}\right]^{1/2}$. The boundary conditions analogous to equations (7a) and (7b) are

$$r\frac{dG_a}{dr}(r,s)\bigg|_R = G_a(R,s)$$

$$G_a(r_o,s) = r_o\Delta N_a(T)$$

and lead to

$$C_5 = -C_6e^{-2\zeta R}\frac{1 + R\zeta}{1 - R\zeta}$$

$$r_o\Delta N_a(T) = C_6\left[e^{-\zeta r_o} - \frac{1 + R\zeta}{1 - R\zeta}e^{-\zeta(2R-r_o)}\right]$$

Under the restricted range of applicability (ζR large),

$$C_6 \approx \Delta r_oN_a(T)e^{\zeta r_o}$$

$$C_5 \approx 0$$

so that

$$G_a(r,s) \approx r_o\Delta N_ae^{-\zeta(r-r_o)}$$

The inverse transform may be obtained by using property 3 and transform number 85, respectively, on pages 243 and 250 of reference 6 as

$$\mathcal{L}^{-1}\left\{G_a(r,s)\right\} = r_o\Delta N_a(T)e^{-\kappa_a\tau}\frac{(r - r_o)e^{-(r-r_o)^2/4\tau D_{ac}}}{2\left(\pi\tau^3D_{ac}\right)^{1/2}}$$

In terms of original variables.

$$\eta_a(r,t) = \frac{\Delta r_o(r - r_o)N_a(T)e^{-\kappa_a(t-t_o)-(r-r_o)^2/4D_{ac}(t-t_o)}}{\sqrt{4\pi D_{ac}(t - t_o)}\, r(t - t_o)} \qquad (t > t_o)$$

$$\eta_a(r,t) = 0 \qquad (t \leqq t_o) .$$

It should be possible under certain conditions to observe responses to changes in the steady-state distribution, the time dependence of which is carried primarily by $\exp(-\kappa_a \tau)$. Time-dependent observations may help to determine at least the magnitude of κ_a when its direct calculation is not feasible.

Numerical Example of Steady-State Solution

A numerical example will help to describe the method and point out the salient features of the solution. If only roughing pumps are used in preparing the absorption vessels, residual total pressures may be as much as 10 μm Hg (1 μm Hg = 10^{-3} torr). When alkali is introduced, it in effect acts as a "getter" for many of the oxygen-containing outgassing constituents. This process removes atomic phase alkali. Outgassing rates depend markedly on temperature and time history of heating, the latter because there is essentially only a finite amount of material to outgas. For the purpose of identifying the level of contamination in this example with a single parameter (time), it is assumed that $p = 10^{-2} \exp(-t/q)$ where p is in torr, t is in hours (1 hour = 3600 sec), and q acts as the pressure time constant. This relationship oversimplifies the actual behavior and overestimates the concentration of harmful constituents, for example, oxygenated species. If q is 3 hours, then this value is consistent with data in figure 4.5 of reference 7 for total outgassing and desorption of nonpolished aluminum chambers at 200° C (472 K) after N_2 flushing. The relationship is used for times greater than or equal to 2 hours. This long time constant would at least be doubled at room temperature on the basis of results in reference 7. Typical diatomic molecular diameters are 3A to 4A $(1A = 10^{-10}$ m$)$. For calculating the cross sections in this example, 3.5A is used as a mean diameter and the mass of C will be taken as 30 amu.

Species A will be Cs and B is taken to be Xe at 400 torr. Vapor pressure data for Cs is taken from page 2425 of reference 8, and the atomic and molecular radii for cross-sectional calculations from reference 9, pages 45 to 47. The activation energy is assumed to be zero since Cs reacts violently with oxygenated compounds even at room temperature. Table I assembles the input data for the example.

Equations (10) and (14) are solved by iteration. An initial guess for $n_c^\infty(r)$ is made to allow κ_a to be estimated from equation (17). The expression for γ is calculable and hence $n_a^\infty(r)$ to first approximation is obtained from equation (10). The quantity κ_c and hence β may be used in equation (14) for a new estimate of $n_c^\infty(r)$ and the procedure repeated until selfconsistency is achieved. Convergence usually occurs within 10 or 20 iterations and, as expected, is slowest in the regions of strong gradients.

TABLE I.- VALUES USED FOR NUMERICAL EXAMPLE

m_a	2.20×10^{-22} g
m_b	2.18×10^{-22} g
m_c	5.00×10^{-23} g
T	473 K
r_o	0.5 cm
R	10.0 cm
n_b	1.42×10^{19} cm-3
$N_a(T)$	2.48×10^{15} cm^{-3}
$N_c(T)$	3.53×10^{14} exp(-t/10 800); t in s
Q_{ac}	83.0×10^{-16} cm^2
Q_{ab}	91.0×10^{-16} cm^2
Q_{bc}	44.0×10^{-16} cm^2
ΔE	0.0
$\bar{g}$	0.01, 0.001

Figure 3 shows computed profiles as the concentration of contaminant depletes in accordance with the simplified time dependence for outgassing and desorption listed in table I. The time intervals are also comparable to run times encountered in the absorption experiments under consideration. The figure is only intended to represent the sharp demarcations that result from this approach. Exact values for the dependence at the reaction zone would require identification of species C and calculation of the associated partition functions, and so forth. The demarcation becomes less abrupt as $\bar{g}$ becomes smaller, which is to say as C becomes more complex. It then takes more encounters to insure a reaction. The example seems to indicate that spatial gradients appear whenever $N_c(T)$ levels approach within three orders of magnitude of $N_a(T)$. Use of diffusion pumps to prepare the experiments would result in approximately four orders of magnitude reductions in the initial $N_c(T)$ levels at the outset and should adequately remove the gradients in small cells loaded by distillation techniques. For large cell loading techniques, as used in reference 1, the alkali may be used as a viable getter if the alkali surface can be maintained in a "clean" state.

Figure 4 shows the effect of reducing the buffer gas pressure by a factor of 50 and is interpreted to mean that the A atom has less interference as it moves away from r_o and less chance of colliding with C so that the demarcation zone moves toward the wall. The experimental evidence (ref. 1) also seems to indicate this result.

CONCLUDING REMARKS

By working with a simplified model it has been shown that the mutual diffusion of chemically reacting species in a medium of inert gas atoms can result in severe spatial gradients of both reacting species. If the alkali annihilation constant κ_a is the second-order rate constant for the reaction of A with C, then rather severe gradients in the concentration of A are expected if $\sqrt{\kappa_a/D_{ac}}\, R \approx 5$ where D_{ac} is the multicomponent diffusion coefficient and R is a characteristic dimension separating the sources of the reactants.

A numerical example for a 400-torr bath pressure showed that when the source strength of one of the reactants approached to within three orders of magnitude of the other, severe spatial gradients of both reactants resulted. This result is germane to some optical absorption measurements with alkali metals, since optical absorption tubes frequently operate in a temperature range that puts the alkali vapor pressure within three orders of magnitude of outgassing levels for oxygenated compounds from the vessel wall. Recent experiments are cited which, in fact, support the predictions of the present model.

The analysis also indicates that the gradients become less severe as the complexity of the reactants increases; for example, gradients are more severe for atom-atom cases than for atom-polyatom situations.

The effect of the inert gas bath pressure is carried through the use of a generalized diffusion constant. Decreasing the bath pressure makes the reaction zone less abrupt and moves it toward the boundary supplying the minor reactant – a result also compatible with observation.

Perturbations in the source strength are shown to propagate toward the reaction zone and to relax there with a time constant inversely proportional to the rate constant for the reaction.

Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Va., April 5, 1974.

APPENDIX

ESTIMATION OF κ_a

The experiments usually neither measure nor identify species C. A reasonable estimate may be given, however, based only on knowing whether the species is atomic or polyatomic. Likely outgassing candidates, when aluminum or stainless steel vessels are involved, might be O, O_2, H_2O, CO_2, CO, and some hydrocarbons from O-rings.

Assume for simplicity that every encounter of A and C removes A as an atomic constituent. Then the loss rate of n_a can be estimated with simple kinetic theory arguments. For a Maxwell-Boltzmann gas, the mean relative speed of A and C is given by $(8kT/\pi m_{ac})^{1/2}$ where m_{ac} is the reduced mass of the pair. An A atom will, on the average, sweep out a volume $Q_{ac}(8kT/\pi m_{ac})^{1/2}$ per unit time where Q_{ac} is the cross section for encounter. Multiplying by the number densities of A and C gives their mean collision rate and a crude estimate for the loss of n_a

$$-\dot{n}_a = \left[Q_{ac}(8kT/\pi m_{ac})^{1/2} n_c\right] n_a \tag{18}$$

In chemical kinetics this condition would be called a second-order reaction because it is of first power in each concentration. The term in brackets is called the rate constant. A generalization of the rate constant will be based on chemical kinetics. (See chapter 3 of ref. 10.) Expression (18) will be modifed by a fraction $\bar{g}$ which is a function of the complexity of C and by an additional temperature-dependent term.

Much of reaction rate theory is based on the assumption that the colliding partners comprise an activated complex which has all the features of a stable molecule save one – that one of its vibrational modes dissociate the complex into its final products. In fact, the frequency of this special vibrational mode is identified with the rate of reaction. Furthermore, both the initial and final products are assumed to be independently in equilibrium with the activated complex. The quantity X^* is the concentration of activated complex. Mathematically,

$$n_a + n_c \rightleftarrows X^* \rightleftarrows \text{Final products}$$

Let Z represent the partition function. Statistical mechanical arguments show that the relative concentrations of various species are related by

$$\frac{X^*}{n_a n_c} = \frac{Z^*}{Z_a Z_c} e^{-\Delta E/kT} \tag{19}$$

where ΔE is the "activation energy" and is defined as the average energy of the molecules which react minus the average energy of all the molecules. (For example, see Rice, ref. 11, p. 513.) Pictorially, ΔE represents a kind of "energy hump," which the colliding partners must overcome to be considered a complex, and empirically ΔE is responsible for the strong temperature dependence of most rate constants.

If the frequency of the vibrational mode which leads to dissociation is $\nu^{(d)}$, then the contribution of this mode to Z^* will be $\left[1 - \exp\left(-h\nu^{(d)}/kT\right)\right]^{-1}$. Since $\nu^{(d)}$ belongs to a very weak coupling, it will be very small with respect to kT/h which is approximately 6×10^{12} sec^{-1} at 300 K. Consequently, the exponential is representable by the first two terms in its Maclaurin expansion. The partition function to this accuracy is $kT/h\nu^{(d)}$. Designate the partition function with this factor removed by Z_*; that is,

$$Z_* = Z^* \Big/ \left(h\nu^{(d)}/kT\right)^{-1} \tag{20}$$

Substitute equation (20) into equation (19) and rearrange to obtain

$$X^*\nu^{(d)} = \left[\frac{kT}{h}\,\frac{Z_*}{Z_a Z_c}\,e^{-\Delta E/kT}\right] n_a n_c \tag{21}$$

which will reduce to equation (18) if C is also an atom.

To the extent that energy in a molecule can be identified as translational, rotational, vibrational, or electronic, it is possible to factor the partition function. Let the partition function for a single mode be z with the superscript identifying the type; then,

$$z^{(t)} = (2\pi mkT)^{1/2}\big/h \tag{22a}$$

$$z^{(r)} = (8\pi^2 IkT)^{1/2}\big/h \tag{22b}$$

$$z^{(v)} = \left[1 - \exp(-h\nu/kT)\right]^{-1} \tag{22c}$$

$$z^{(e)} = \text{Degeneracy of lowest state} \tag{22d}$$

where I in equation (22b) is the moment of inertia, equation (22c) is the harmonic oscillator approximation, and equation (22d) is true only for temperatures below 1000 K. Order of magnitude estimates (in cgs units) for the individual modes are 10^8 for $z^{(t)}$, 10 to 100 for $z^{(r)}$ and 1 for $z^{(v)}$ and $z^{(e)}$. It is convenient to define $z^{(v)}/z^{(r)} \equiv \epsilon$; then $0.01 \leqq \epsilon \leqq 0.1$.

APPENDIX

If A and C are atoms, X^* is a diatomic molecule. The electronic mode is neglected. Each atom has three degrees of translational freedom. The quantity Z^* has its only degree of vibrational freedom removed to form Z_*; therefore

$$Z_a = z_a^{(t)3} \approx z^{(t)3}$$

$$Z_c = z_c^{(t)3} \approx z^{(t)3} .$$

$$Z_* = z_*^{(t)3} z_*^{(r)2} \approx z^{(t)3} z^{(r)2}$$

Substituting these relations into equation (21)

$$X^*{}_\nu{}^{(d)} = \left\{ \left\langle \left[\frac{kT}{h} \frac{z_*^{(t)3} z_*^{(r)2}}{z_a^{(t)3} z_c^{(t)3}} e^{-\Delta E/kT} \right]_{n_c} \right\rangle \right\}_{n_a} \qquad (23)$$

If the z terms are calculated with equations (22) and it is noted that $I = Q_{ac}\, m_{ac}/\pi$, then equation (23) reduces exactly to equation (18) except for the activation energy term. Identify $\bar{g}$ times the expression in braces with κ_a. Then $\bar{g}$ is 1 if C is atomic.

If C is diatomic, then X^* is triatomic less one degree of freedom

$$Z_a \approx z^{(t)3}$$

$$Z_c \approx z^{(t)3} z^{(r)2} z^{(v)}$$

$$Z_* \approx z^{(t)3} z^{(r)3} z^{(v)2}$$

and

$$\left(\frac{Z_*}{Z_a Z_c}\right)_{\text{atom-diatom}} \approx \epsilon \left(\frac{Z_*}{Z_a Z_c}\right)_{\text{atom-atom}}$$

If C has three or more atoms, $\bar{g}$ is ϵ^2. In summary

$$\kappa_a = \bar{g} Q_{ac} \left(8kT/\pi m_{ac} \right)^{1/2} n_c e^{-\Delta E/kT}$$

where $\bar{g} \approx 1$ if C is atomic; $0.01 \leqq \bar{g} \leqq 0.1$ if C is diatomic; and $0.0001 \leqq \bar{g} \leqq 0.01$ if C has more than two atoms.

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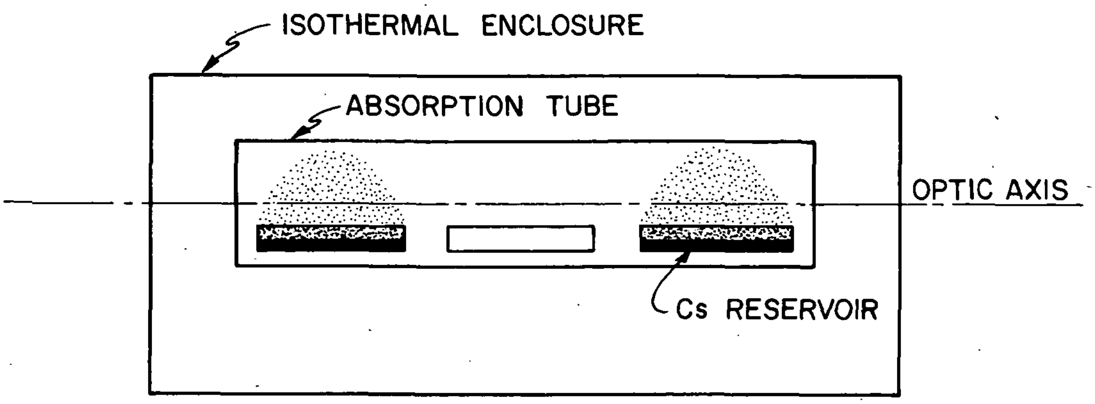
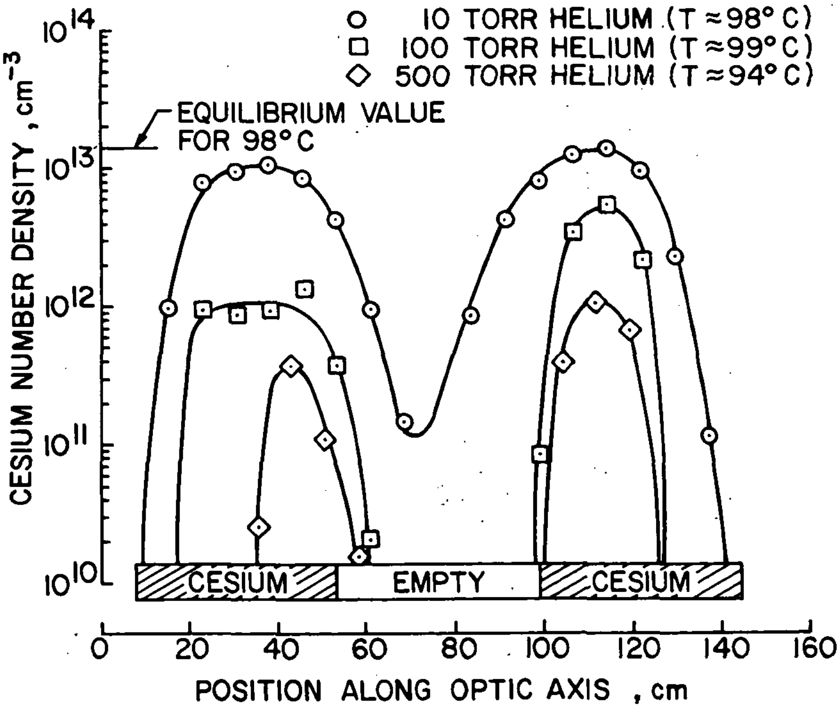


(a) Schematic of a typical absorption cell set up to indicate the location of Cs reservoirs with respect to optical axis.



(b) Data showing the Cs vapor distribution above two separated reservoirs for loading pressures of 10, 100, and 500 torr He. Measurements are made along the optical axis depicted in figure 1(a).

Figure 1.- Experimental alkali concentration measurements from reference 1.

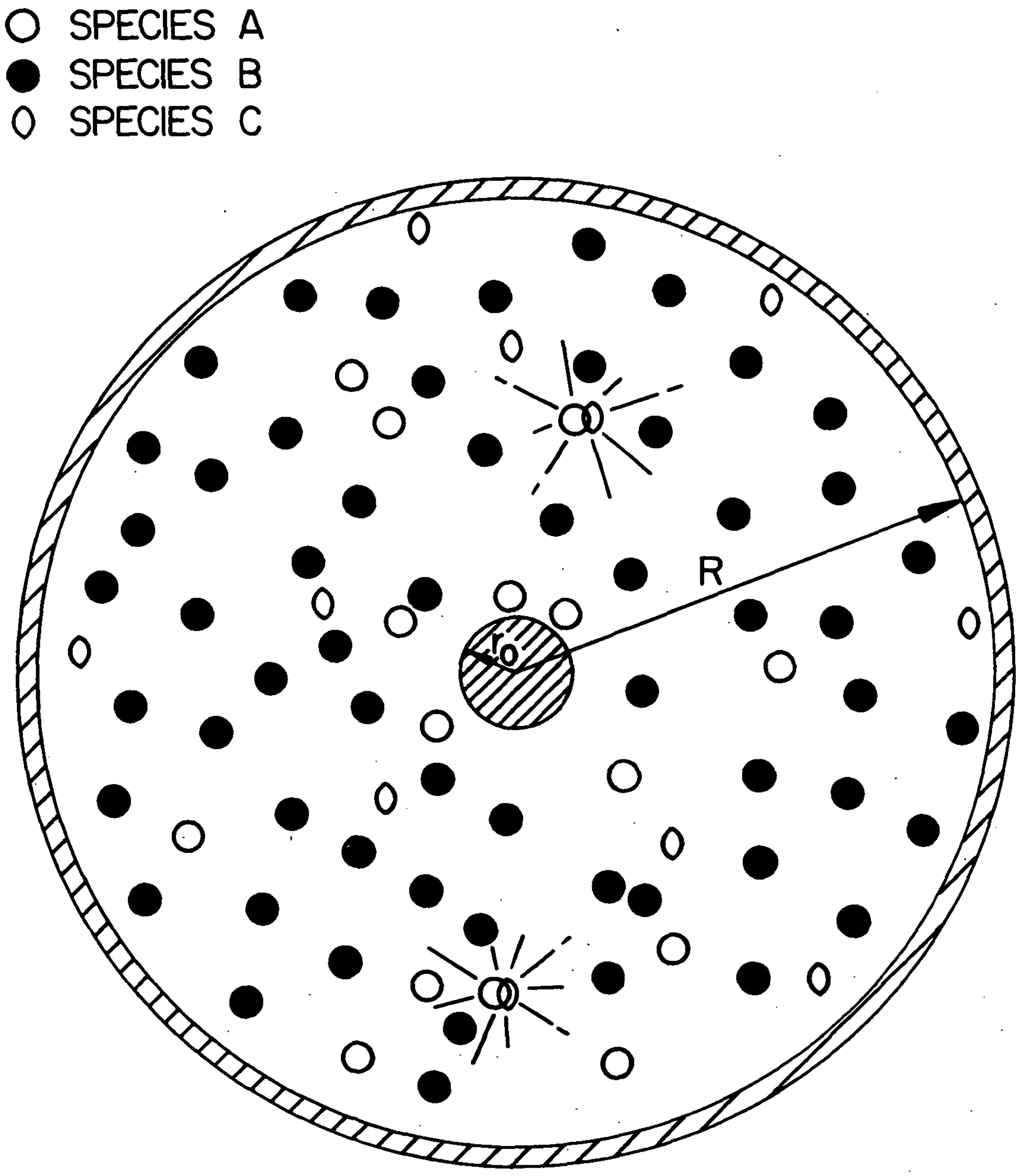


Figure 2.- Cross section of container and alkali bead showing gas phase species.

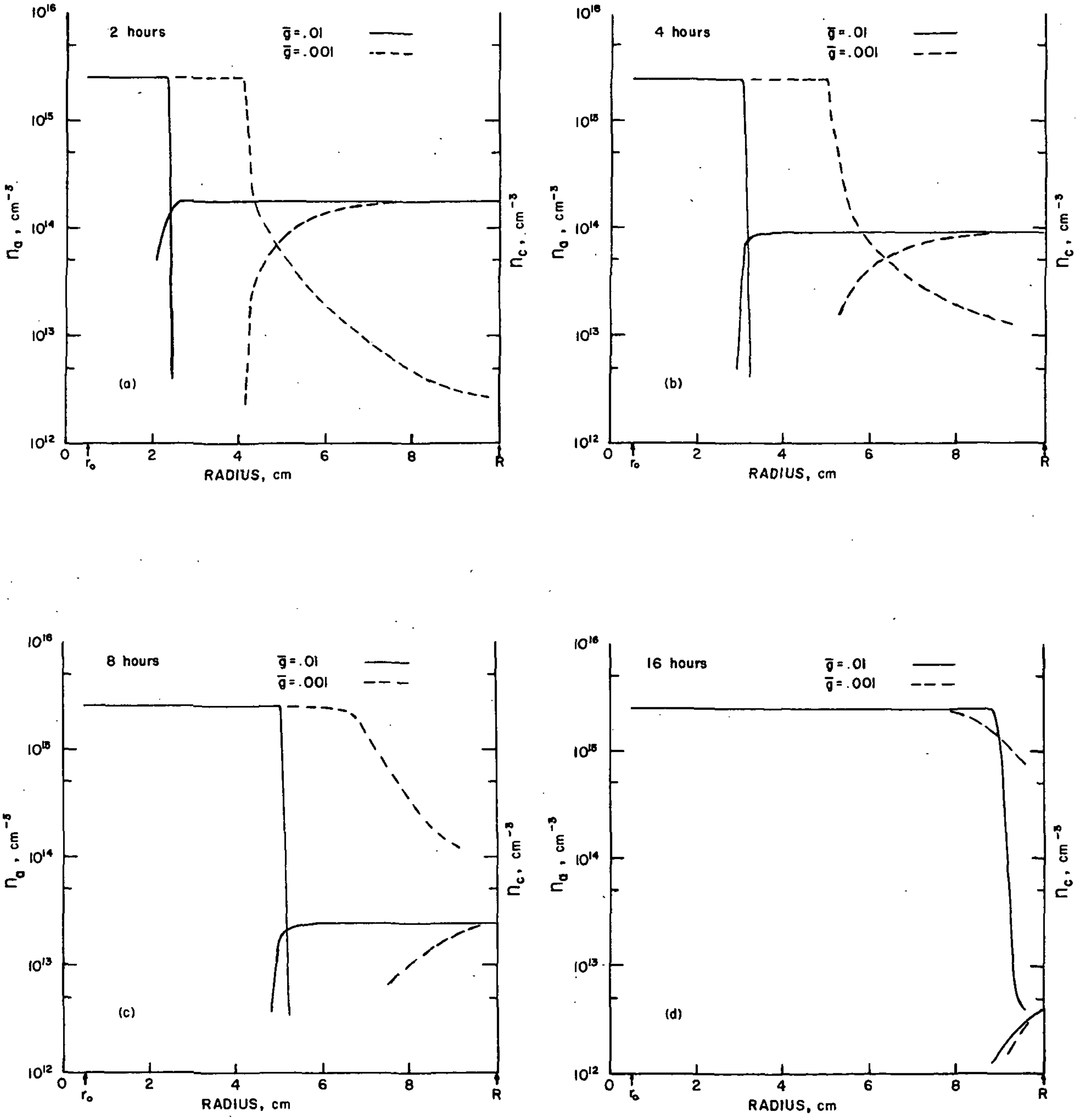


Figure 3.- Steady state distributions (a) to (d) which result when the contaminant level n_c changes at the boundary $r = R$ while the alkali density n_a is held at the 200° C vapor pressure value at the bead's surface $r = r_0$. Contaminant level is parametrized by time according to the simplified model in table I. Buffer gas pressure is 400 torr.

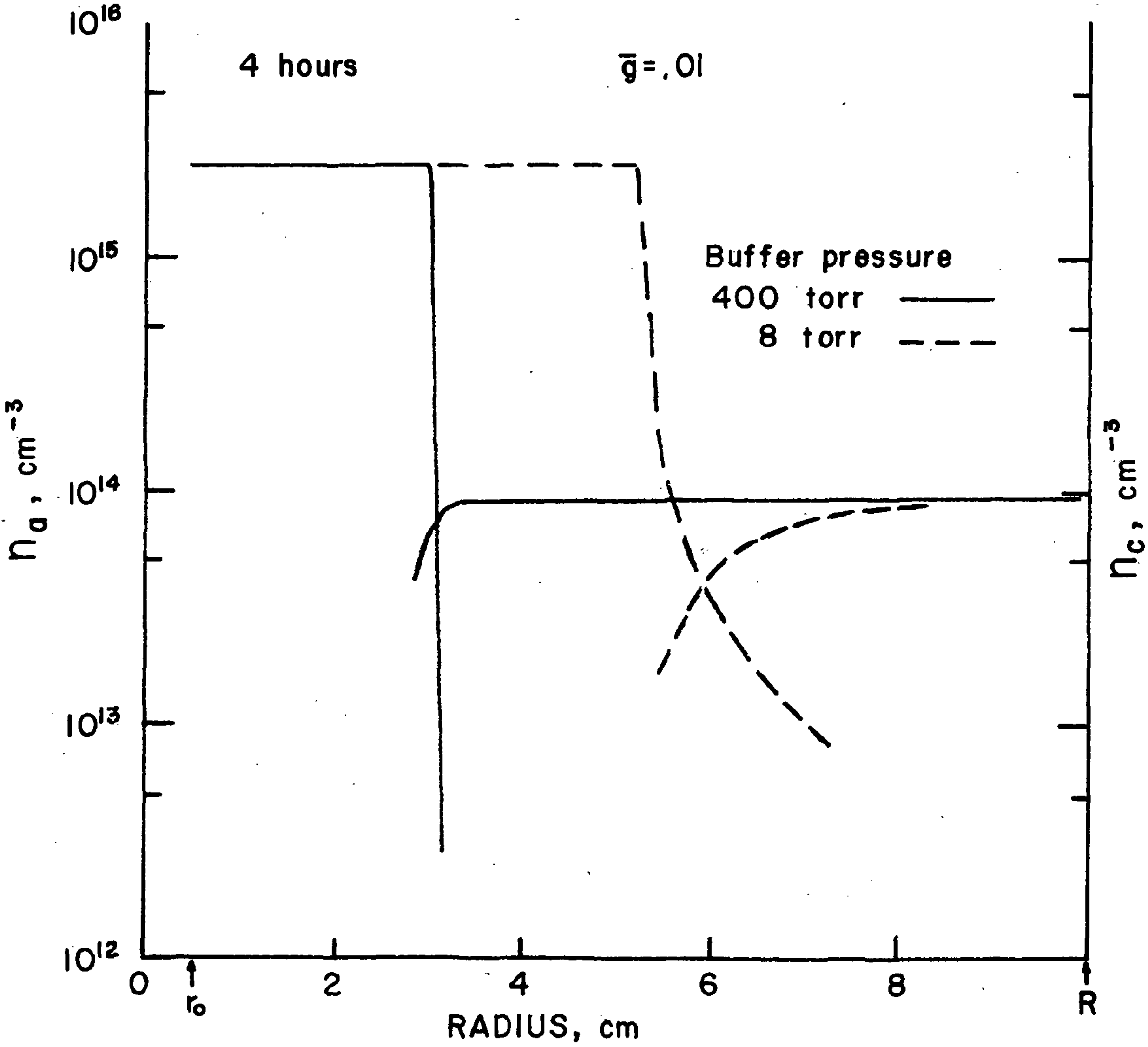


Figure 4.- The effect of buffer gas pressure on alkali concentration.

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