A MOLECULAR DYNAMIC THEORY OF CHROMATOGRAPHY[1]

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The molecular dynamic problem of passage of substances through a chromatographic column is investigated for the linear range of the adsorption isotherm. It is found, assuming uniform adsorption sites of only one type, that a reasonable concentration distribution of molecules in the effluent of a column can be obtained. Equations are also derived for the case in which there are two and more different type sites. The sorption rate constants of a typical chromatographic process are experimentally determined.

Introduction

The general problem of chromatography is, in a practical sense, not solvable. For ordinary column chromatography unknowable variables exist involving everything from the nature of the complex multi-site surface to the details of the method of packing the column. Assumptions can be, and have been made that allow for an approximate solution to the theoretical problem. The approximate results have been shown to check experience to a fair degree.

The principal problem of chromatography is the separation of substances. In a typical procedure the material of interest is started from a band near the top of the column and is washed down the column with pure solvent. As the washing proceeds, there is a separation of the original band into component substances. The value of the method is enhanced by any factor that can further the separation of the component bands, and that can minimize each band's dispersion. If there is extensive dispersion, the bands of two neighboring components may considerably overlap. The theory developed in this paper sheds some light upon the dispersion of bands of separable solutes.

It has been found elsewhere, and is true here, that reasonable solutions to the chromatography problem can be obtained only if the adsorption isotherm is linear.[2] For cases in which it is not linear, dispersion may still be important, and it should be affected in roughly the same way as in the linear case.

If the isotherm is linear, each molecule behaves independently of the others. The problem of dispersion of these molecules is analogous to the random walk problem. The number of steps may qualitatively be considered as the number of reactions to the surface. It is a well-known result that any factor increasing the number of steps, and correspondingly decreasing their length, decreases the dispersion. Thus, in going between two points in the chromatographic column, we might guess that we can decrease dispersion if we can find ways of increasing the number of combinations with the surface. For one thing, this is simply done by decreasing the rate of solvent flow. And, as our theory verifies, the dispersion is proportional to the square root of flow rate.

In actual cases, there are two other causes of dispersion. Channeling, for one thing, smears individual bands. This dispersion will not depend strongly upon the flow rate—it is minimized by careful packing of the column. Diffusion also causes dispersion. The dispersion due to diffusion is inversely proportional to the square root of flow rate. Thus, flow rate affects oppositely dispersion due to diffusion and dispersion due to "random walk." In practice, one should be able to find the optimum flow rate for minimum dispersion. Unless the rate of adsorption is very high, or the rate of flow very low, the "random walk" dispersion will be the more important of the two.

The majority of papers written on chromatography have started with the partial differential equations expressing the conservation of solute molecules.[2-7] Thomas[2] has solved these equations for several interesting cases with a finite rate of adsorption and desorption explicitly included. He has thereby obtained the values of adsorption and desorption constants from experimental data. When the adsorption isotherm is not linear, the equations can be solved only by assuming instantaneous equilibrium between solute and surface. These solutions are of great practical interest, but will not be considered here. Papers[8,9] also have been written which compare chromatographic separation with distillation. The results are useful in demonstrating the efficiency of column separation as compared to distillation, but the theory is not based on considerations of actual molecular processes.

Single Site Adsorption

The problem we first wish to consider is that in which a narrow band of solute is started at the top of the column and then washed through with pure solvent. Experimentally, the same velocity of flow, w, must be maintained in the column throughout the course of the experiment. We define $t°$ by the equality $wt° = L$, where L is the length of the column. $t°$, then, is the time it takes the solvent to flow completely through the column. The theory here presented is based on the following assumptions.

1. There is negligible net diffusion of any given solute molecule within the solvent in the direction of the column.

(2) H. C. Thomas, *Ann. N. Y. Acad. Sci.*, **49**, 161 (1948).

(3) (a) J. N. Wilson, *J. Am. Chem. Soc.*, **62**, 1583 (1940); (b) D. DeVault, *ibid.*, **65**, 532 (1943).

(4) J. Weiss, *J. Chem. Soc.*, 297 (1943).

(5) H. C. Thomas, *J. Am. Chem. Soc.*, **66**, 1664 (1944).

(6) J. E. Walter, *J. Chem. Phys.*, **13**, 229 (1945).

(7) E. Glueckauf, *Proc. Roy. Soc. (London)*, **A186**, 35 (1946); *J. Chem. Soc.*, 1302 (1947).

(8) A. J. P. Martin and R. L. M. Synge, *Biochemical J.*, **35**, 1358 (1941).

(9) S. W. Mayer and E. R. Tompkins, *J. Am. Chem. Soc.*, **69**, 2866 (1947).

2. When a molecule is in the liquid phase there is a definite, non-varying constant k_1 representing the probability per unit time that the molecule will adsorb on the surface. Also, when the molecule is on the surface, there is a definite probability per unit time of desorption which we call k_1'. k_1' is simply the unimolecular rate constant for dissociation of the surface and the solute molecule. k_1 is a rate constant for adsorption multiplied by the concentration of sites.

Assumption (2) implies several things. For one thing, it is a sufficient (but not necessary) condition for the existence of a linear adsorption isotherm. It further ensures that there is only one type of non-interacting site available to adsorb on. Since assumption (2) must hold at all times, it implies also that diffusion is not the rate-controlling step for adsorption (otherwise there would be a greater probability for adsorption of a molecule immediately following its desorption, since it would then be near the surface, but we have assumed that the probability of adsorption is a constant). Even for the most carefully packed column, assumption (2) is not realizable simply because of the fact that k_1 will be larger when the molecule is passing between two closely adjacent surfaces than when the surfaces are farther apart. However, an average k_1 is satisfactory provided that k_1 for a molecule goes through its range of fluctuations many times between successive adsorptions.

Because of assumption (1) we may say that a given solute molecule spends exactly a time $t°$ in the liquid phase while it is in the chromatographic column. The molecule will then spend time t adsorbed on the surface. By the application of probability theory we wish to find a distribution function in t representing the chance that in unit time the solute molecule will be eluted from the bottom of the column. Let us say to begin with that the particular molecule under study is in the liquid phase at the top of the column. In the course of its descent through the column it will adsorb on the surface, in general, r times. Assumption (2) assures us that the probability of reacting exactly r times is given by Poisson's probability law

$$\gamma_r = \frac{(k_1 t°)^r}{r!} e^{-k_1 t°} \tag{1}$$

Since the molecule must be in the liquid phase to pass through the bottom of the column, the molecule must also desorb exactly r times. The chance that this rth desorption occurs between the time t and $t + dt$ is the chance that just $r - 1$ desorptions occur in time t, multiplied by the chance that the rth desorption occurs between t and $t + dt$. The probability differential is

$$dP_r = P_r dt = \frac{(k_1't)^{r-1}}{(r-1)!} e^{-k_1't} k_1' dt \tag{2}$$

The quantity we want, of course, is the total probability differential, which is the sum over r of dP_r, weighted by the chance of exactly r reactions.

$$dP = \sum_{r=1}^{\infty} \gamma_r dP_r = P\, dt \tag{3}$$

Substituting (1) and (2) into (3) we arrive at the equation

$$P = e^{-k_1't - k_1 t°} \left(\frac{k_1 k_1' t°}{t}\right)^{1/2} \sum_{r'=0}^{\infty} \frac{\left(\frac{\sqrt{4 k_1 k_1' t t°}}{2}\right)^{2r'+1}}{r'!(r'+1)!} \tag{4}$$

where $r' = r - 1$. This is also equal to

$$P = e^{-k_1't - k_1 t°} \left(\frac{k_1 k_1' t°}{t}\right)^{1/2} I_1\left(\sqrt{4 k_1 k_1' t° t}\right) \tag{5}$$

It will be noticed that the argument, x, of the Bessel function, $I_1(x)$, is twice the geometrical mean of the expected number of adsorptions to the surface in time $t°$, and the expected number of desorptions in time t. For most cases of interest, and for most values of t this will be a large number. To a good degree of approximation we may use the first term of the asymptotic expansion of $I_1(x)$, obtaining the result

$$P = \frac{(k_1' k_1 t°)^{1/4}}{2\sqrt{\pi}} \frac{e^{-(\sqrt{k_1' t} - \sqrt{k_1 t°})^2}}{t^{3/4}} \tag{6}$$

It is to be noted that in equation 3 we allowed for any number of reactions from one to infinity. We did not allow for zero number of reactions, which event has a definite probability. If no reactions to the surface occur, then the molecule will be eluted from the column in exactly the time $t = 0$ (throughout the paper we use as the origin of the t axis the time $t°$ after the beginning of the experiment). The probability that there is no adsorption in passing through the column is $e^{-k_1 t°}$. This will be negligibly small under the same conditions which allow us to make the asymptotic expansion leading to (6).

To derive equation 6 we have assumed that the molecule started in the liquid phase. However, the molecule might initially be found attached to the surface. This leads to a slightly different distribution $P(t)$. As a matter of practice we can usually state the fraction of molecules of this thin band that are adsorbed on the surface. If the band is introduced rapidly into the column and the experiment started at once, nearly all molecules will start in the liquid phase. If the band is allowed to stay at the top of the column for a time, then equilibrium with the surface will be reached, and the fraction $k_1/k_1' + k_1$ of total molecules will start from the surface.

Centering our attention on a particular molecule initially adsorbed on the surface, the chance that it will adsorb exactly r times before reaching the bottom of the column is given, as before, by (1). However, r adsorptions are now associated with $r + 1$ desorptions, and the probability distribution function in t is given by

$$P_r = \frac{(k_1't)^r}{r!} e^{-k_1't} k_1' \tag{7}$$

Unlike the previous case, we can find the total distribution P by summing from zero to infinity

$$P = \sum_{r=0}^{\infty} \gamma_r P_r \tag{8}$$

Upon substitution we find that

$$P = e^{-k_1 t° - k_1't} k_1' I_0\left(\sqrt{4 k_1 k_1' t° t}\right) \tag{9}$$

The asymptotic expansion of the Bessel function,

$I_0(x)$, is allowable under the same conditions as before, and leads to

$$P = \frac{k_1'}{2\sqrt{\pi}(k_1 k_1' t^\circ)^{1/4}} \frac{e^{-(\sqrt{k_1' t} - \sqrt{k_1 t^\circ})^2}}{t^{1/4}} \quad (10)$$

Equations 6 and 10, weighted by the probability of the initial state of the molecule, should approximately yield the distribution curve for elution.

Multiple-site Adsorption

The surfaces encountered in adsorption work will always contain many different types of sites, each with different constants of adsorption and desorption. A more general treatment of chromatography would include the effect of n different types of sites with adsorption constants k_1, $k_2, \ldots, k_n$, and desorption constants $k'_1, k'_2, \ldots, k_n'$. The expressions found for such a general treatment are very cumbersome. Instead of giving a general solution of the n-site system we will solve the 2-site system. This may be of practical interest for certain surfaces—but many more quantitative measurements must be made to establish the extent of its value.

Just as we did for the single-site system, we will neglect diffusion along the column. We also state that the constants $k_1, k_2, \ldots, k'_1, k'_2, \ldots$, represent probabilities of reaction per unit time, and that they are constants independent of time, distance along the column, presence of other molecules, etc. These assumptions, as before, guarantee the existence of a linear adsorption isotherm, and assure us that diffusion is not the rate-controlling step for adsorption.

In the 2-site problem the molecule may initially be found in one of three places: in the liquid phase, on site 1, or on site 2. This is treated just as before.

To begin with, we will find the function P for a molecule that begins in the liquid phase. In the time t°, the independent probabilities that the molecule will adsorb r times on site 1 and s times on site 2 are given by equations 1 and 11, respectively.

$$\gamma_s = \frac{(k_2 t^\circ)^s}{s!} e^{-k_2 t^\circ} \quad (11)$$

Having reacted in this manner, the respective probabilities per unit time of remaining with sites of type 1 for time t_1, and sites of type 2 for time t_2, are given by equations 12a and 12b.

$$P_r = \frac{(k_1' t_1)^{r-1}}{(r-1)!} e^{-k_1' t_1} k_1' \quad (12a)$$

$$P_s = \frac{(k_2' t_2)^{s-1}}{(s-1)!} e^{-k_2' t_2} k_2' \quad (12b)$$

We are not interested in the unobservables t_1 and t_2, but only in their sum $t_1 + t_2 = t$, since this is the measure of the elution time. To obtain the distribution function in t, we combine these independent probabilities in the standard manner, and obtain

$$P_{rs}(t) = \int_0^t P_r(t_1) P_s(t - t_1) \, dt_1 \quad (13)$$

$$= \frac{k_1'^r k_2'^s}{(r-1)!(s-1)!} e^{-k_2' t/(r+s-1)} \int_0^1 x^{r-1}(1-x)^{s-1} e^{ktx} dx$$

where we have made use of the substitution $t_1 =$

tx and $k = k'_2 - k'_1$. If we use the series expansion of e^{ktx}, we obtain

$$P_{rs} = \frac{k_1'^r k_2'^s}{(r-1)!} e^{-k_2' t/(r+s-1)}$$

$$\sum_{m=0}^{\infty} \frac{(kt)^m}{m!} \frac{(r+m-1)!}{(r+m+s-1)!} \quad (14)$$

For the total probability expression, we must allow properly for all values of the subscript r and s. Following the example of 1-site theory, we can write

$$P = \sum_{r=1}^{\infty} \sum_{s=1}^{\infty} P_{rs} \gamma_r \gamma_s + e^{-k_1 t^\circ} \sum_{s=1}^{\infty} \gamma_s P_s(t) +$$

$$e^{-k_2 t^\circ} \sum_{r=1}^{\infty} \gamma_r P_r(t) \quad (15)$$

There is also the probability $e^{-(k_1 + k_2)t^\circ}$ that the molecule will be eluted at exactly $t = 0$.

The last two terms of equation 15 allow for the distribution in time if there are no reactions to site 1 and if there are no reactions to site 2, respectively. The reason that these terms (and also the term $e^{-(k_1 + k_2)t^\circ}$) cannot be included in the first term merely by summing from zero, instead of one, is that P_r and P_s of equation 12 are without meaning for $r = 0$ and $s = 0$. In general, a site of a given type will affect the distribution very little unless a molecule adsorbs on this type site very many times on the average. A molecule's probability, then, of adsorbing zero times is negligible, unless the site is of no importance and can be neglected from the treatment altogether. A possible exception to this rule, which neglects the probability of zero reactions, would result from a site that would hold molecules very tightly, making k'_1 a very small number. Neglecting the probability of zero reactions we can write

$$P = \sum_{r=1}^{\infty} \sum_{s=1}^{\infty} P_{rs} \gamma_r \gamma_s$$

$$= [e^{-k_2' t - (k_1 + k_2)t^\circ}] X \quad (16)$$

$$\left[\sum_{m=0}^{\infty} \sum_{r=1}^{\infty} \sum_{s=1}^{\infty} \frac{(k_1' k_1)^r (k_2' k_2)^s k^m t^{\circ r + s} t^{r+m+s-1}(r+m-1)!}{(r-1)!(r+m+s-1)! m! r! s!} \right]$$

It is hoped that in future work this expression can be reduced to a more usable form.

Experimental

Exploratory experiments were run to determine the approximate rate of adsorption and desorption for a typical chromatographic process. A five cm. wide chromatographic column was filled with a 2.5:1 mixture, by volume, of commercial grade Magnesol and Celite. The solvent used was water. The column was kept under a continuous vacuum of approximately 60 cm. from before the solute was introduced to the end of the experiment. 0.001737 gram of brilliant scarlet 3R[10] dissolved in 15 ml. of water was introduced into the top of the column. A narrow band with original approximate width of 0.5 cm. was then washed on

(10) Information on this dye has kindly been provided by Allied Chemical and Dye Corporation, National Aniline Division, 40 Rector Street, N. Y. 6, N. Y. The structure is
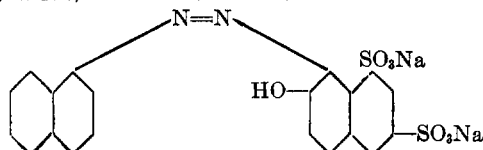
through the 20 cm. long column. Despite the wide column used, the dispersion due to channeling was kept down to about 0.5 cm. (as estimated visually), a small value compared to the total dispersion. The temperature was kept within a few degrees of 24°. When quantities of solute much greater than that mentioned above were run through the column, they passed through much faster, indicating that many sites were taken up and that the isotherm was not linear. The above quantity of solute is that at which the center of the band moves no faster upon further dilution. Samples were collected every 25 ml. The concentration of each sample was determined by a Beckman quartz spectrophotometer set at a wave length of 500 mμ.

Figure 1 shows the experimentally determined effluent curve, and that predicted from one-site theory with $k_1' = 0.01$ sec.$^{-1}$ and $k_1 = 0.0176$ sec.$^{-1}$. Plotted along the abscissa is the reduced volume, $V/V° = X$ where V_0 is the total volume of solvent within the column, and V is a measure of input volume. For consistency with the equations derived in the last section, we let $V + V°$ be the measure of input volume from the beginning of the experiment. The ordinate is a measure of the concentration in arbitrary units.
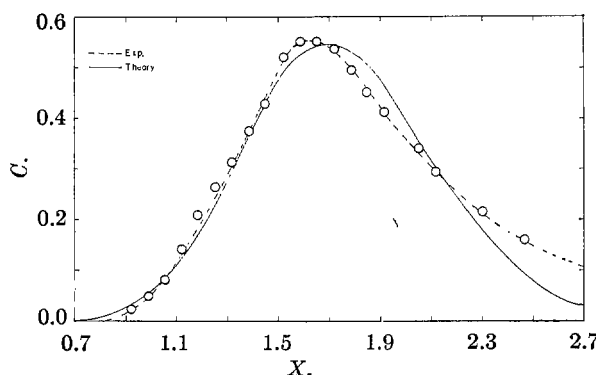

Fig. 1.

Equation 6 was used in plotting the theoretical curve since the solute molecules were introduced into the column directly from the liquid phase, and there was not a time lag which would allow unaccounted for equilibration. If equation 6 is written in terms of our new variable, X, we have

$$P = \frac{Ae^{-t°(\sqrt{k_1'X} - \sqrt{k_1})^2}}{X^{3/4}} \qquad (17)$$

where A is a normalization constant. $t°$ may also be written as $V°/\dot{V}$. $\dot{V}$ is the rate of input flow measured in cm.^{3} sec.$^{-1}$. Written in terms of $\dot{V}$, the dependence of the dispersion upon flow rate is easily appreciated.

$t°$, in our particular experiment, was equal to 2480 sec. $V°$ and $\dot{V}$ were 300 cm.^{3} and 0.121 cm.^{3} sec.$^{-1}$, respectively. The expected number of reactions to the surface of a molecule during its course of descent down the column, $k_1t°$, was 43.7.

The measured value of concentration fits equation 17 quite well for the front boundary, but the back boundary is significantly different, and so is the curvature near the maximum. It is probable that with the use of meticulously prepared adsorbents, a better fit could be made. It is possible that the observed discrepancy is due to a second type site which, because of its scarcity, does not adsorb molecules very often, but holds solute molecules very strongly when it does adsorb them (k'_1 very small). This could well increase the concentration for large value of X, and leave it unaffected for the front boundary. No attempt has been made, however, to fit the data to the more difficult two-site theory.

Harris and Tomkins[11] have collected data on the effluent curves of rare earth ions. In their experiments, the band was eluted with a complexing agent. Assumption two should hold provided the rate constant of complexing is fast. Otherwise, the rare earth ions would be more prone to return to the surface immediately after they had left it.

(11) O. H. Harris and E. R. Tompkins, J. Am. Chem. Soc., **69**, 2792 (1947).

The fact that some of the reactions are bimolecular is of no significance providing the other reactant (complexing agent, and ions of a given type on the surface) is at constant concentration.

Figure 2 shows the experimental points for praseodymium from Table IV of their paper, and the theoretical curve plotted with $k_1 = 0.02174$ and $k'_1 = 0.0001890$ sec.$^{-1}$. Equation 10 was used in this case, since it is assumed that nearly all molecules were on the surface when the complexing agent was added. (Equations 6 and 10, however, yield nearly identical curves.) In their experiment, $t°$ was 17,420 seconds and the expected number of combinations of a given ion, with the surface, is 378.7. The fit is seen to be quite satisfactory.
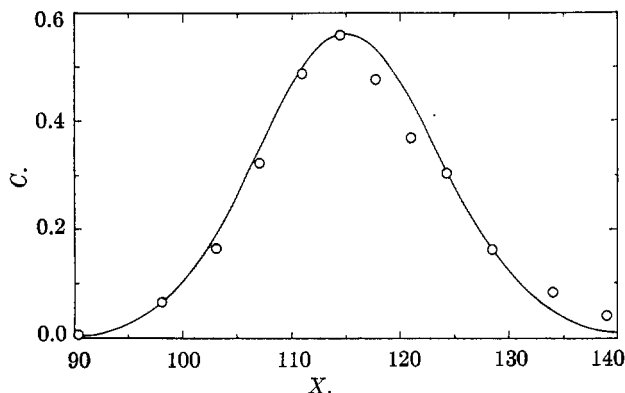

Fig. 2.

We will now show that the dispersion is nearly proportional to one over the square root of $t°$. To do this, we assume that $X^{3/4}$ is a slowly varying function of X as compared to the exponential. Equation 17, then, goes over into

$$P \sim e^{-t°(\sqrt{k_1'X} - \sqrt{k_1})^2} \qquad (18)$$

For our purposes, $X_{1/2} - X_m$ is a sufficiently good measure of dispersion. $X_{1/2}$ is the value of the coördinate X for which the concentration has dropped to half of its highest value. X_m is the value of X for which the concentration is a maximum. The above distribution yields

$$X_m = k_1/k_1' \qquad (19)$$

$$X_{1/2} - X_m = (\ln 2)^{1/2}(k_1/k_1')\left(\frac{(\ln 2)^{1/2}}{E} + \frac{2}{E^{1/2}}\right)$$

where $E = k_1t°$ is the expected number of reactions to the surface. $1/E$ is ordinarily small compared to $1/E^{1/2}$, so that we can write

$$X_{1/2} - X_m \cong \pm 2\left(\frac{\ln 2}{E}\right)^{1/2}\left(\frac{k_1}{k_1'}\right) \qquad (20)$$

Since E is proportional to $t°$ (and inversely proportional to $\dot{V}$), our assumption is true. It is not surprising that any factor altering the rate constant can strongly affect the separability of compounds when we notice the way in which dispersion depends upon rate constants. Factors such as pH, ionic strength, and especially temperature, are significant, and could be studied for individual cases.

It is interesting that the distribution curves predicted from theory are not symmetric, and thus not of the same form as the Gaussian function. As demonstrated in Fig. 1, these distributions are characterized by a positive skew.

A More General Case

In previous sections of this paper various cases in which the solute molecules were originally found within the confines of a narrow band were considered. There are, however, many other initial conditions of importance. Some of these will be treated in the following general discussion. It is unfortunate that simple expressions do not result in a majority of cases.

The expressions that we derive will be more useful if we let V (volume) instead of t (time) be the independent variable. In this case, $V = \dot{V}t$ and $V^\circ = \dot{V}t^\circ$. With this transformation equations 4 and 9, respectively, go over into (21) and (22), respectively.

$$P(V) = \frac{1}{V} e^{-\frac{1}{V}(k_1 V^\circ + k_1' V)} \left(\frac{k_1 k_1' V^\circ}{V}\right)^{1/2} \times$$
$$I_1 \left(\frac{1}{V} \sqrt{4k_1 k_1' V^\circ V}\right) \quad (21)$$

$$P(V) = \frac{k_1'}{V} \exp\left[\frac{1}{V}(k_1 V^\circ + k_1' V)\right] \times$$
$$I_0 \left(\frac{1}{V} \sqrt{4k_1 k_1' V^\circ V}\right) \quad (22)$$

It will be useful to review the significance of the above equations. If N molecules all start from a single narrow band at the beginning of the experiment $(t = -t^\circ, V = -V^\circ)$, $P(V)\,dV$ represents the chance that any given molecule will be eluted between volume V and $V + dV$. The probable number of molecules eluted between V and $V + dV$ will then be $NP(V)\,dV$. $NP(V)$ is the number of molecules per unit volume and thus is the concentration, C.

Suppose now that the molecules are not all originally contained within the small band at the top of the column. Instead, let the first small volume element, dV', and every small volume element thereafter contain a number of molecules equal to $C_0(V')\,dV'$. (We have introduced V' as representing the volume introduced into the top of the column. At $V' = 0$ the first solute molecule enters the top layer of adsorbent. Eventually, we will want to write $C(V)\,dV$, the number of molecules in the volume between V and $V + dV$, as a function of V. The sum of the molecules eluted between V and $V + dV$ will be the sum of the molecules contributed to this particular band by all of the small volume elements, dV'. Since many small volume elements, dV', contribute to one measured concentration, $C(V)$, we will have to integrate over V'. It is well to remember that $C_0(V')$ is an initial, but not necessarily constant, concentration.) Since all molecules will be in the liquid phase upon first entering the column, equation 20 must be used. The concentration of solute molecules in the column efflux is

$$C(V) = \int_{V'=0}^{V} C_0(V')P(V - V')\,dV' \quad (23)$$

The upper integration limit is V since molecules arriving at the top of the column after $V' = V$ do not contribute at all to $C(V)$. In rare cases those molecules that adsorb on the surface zero times must be considered. In those cases we add the term $[e^{(-(k_1 V^\circ/\dot{V}))}]C_0(V)$ to the right-hand side of (23). The value of this term for the experiment considered in the last section is approximately $10^{-18} C_0(V)$.

If a band of considerable width is introduced into the column, $C_0(V')$ may be of the following form

$$C_0(V') = C_0 \quad 0 < V' < V'' \quad (24)$$
$$C_0(V') = 0 \quad V' > V''$$

If we may approximate a given finite band by the expression

$$C_0(V') = N\delta(V') \quad (25)$$

where $\delta(V')$ is the Dirac delta function, we obtain from (23)

$$C(V) = NP(V) \quad (26)$$

As has been pointed out, this is the concentration obtained by assuming a very thin band. We have used this equation throughout the paper.

As a second general case, suppose that the solute molecules are somehow initially distributed in the column, and then be washed through with pure solvent. It will be convenient to introduce a new independent variable, $v = V + v'$, where V is the measure of volume used previously, and v' is equivalent to V° for any given band of solute within the column. v is the volume of liquid passed through the column after the initial conditions have been specified.

The concentration of molecules in the liquid phase is given by $C_1(v')$, and if all the molecules in the surface phase were suddenly desorbed, their concentration would be $C_s(v')$. The concentration in the effluent is the sum of several terms. One term is contributed by original liquid phase molecules, and another by surface phase molecules. For the concentration of molecules originally in the liquid phase, $C^1(v)$, we can write

$$C^1(v) = \int_{v'=0}^{v} C_1(v')P(v - v')\,dv' \quad (27)$$

$P(v - v')$ is given by equation 21, providing $v' = V^\circ$.

Molecules beginning in the surface phase contribute the following to the concentration

$$C^s(v) = \int_{v'=0}^{v} C(v')P(V - v')\,dv' \quad (28)$$

$P(v - v')$ is now given by (22). If there are molecules near the lower end of the column at the beginning of the experiment, the probability of zero reactions may well be important. This case will contribute a term

$$C^\circ(v) = [e^{-k_1 v''/\dot{V}}]C_1(v) \quad (29)$$

The final concentration, $C(v)$, is given exactly by

$$C(v) = C^1(v) + C^s(v) + C^\circ(v) \quad (30)$$

Appendix

1. **Normalization.**—To assure us that the equations for effluent distribution are *bona fide* probability functions, we will show that they are normalized. Equation 21 can be written as

$$P(V) = e^{-\left(\frac{k_1 V^\circ}{\dot{V}} + \frac{k_1' V}{\dot{V}}\right)} \sum_{r=1}^{\infty} \frac{\left(\frac{k_1 k_1' V^\circ}{\dot{V}^2}\right)^r V^{r-1}}{(r-1)!\,r!} \quad (31)$$

The integral of $P(V)\,dV$ from zero to infinity should give the total probability that there are one or more adsorptions on the surface.

$$\int_0^\infty P(V)\,dV = 1 - e^{-(k_1 V^\circ/\dot{V})} \quad (32)$$

We have mentioned that the probability of zero adsorptions is $e^{-k_1 V^\circ/\dot{V}}$. Adding this term to (32), we arrive at the value unity. Equation 22 can likewise be shown to be normalized.

2. Expectation Values.—Equation 4 can be written

$$P(t) = e^{-E - k_1't} \sum_{r=1}^{\infty} \frac{(k_1'E)^r\, t^{r-1}}{r!\,(r-1)!} \qquad (33)$$

where $E = k_1 t^\circ$. The expectation value of the Nth power of t is

$$Ex(t^n) = \int_0^\infty P(t) t^n dt = \frac{E e^{-E}}{(k_1')^n} \sum_{r=0}^{\infty} \frac{E^r}{r!} \frac{(r+n)!}{(r+1)!} \qquad (34)$$

We can approximately evaluate (34) by assuming that $E^r/r!$ is a rapidly varying function of r as compared to the other terms. $E^r/r!$ is near its maximum when $r = E$. If we factor the other terms out with r equal to this value, we obtain

$$Ex(t^n) \cong \frac{(E+n)!}{(E+1)!} \times \frac{E}{(k_1')^n}$$

$$Ex(t) = \frac{E}{k_1'} = \frac{k_1 t^\circ}{k_1'} \qquad (35)$$

$$Ex(t^2) \cong \frac{(E+2)E}{k_1'^2}$$

3. Position of Mode.—The single-site distribution can be written

$$P \sim \exp \frac{[-t^\circ(\sqrt{k_1'X} - \sqrt{k_1})^2]}{X^n} \qquad (36)$$

where n $^3/_4$ or $^1/_4$. By setting the derivative of P with respect to X equal to zero, we can solve for X (max.), the maximum point of the distribution. This is

$$X\,(\text{max.}) = \frac{k_1}{k_1'} \left(1 - \frac{2n}{E}\right) \qquad (37)$$

provided that $X \gg n$.

4. Reduction of Two-site Theory for Identical Sites.—If $k_1' = k_2' = k'$ in equation 13, P_{rs} reduces to

$$P_{rs} = \frac{(k')^{r+s}\, e^{-k't}\, t^{r+s-1}}{(r+s-1)!} \qquad (38)$$

Let $r + s = n$.

$$P_n = \frac{(k_1't)^{n-1}}{(n-1)!} k_1' \qquad (39)$$

This is the equation derived for one site theory.

THE VAPOR PRESSURES OF LITHIUM AND SODIUM OXIDES[1]

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Theoretical calculations of the stability of alkali oxide gaseous molecules have been checked experimentally for Li_2O and Na_2O. The results indicate that Li_2O vapor under neutral conditions may contain gaseous molecules in concentrations comparable to the gaseous elements. It is possible that both Li_2O and LiO gaseous molecules may be important, especially under oxidizing conditions. Na_2O vapor consists predominately of Na atoms and O_2 molecules with any oxide molecules being less important than the elements under neutral conditions. Thus Na gas and O_2 gas do not react with one another unless they are at high enough pressures to deposit solid or liquid Na_2O. No experimental data are available for the heavier alkali oxides but the calculations indicate that gaseous MO molecules might be of importance even under neutral conditions. The M_2O gaseous molecules are expected to be less important than the MO or elemental molecules. In a hydrogen–oxygen system all of the alkali metals react to form stable gaseous hydroxides.

Theoretical

Brewer and Mastick[3] have calculated the vapor pressures of the alkali oxides using the Born–Haber cycle with an ionic model to calculate the heats of formation of the gaseous molecules. In this work their calculations have been extended and the vapor pressures of Li_2O and Na_2O have been experimentally determined to check these calculations.

The calculations of Brewer and Mastick indicated that none of the M_2O gaseous molecules should be of chemical importance except possibly for the Li_2O molecule. The calculations of Rittner[4] for the gaseous alkali halide molecules and those of Klemperer and Margrave[5] indicate that it might be possible to extend these calculations to consider in detail the polarization and repulsive contributions to the stability of the molecules. Use of the gaseous ionic radii given by Rittner would indicate that the interatomic distances should be larger and therefore the M_2O molecules less stable than calculated by Brewer and Mastick. However the Li_2O calculations indi-

(1) Presented at the 121st Meeting of the American Chemical Society, Buffalo, New York, March, 1952.
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(3) L. Brewer and D. Mastick, *J. Am. Chem. Soc.*, **73**, 2045 (1951).
(4) E. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951).
(5) W. Klemperer and J. Margrave, *ibid.*, **20**, 527 (1952).

cate that it still might be of chemical importance in oxidizing systems and possibly even in neutral systems.

The stabilities of the MO gaseous molecules were calculated by considering that the O^- ion would be intermediate in size between F^- and Cl^-. The heats of formation of the gaseous alkali halide molecules from the gaseous ions as given by Rittner do not differ by more than 20 kcal. Thus the corresponding values for the MO gaseous alkali oxide molecules were taken as the mean of the fluoride and chloride values with a maximum uncertainty of 10 kcal. These values combined with the ionization potentials of the alkali metals and the electron affinity of 53.8 kcal. for oxygen yielded the following heats of dissociation of the MO gaseous molecules to the gaseous atoms or D_0 values going from Li to Cs: 97, 71, 81, 79 and 80 kcal. By combining these values with the heats of sublimation of the metals and the heat of dissociation of O_2, one obtains for the ΔH of formation of gaseous MO molecules from the elements in the standard states going from Li to Cs: 0, +14, 0, +1 and −2 kcal. with an uncertainty of 10 kcal.

Free energy functions were estimated for the MO gaseous oxides and the above heats used to calcu-