# The Approach to Equilibrium in Fractionation*

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The differential equations for a plate column are solved for cases that arise in the concentration of isotopes, where there is a small difference in the concentration in the liquid and gas phases, or where the equilibrium constant for ion exchange is very nearly unity. A formula suitable for computation is deduced, and curves are given showing the rate of approach to equilibrium for various numbers of plates.

THE gradual approach of a fractionating plate column to an equilibrium condition after it has been put into operation has been treated by methods in which the equations for the discrete series of plates are replaced by a single differential equation in which the concentrations throughout the column are considered to vary continuously.[1–5]

In this paper it is shown that in many cases the simultaneous differential equations that govern the change of concentration at each plate can be solved directly.[6] In many cases in which the equilibrium constant differs from unity by a small amount, and the number of plates is not too great, the equations have particularly simple solutions. These cases will be considered in this paper, reserving the more general case for a later paper.

## FUNDAMENTAL EQUATIONS

We shall consider the case of a column of $p$ equal plates in which concentrations are kept normal at one end, and in which no material is withdrawn at the other. As an example, we may consider the concentration of the nitrogen isotope of mass 15, by means of the equilibrium between ammonia gas and ammonium hydroxide solution. The equilibrium ratio of the fraction of $N^{15}$ atoms in the liquid to the fraction in the gas was determined by Urey, Huffman, Thode, and Fox[7] to be 1.006. This difference was made use of in a packed fractionating column to prepare samples of ammonia enriched in the $N^{15}$ isotope. The flow of solution and gas in an equivalent plate column is shown diagrammatically in Fig. 1.

The column is filled with ammonia gas and a solution of $NH_4OH$ is introduced at the left and leaves at the right. Care is taken to separate all the ammonia from the solution leaving at the right and to return it to the end of the column, so that no ammonia is removed or added at the right. The surplus ammonia escapes at the left. An increase in the ratio of the $N^{15}$ takes place at the right as its ratio is greater in the liquid than in the gas, while the ratio of the isotopes at the left remains 1:131, the normal value.

In symbols, if we denote the fraction of nitrogen atoms of mass 15 in the liquid by $N(N_1, N_2 \cdots N_p)$ for the different plates, and in the gas by $n$, the ratio of $N_k$ to $n_k$ for each plate is $\alpha$. If $w$ is the total number of nitrogen atoms flowing per second to the right as liquid and to the left as gas, the loss of nitrogen atoms of mass 15 at plate $k$ is given by the sum of two terms; $wN_k$ move to the right in the liquid and $wn_k$ move to the left in the gas. On the other hand, the gain of nitrogen atoms of mass 15 at plate $k$ is likewise made up of two terms; $wN_{k-1}$ are received from the left in the liquid, and $wn_{k+1}$ are received from the right as gas. If $h$ is the total number of nitrogen atoms on each plate, the equation governing the rate of change of the number of atoms of nitrogen 15 is, since $n_k$

* This paper was completed in 1941, and was voluntarily withheld from publication.

[1] W. H. Keesom and H. van Dijk, *Communications from the Kamerlingh Onnes Laboratory* (Leiden, 1932), Supplement 71C.

[2] H. Barwich, Zeits. f. Physik **100**, 184 (1936).

[3] J. R. Huffman and H. C. Urey, Ind. Eng. Chem. **29**, 531 (1937).

[4] J. Bardeen, Phys. Rev. **57**, 35 (1940).

[5] K. Cohen, J. Chem. Phys. **8**, 588 (1940).

[6] The authors are indebted to Professor Carl Eckart who pointed out in conversation with one of the authors that this possibility should be investigated.

[7] H. C. Urey, J. R. Huffman, H. G. Thode, and M. Fox, J. Chem. Phys. **5**, 856 (1937).

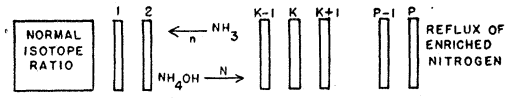


FIG. 1. Plate column for the enrichment of the nitrogen isotope of mass 15.

$$=\alpha^{-1}N_k,$$

$$\frac{h}{w}\frac{dN_k}{dt}+N_k(1+\alpha^{-1}) =N_{k-1}+\alpha^{-1}N_{k+1} \quad (k=1\cdots p-1),$$

and for the last plate, $k=p$,

$$\frac{h}{w}\frac{dN_n}{dt}+N_p\alpha^{-1}=N_{p-1}.$$

Let us put $h/w=a$ and write $X_k$ in place of $N_k$ as the dependent variable. Then the equations are:

$$\begin{aligned}(aD+1+\alpha^{-1})X_k&=X_{k-1}+\alpha^{-1}X_{k+1} \quad (k=1, 2\cdots p-1),\\ (aD+1+\alpha^{-1})X_p&=X_{p-1}+X_p \quad (k=p).\end{aligned} \tag{1}$$

These equations may be reduced to a simpler form by introducing the variable $Z_k$ by the substitution

$$X_k=X_0\{\alpha^k+\alpha^{k/2}Z_k\exp[-(1+\alpha^{-1})t/a]\}. \tag{2}$$

For $t=\infty$, $X_k=X_0\alpha^k$.

Let us put $\tau=(1/a\alpha^{\frac{1}{2}})t$. As $\alpha$ is nearly unity, $\tau$ becomes unity at a time $t=a=h/w$ approximately, that is, the time required to remove the material on one plate, and the value of $\tau$ gives the ratio of the total flow of atoms to the number of atoms on one plate.

The equations then take the form:

$$\begin{aligned}\frac{dZ_1}{d\tau}&=Z_2,\\ \frac{dZ_2}{d\tau}&=Z_1+Z_3,\\ &\cdots\cdots\\ \frac{dZ_k}{d\tau}&=Z_{k-1}+Z_{k+1},\\ &\cdots\cdots\\ \frac{dZ_p}{d\tau}&=Z_{p-1}+\alpha^{\frac{1}{2}}Z_p.\end{aligned} \tag{3}$$

The initial conditions will be taken to be uniform concentration throughout the column, that is, all $X$'s alike;

$$t=t_0, \quad X_k=X_0, \quad \text{and} \quad Z_k(0)=\alpha^{-k/2}-\alpha^{k/2}. \tag{4}$$

These equations apply to many cases in which increased concentration of a faint isotope occurs at the closed end of a fractionating column. Among them may be listed the concentration of $Ne^{22}$ by evaporation from liquid neon,[8] the concentration of $O^{18}$ by evaporation of $H_2O$,[9–12] the concentration of $C^{13}$ and $N^{15}$ by ion exchange[13,14], and the enrichment of the light isotopes in mercury.[15] In these cases normal isotopic abundance is maintained at one end and none of the element escapes from the other. In the cases of chemical equilibrium, the constant of the reaction $\alpha$ is given by $(N/1-N)/(n/1-n)$, where $N$ is the fraction of special atoms or molecules under consideration in the liquid, and $n$ is the corresponding fraction for the gas. Rearranging terms, $N/n=\alpha+(\alpha-1)N$. We have put $N/n=\alpha$ in (1) since in the cases considered both $\alpha-1$ and $N$ are very small. In the case of liquid neon in equilibrium with its vapor, $N$ and $n$ give the fraction of $Ne^{22}$ atoms in the liquid and in the vapor.

Similar relations also hold for the concentration of the isotopes $Ne^{22}$, $A^{36}$, $O^{18}$ by means of diffusion into a stream of mercury vapor.[16–19] The successive plates in Fig. 1 represent the series of mercury vapor pumps which may be connected so as to transfer the gas enriched in the faint isotope either to the right or to the left.

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[8] W. H. Keeson and H. van Dijk, Proc. K. Akad. Wiss. Amsterdam **34**, 42 (1931); **36**, 248 (1933); Physica **1**, 1109 (1934).
[9] G. N. Lewis and R. E. Cornish, J. Am. Chem. Soc. **55**, 2616 (1933).
[10] M. W. Wahl and H. C. Urey, J. Chem. Phys. **3**, 411 (1935).
[11] H. C. Urey, G. B. Pegram, and J. R. Huffman, J. Chem. Phys. **4**, 623 (1936).
[12] A. E. Brodsky and O. C. Scarre, Acta Physicochem. U.R.S.S. **10**, 729 (1939).
[13] C. A. Hutchison, D. W. Stewart, and H. C. Urey, J. Chem. Phys. **8**, 532 (1940).
[14] H. G. Thode and H. C. Urey, J. Chem. Phys. **7**, 34 (1939).
[15] A. Keith Brewer and S. L. Madorsky, J. Research Nat. Bur. Stand. **38**, 129 (1947).
[16] G. Hertz, Zeits. f. Physik **79**, 108, 700 (1932); **91**, 810 (1934).
[17] H. Barwich, Zeits. f. Physik **100**, 166 (1936).
[18] H. Barwich and W. Schutze, Naturwiss. **24**, 667 (1936).
[19] R. Scherr, J. Chem. Phys. **6**, 251 (1938).

In case the isotope to be concentrated is the lighter one, as in the case of $A^{36}$, we connect the pumps so as to transfer it to the right; the equations deduced above apply directly where $\alpha$ is the ratio of the concentration of $A^{36}$ in the mercury vapor leaving a pump to that in the argon in the pump reservoir itself. In case we wish to concentrate a faint heavy isotope such as $Ne^{22}$, we connect the pumps so that the lighter isotope $Ne^{20}$ is transferred to the left in Fig. 1 by the stream of mercury, and an equal number of heavy isotopes are transferred to the right, thus giving again the relations expressed in Eq. (1) for the concentration of the heavy isotope.

It is also possible to connect the pumps so that they transport an extra number of light atoms such as $A^{36}$ toward the end where normal abundance is maintained, that is, to the left in Fig. 1, thus producing a depletion of these atoms at the closed end. In this case the equations are the same as in the former case, except that $\alpha$ is replaced by its reciprocal.

In this paper we shall find the solution of Eq. (3) for the cases in which $\alpha^p$ may be replaced by $1+p(\alpha-1)$. If $\alpha=1+\epsilon$, $\alpha^p=1+p\epsilon$ and $p\epsilon$ must be small compared with unity for the solutions to apply. In these cases the solutions of the differential equations are specially simple and are applicable to many important problems. Enrichments of ten percent or less in the abundance of many isotopes may be treated in this manner, and experimentally such enrichments can be measured with considerable accuracy with a mass spectrometer. Tables of $\alpha$ are given in most of the references cited, and particularly in references 19 and 20.[20] We shall first find expressions for $X_k$ and the fraction of the isotopes on the last plate $X_p$ as functions of the time. In a later paper we shall give the corresponding solutions for cases in which $p\epsilon$ is not small.

## SOLUTION OF DIFFERENTIAL EQUATIONS FOR SMALL ENRICHMENTS

The system of Eq. (3) is satisfied by solutions of the form:

$$Z=\sin k\phi e^{2\tau\cos\phi}, \tag{5}$$

since for $k=1, 2\cdots p-1$

$$\frac{dZ_k}{d\tau}=2\sin k\phi\cos\phi e^{2\tau\cos\phi}$$
$$=[\sin(k-1)\phi+\sin(k+1)\phi]e^{2\tau\cos\phi},$$

and consequently,

$$\frac{dZ_k}{d\tau}=Z_{k-1}+Z_{k+1} \text{ for } k>1,$$
$$\frac{dZ_1}{d\tau}=Z_2 \text{ for } k=1.$$

It is also necessary to satisfy the equation for the last plate $k=p$. For this we must choose $\phi$ in (5) so that $2\sin p\phi\cos\phi=\sin(p-1)\phi+\alpha^{\frac{1}{2}}\sin p\phi$, that is

$$2\sin p\phi\cos\phi-\sin p\phi\cos\phi+\cos p\phi\sin\phi$$
$$=\alpha^{\frac{1}{2}}\sin p\phi,$$
$$\sin(p+1)\phi=\alpha^{\frac{1}{2}}\sin p\phi. \tag{6}$$

There are $p$ distinct values of $\phi$, $(0<\phi<\pi)$ which make (5) a solution. To find them put $\alpha^{\frac{1}{2}}=(1+\epsilon)^{\frac{1}{2}}=1+\frac{1}{2}\epsilon$. Then (6) becomes

$$\sin(p+1)\phi-\sin p\phi=\tfrac{1}{2}\epsilon\sin p\phi,$$
$$2\sin\tfrac{1}{2}\phi\cos(p+\tfrac{1}{2})\phi=\tfrac{1}{2}\epsilon\sin p\phi.$$

Since the right-hand term is very small, the values of $\phi_r$ are those $p$ values which make $\cos(p+\frac{1}{2})\phi_r$ very nearly zero, that is:

$$\phi_r=r\pi/(2p+1) \quad (r=1, 3, 5,\cdots 2p-1).$$

The most general solution of (5) is thus seen to be:

$$Z_k=\textstyle\sum_r A_r\sin k\phi_r e^{2\tau\cos\phi_r}. \tag{7}$$

## INITIAL CONDITIONS

The initial conditions (4) may be satisfied by the proper choice of the constants $A_r$. The initial values are:

$$Z_k(0)=\alpha^{-\frac{1}{2}k}-\alpha^{\frac{1}{2}k}=(1-\tfrac{1}{2}k\epsilon)-(1+\tfrac{1}{2}k\epsilon)=-k\epsilon. \tag{8}$$

Thus

$$\textstyle\sum A_r\sin kr\pi/(2p+1)=-k\epsilon$$
$$(r=1, 3, 5,\cdots 2p-1). \tag{9}$$

Set

$$A_r=-\epsilon B_r \quad \text{and} \quad \omega=\pi/(2p+1). \tag{10}$$

The $p$ equations for determining $A_r$ or $B_r$ are

[20] H. C. Urey and L. V. Greif, J. Am. Chem. Soc. **57**, 321 (1935).

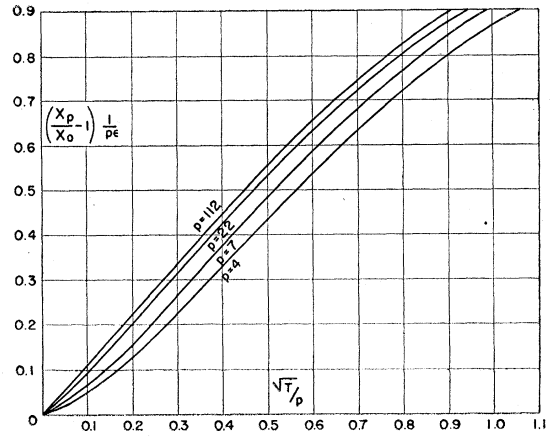


FIG. 2. Curves showing the rate of approach to equilibrium for various numbers of plates ($P$).

then:

$$1=B_1\sin\omega+B_3\sin3\omega+\cdots+B_{2p-1}\sin(2p-1)\omega,$$

$$2=B_1\sin2\omega+B_3\sin6\omega+\cdots+B_{2p-1}\sin2(2p-1)\omega,$$

$$\cdot\quad\cdot\quad\cdot$$

$$p=B_1\sin p\omega+B_3\sin3p\omega+\cdots+B_{2p-1}\sin p(2p-1)\omega. \quad (11)$$

Any $B_r$ can be found by multiplying each of the $p$ equations in order by $2\sin r\omega$, $2\sin2r\omega\cdots2\sin pr\omega$ and adding. Using the value $\omega=\pi/(2p+1)$, all the sums are found to be zero except the one multiplying $B_r$, which has the value $p+\frac{1}{2}$. The sum on the left is given in tables,[21] and the values of $B_r$ are found to be:

$$B_r=(-1)^{(r-1)/2}\frac{1}{2p+1}\frac{\cos\frac{1}{2}r\omega}{\sin^2\frac{1}{2}r\omega}\qquad(r=1,3,5\cdots2p-1). \quad (12)$$

Substituting in (10) and (7) we obtain the $Z$'s which satisfy the system of differential Eqs. (3) with the particular initial conditions (8). Substituting these $Z$'s in Eq. (2) we find for the concentration on the $k$ plate at various times:

$$\frac{X_k}{X_0}=1+k\epsilon-\frac{\epsilon}{2p+1}\sum_r(-1)^{(r-1)/2}\frac{\cos(r\omega/2)}{\sin^2(r\omega/2)}\times\sin kr\omega\exp[-(2t/a)(1-\cos r\omega)]. \quad (13)$$

For the last plate Eq. (13) takes a simpler form since all the $r$'s are odd. Substituting the value of $\omega=\pi/(2p+1)$,

$$\sin pr\omega=\sin\frac{2p}{2p+1}\cdot\frac{r}{2}\pi=\sin\left(1-\frac{1}{2p+1}\right)r\frac{\pi}{2}$$

$$=\sin\left(r\frac{\pi}{2}-\frac{\omega r}{2}\right)=\sin r\frac{\pi}{2}\cos\frac{\omega r}{2}$$

$$=(-1)^{(r-1)/2}\cos\frac{\omega r}{2}.$$

Hence (13) becomes, for the last plate:

$$\frac{X_p}{X_0}=1+p\epsilon-\frac{\epsilon}{2p+1}\sum\cot^2\frac{\omega r}{2}\times\exp\left[-\frac{2t}{a}(1-\cos r\omega)\right]. \quad (14)$$

If we put

$$\frac{1}{2p+1}\cot^2\frac{\omega r}{2}=C(r)$$

and

$$\frac{1}{p}\exp\left[-\frac{2t}{a}(1-\cos r\omega)\right]=D(r,\tau)$$

Eq. (14) may be written in the form:

$$X_p/X_0=1+p\epsilon-p\epsilon[\textstyle\sum_r C(r)D(r,\tau)].$$

In this the bracket is independent of $\alpha(=1+\epsilon)$ and has the values unity for $t=0$ and zero for $t=\infty$. Both $C(r)$ and $D(r,\tau)$ decrease rapidly with increasing $r$, and the expression is very convenient for computing $X_p$ in any particular case. A series of values were computed for different values of $\tau$ for columns with various numbers of plates and the rate of approach to equilibrium is shown by the plot of $1-\sum C(r)D(r,\tau)=(X_p/X_0-1)/p\epsilon$ in Fig. 2. The abscissa is chosen as $(\tau)^{\frac{1}{2}}/p$ for convenience in plotting the curves for different numbers of plates. Curves

[21] *Smithsonian Mathematical Formulae and Tables* (Smithsonian Institute, Washington, D. C., 1939), p. 82.

are drawn for $p=4$, 7, 22, and 112 plates. A curve for $p=337$ is indistinguishable from that for 112 plates. From these curves we may find the time required to reach any fraction of the maximum enrichment. Thus in a column with 22 plates, 70 percent of the final enrichment is reached, according to Fig. 2, at $(\tau)^{\frac{1}{2}}/22=7$, or $\tau=23{,}700$; that is, a time equal to 23,700 times the time required for an amount of material equal to that on one plate to be transported to the next.

The curves in Fig. 2 indicate that for columns with a large number of plates the curves become straight lines with a slope of 1.12 from zero up to approximately 60 percent of the maximum enrichment. This gives the simple formula for this range,

$$X_p/X_0=1+1.12\epsilon(\tau)^{\frac{1}{2}}.$$

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# Surface Catalysis

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IT is the purpose of this paper to review some of the work of the author and his associates in the field of surface catalysis. This work was begun in a fundamental way through some experiments on positive ions[1,2] while the author was in residence at the California Institute of Technology. No complete discussion of the literature on the subject is attempted.

Perhaps most closely related to the author's earlier work at California Institute of Technology are some studies carried out in the middle thirties on the heterogeneous thermal decomposition of hydrocarbon molecules by a molecular ray method in which a beam of hydrocarbon molecules enters an otherwise closed vessel through an aperture (short channel) and sets up an equilibrium pressure of $10^{-5}$ to $10^{-6}$ mm Hg which could be measured with an accuracy of $10^{-9}$ mm Hg by a balanced high sensitive Pirani gauge circuit. The gauges could be maintained at any desired temperature including liquid nitrogen temperature. Inside the vessel was mounted an electrically heated platinum foil, the geometric arrangement of which was such that the incoming beam had to strike the hot surface, which was not much larger than the cross section of the beam—that is, not more than a few square millimeters. Since the total gas pressure, including the background pressure, was only of the order of some $10^{-5}$ mm Hg, gas molecules would only suffer collisions with the cold walls of the vessel except for about ten collisions with the hot foil before leaving the vessel altogether.

Some interesting results were obtained by this method. Saturated hydrocarbons dried over crystals of triphenylmethylsodium or fresh phosphorous pentoxide remained unaffected by the hot foil up to about 1600°C when they apparently decompose completely into atoms or such radicals as would be readily adsorbed on the cold walls of the vessel, reducing the pressure set up by the molecular beam to zero. A trace of water or hydrogen sulfide added to these gases would cause the beam molecules to be decomposed at much lower temperatures. These findings, which led to some practical application, were briefly reported in Nature[3] and are the basis of a patent[4] dealing with the influence of water or $H_2S$ on the catalytic dehydrogenation of hydrocarbons. As it appears likely that a molecule such as water will be dissociated on the hot surface with subsequent temporary adsorption of the

[1] O. Beeck and C. Mouzon, Ann. d. Physik **11**, 858–62, 737–40 (1931); O. Beeck, Ann. d. Physik **18**, 414–16 (1933); W. Weizel and O. Beeck, Zeits. f. Physik **76**, 250–7 (1932); O. Beeck (review), Physik. Zeits. **35**, 36–52 (1934).

[2] O. Beeck, Proc. Nat. Acad. Sci. **18**, 311–13 (1932); O. Beeck and H. Wayland, Ann. d. Physik **19**, 129–42 (1934).

[3] O. Beeck, Nature **136**, 1028–9 (1935).

[4] O. Beeck, J. Burgin, and H. P. A. Groll, "Activating and maintaining the activity of dehydrogenation catalysts," U. S. Patent 2,131,089.