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THE CALCULATION OF EQUILIBRIUM COMPOSITIONS IN EXCHANGE REACTIONS

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ABSTRACT

A simple calculational method for deducing equilibrium mixtures in isotopic exchange reactions, in particular those involving mixed hydrogen isotope lithium hydride-hydrogen systems, is described. The method relies heavily on an approximate graphical technique. Several examples based on the Li(D,T)-DT system are discussed using assumed values of equilibrium constants for this particular system.

I. INTRODUCTION

A convenient technique for preparing mixed-isotope compounds is to react an isotopically pure compound with a gaseous compound or mixture containing a second isotope.[1,2] Thus, for example, to prepare Li(D,T) one can react LiD with T_2 gas (or often a mixture of tritium-rich DT gas), and allow the mixed system to equilibrate at high temperatures. By varying the relative amounts of the two starting materials the final composition of the solid phase at equilibrium can be adjusted to any desired value. Such equilibrium compositions are determined from experimental exchange constants; however, the calculations are tedious.

A method of calculating such equilibrium compositions and of following the compositions during the course of the reaction is presented herein. The method is based on a graphical technique and thus yields only approximate values, but the reliability of the results is probably more limited by the uncertainties of experimentally determined exchange constants. Several examples of this method will be given based on practical problems. All the examples discussed will be limited to the Li(D,T)-DT system, but the method could obviously be applied to others.

Calculational Method

The two exchange constants which will be used in this discussion of the Li(D,T)-DT system are defined by

$$K_1 = \frac{(\mathrm{LiT})(\mathrm{DT})}{(\mathrm{LiD})(\mathrm{T_2})} \qquad (1)$$

and

$$K_2 = \frac{(\mathrm{LiT})(\mathrm{D_2})}{(\mathrm{LiD})(\mathrm{DT})} \qquad (2)$$

where (LiT) and (LiD) are the concentrations of tritium and deuterium atoms in the salt mixture and (T_2), (D_2), and (DT) are the gas phase compositions of these molecular species in equilibrium with the salt. Other equilibrium constants can be defined for this system but only two are dependent and Eqs. (1) and (2) are the most convenient set for the method.

We begin by defining T_g as the number of moles of <u>atomic</u> tritium and D_g as the number of moles of <u>atomic</u> deuterium both in the gas phase. Although it is somewhat unconventional to define these values in terms of atoms rather than molecules, again it is more convenient. By these definitions

$$T_g = 2(T_2) + (\mathrm{DT}) \qquad (3)$$

and

$$D_g = 2(D_2) + (DT) . \tag{4}$$

Defining R_s as the isotopic ratio in the salt = (LiT)/(LiD) and substituting Eqs.(1) and (2) into (3) and (4) yields (for a system at equilibrium)

$$T_g = \left(\frac{2R_s}{K_1} + 1\right)(DT) \tag{5}$$

and

$$D_g = \left(\frac{2K_2}{R_s} + 1\right)(DT) . \tag{6}$$

Thus it follows, defining R_g as the ratio of tritium to deuterium in the gas phase, that

$$R_g = \frac{T_g}{D_g} = \frac{2R_s^2 + R_sK_1}{2K_1K_2 + R_sK_1} . \tag{7}$$

For any given mixture consisting of Li(D,T) and DT mixed gas it is possible to define values of R_s and R_g at any time. As the reaction progresses these values will of course vary; however, Eq. (7) linking R_s and R_g holds only when the system has attained equilibrium. Therefore, if the system is equilibrated, one can calculate R_g from R_s (or vice versa) with this equation, and further all equilibrium compositions must have corresponding values of R_s and R_g whose coordinates lie on the curve described by this equation.

It is also possible to analytically describe R_s and R_g as they vary during the course of the reaction by a second expression. To do this we define T_g' and D_g' as the amounts of T and D atoms in the initial gas mixture and T_s' and D_s' as the amounts in the salt before the reaction. (Generally, T_s' is zero.) Then, letting x equal the number of moles of T atoms exchanged for D atoms in the salt

$$R_g = \frac{T_g' - x}{D_g' + x} \tag{8}$$

and

$$R_s = \frac{T_s' + x}{D_s' - x} . \tag{9}$$

Removing x from these two parametric equations and rearranging yields,

$$R_g = \frac{T_g'(R_s + 1) - R_sD_s' + T_s'}{D_g'(R_s + 1) + R_sD_s' - T_s'} . \tag{10}$$

From this equation a curve can be obtained which describes R_s and R_g as they vary during the exchange process. The point at which this curve crosses that defined by the Eq. (7) gives the equilibrium compositions.

To find the gas- and solid-phase compositions at equilibrium one can thus substitute the initial values into Eq. (10) then solve Eqs. (7) and (10) for R_s and R_g. Since these are complicated expressions it is far simpler to solve them graphically. The general technique to be illustrated in the next section is as follows:

- Plot Eq. (7) using known values of K_1 and K_2.
- Substitute the starting values of T_s', D_s', T_g', and D_g' into Eqs. (8) and (9).
- Picking convenient values of x and using (8) and (9) plot Eq. (10).
- From the plot of Eq. (10) one can follow the changes in composition in both of the gas and solid phases during the exchange.
- Finally, the equilibrium values of R_s and R_g can be found from the intersection. From these two values all equilibrium values of (LiT) and (LiD) (and also the composition of the three molecular gases if needed) can be readily calculated.

II. RESULTS AND DISCUSSION

For this discussion values of $K_1 = 2$ and $K_2 = 0.5$ will be used. These are reasonable values which also, when substituted into Eq. (7), yield $R_g = R_s$ under equilibrium conditions. This equation is plotted in Fig. 1 (line A) on a log-log plot. In addition these values of K_1 and K_2 lead to

$$K_3 = \frac{(DT)^2}{(T_2)(D_2)} = 4.0 , \tag{11}$$

which happens to be the high-temperature limit for K_3.[3] For actual problems, values of K_1 and K_2 must be determined experimentally at the temperature used for an exchange.

In Fig. 1 several examples using this method are also depicted. These will now be discussed in

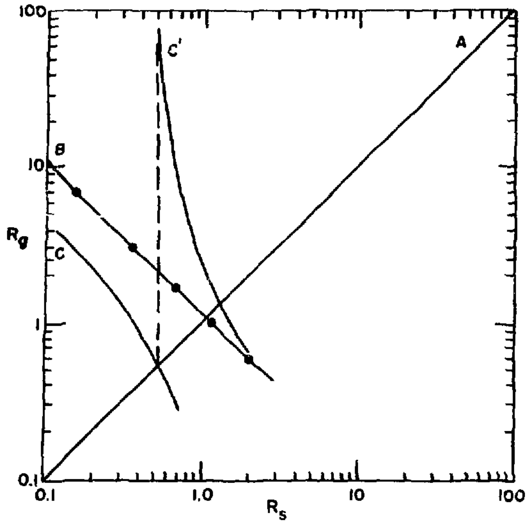

Fig. 1. Plots of R_g, the ratio of T to D in the gas phase, and R_s, the same ratio in the solid phase. Curve A plots the relationship of R_g to R_s for any equilibrium mixture. The remaining curves display the variations during particular reactions as discussed in the text.

more detail.

Example 1.

For the first example let us assume that 15 moles of LiD are to be equilibrated with 8 moles of pure T_2. Then $D_s' = 15$, $T_g' = 16$, $D_g' = T_s' = 0$; and $R_g = (16 - x)/x$ and $Rs = x/(15-x)$. From these two equations a table can be constructed by picking convenient values of x up to and past the expected end point:

x	R_g	R_s
2	7	0.15
4	3	0.36
6	1.67	0.67
8	1	1.14
10	0.6	2

These values are then plotted in Fig. 1 (circled points) and the resultant curve (B in Fig. 1.) drawn in. From the intersection of the two curves, we obtain $R_s = R_g = 1.08$ indicating the salt from the equilibrium mixture would have the composition $Li(D_{0.48}, T_{0.52})$. If it were desired to calculate the composition of the equilibrium gas, this could be done by substituting $T_g = 8.3$ moles and $D_g = 7.7$ moles, obtained from the value of R_g, into Eqs. (1), (2), and (11) then solving for the three unknowns (T_2), (D_2), and (DT).

Note that it would be experimentally possible to obtain a salt of such a composition that R_s was less than the equilibrium value by stopping the reaction prematurely. Thus, if one desired in this case a salt of composition $R_s = 0.4$, the reaction would be stopped when R_g for the gas over the salt reached a value of 2.7.

Example 2.

As in the first example, except the 15 moles of LiD is to be successively equilibrated with two batches of T_2 gas, each with half the tritium (4 moles). For the first equilibration the reaction is represented by $R_g = (8-x)/x$ and $R_s = x/(15-x)$. This is depicted by the curve marked C in Fig. 1 and leads to the value at equilibrium of $R_g = R_s = 0.53$. This gives the first product $Li(D_{0.65}, T_{0.35})$. When this salt is reacted with 4 more moles of T_2 the equations are $R_g = (8-x)/x$ and $R_s = (5.2 + x)/(9.8-x)$, represented by the line C'. The final equilibrium values are $R_g = R_s = 1.32$ and $Li(D_{0.43}, T_{0.57})$.

Note that curve C' must start from a point lying on a line rising vertically from the intersection of C and A (dashed line in Fig. 1). This is because the values of R_s at the end of the first exchange and the begining of the second must be the same.

The results of these first two examples illustrate that more exchange gas is taken up when the process is broken up into more than one step. Such a stepwise technique would be worthwhile when the reactant is expensive.

Example 3.

The final example is more practical. Suppose one desires 10 moles of a composition $Li(D_{0.25}, T_{0.75})$ and one has a gas of composition 90% T and 10% D, how many moles of the gas are needed?

Here, R_s at equilibrium is 3 and from the curve R_g has the same value. Let y = the number of atom-moles of gas originally added and let x = the quantity reacted at equilibrium. Then (LiT) at equilibrium = x - 7.5 moles and $R_g = 3 = (0.9y-x)/(0.1y+x)$. Substituting the value of x and solving this equation gives y = 50 moles which implies 25 moles of the mixed gas are to be added initially.

III. CONCLUSION

The technique presented here offers a convenient means of calculating starting amounts in exchange reactions. Although more exact results can be obtained by solving the equations derived, the graphical plotting of the reaction parameters serves as a check on such calculations if they are undertaken. The plots, however, serve the more important function of allowing one to previsualize the course of the reaction. Thus, by periodically monitoring the gas phase mixture it is possible to monitor the reaction using such curves.

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