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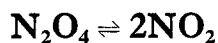
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Effect of chemical reaction on diffusion in the system



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Abstract. The diffusion of krypton into the dissociating system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ has been measured by the radioactive tracer technique. The results show that, as pointed out by Rai Dastidar and Barua, chemical reaction exerts a retarding influence on the diffusion process in reacting systems.

1. Introduction

Let us consider a chemically reacting gas mixture placed in a thermal conductivity cell. It is known (Hirschfelder *et al.* 1954) that the energy of the reaction is transported from one surface of the cell to the other through a diffusion mechanism; the concentration gradient across the gas set up by the continuously varying state of chemical equilibrium along the temperature gradient gives rise to the diffusion process. Theories of heat transfer in a reacting gas system have been worked out by Butler and Brokaw (1957) and by Brokaw (1960) along this line.

It has, however, been recently found by Rai Dastidar and Barua (1966, 1967) that the experimental thermal conductivity of the reacting system $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ yielded a value of the diffusion flux which was noticeably smaller than the value calculated from the Chapman-Enskog theory. Without going into mathematical details, it was shown that the evidence pointed to a retarding influence of the chemical reaction upon the diffusional transfer when the latter tended to disturb the instantaneous local equilibrium.

Ordinarily, the concentration gradient between the two surfaces of the cell would be given by the chemical equilibria at the temperatures of the two surfaces. However, unless the reaction is ideally fast, the concentration gradient tends to decrease from this calculated value on account of the effects of relaxation of chemical energy. Consequently, the measurement of this effect of the reaction upon diffusion from the thermal conductivity data is somewhat involved, inasmuch as the diffusional energy transfer has to be corrected for relaxation effects before the other effect can be observed separately. Such an analysis has been carried out by Rai Dastidar and Barua (1967) with the aid of the theory of heat transfer in reacting gases, as given by Brokaw (1961), which takes account of the relaxation of chemical energy in the system. The results confirmed that the effect upon diffusion was independent of the relaxation effects.

The present work was undertaken to observe this effect of chemical reaction upon diffusion in a more direct way. Because of the corrosive nature of the N_2O_4 - NO_2 system, it is difficult to observe diffusion phenomena in this gas by any physical means. It was therefore decided to introduce an inert gas into the reacting system and to measure the diffusion coefficient of the inert component within the mixture by the tracer technique. Effects of relaxation of chemical energy were fully eliminated by maintaining the apparatus at a uniform temperature throughout. By allowing the diffusion process alternately (i) to disturb, and (ii) not to disturb, the reaction equilibrium, the effect could be directly observed by measuring the diffusion coefficient in the two cases.

2. Apparatus and theory

The inert gas used in the experiment was krypton supplied by British Oxygen Ltd. The two-bulb technique of Ney and Armistead (1947) was employed for measuring the diffusion coefficient, with radioactive ^{85}Kr as the tracer.

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The diffusion apparatus consisted of two stainless-steel cubical chambers connected by means of a metal stop-cock. A small mica window was fitted at the top of one of the chambers, above which the counting probe was mounted. This chamber was connected to a manometer by a stainless-steel capillary tube. To prevent any reaction of nitrogen tetroxide with mercury, the manometer level was covered with a little silicone oil. The counting was performed by a scintillation counter with the usual accessory circuits.

The relaxation time $1/\alpha$ of the gas, defined as

$$\frac{C_1^t - C_1^\infty}{C_1^0 - C_1^\infty} = \exp(-\alpha t) \quad (1)$$

is given by

$$\alpha = D_p \frac{A}{l} \frac{V_0}{V_1 V_2} \quad (2)$$

where C_1^0 , C_1^t and C_1^∞ are the radioactive counting rates initially, at time t and after complete mixing, respectively. V_1 and V_2 are the volumes of the two chambers: $V_0 = V_1 + V_2$; A and l are the effective cross-sectional area and length of the diffusion path.

3. Experimental details

Pure N_2O_4 was prepared by heating crystals of $Pb(NO_3)_2$, as described in detail by Srivastava and Barua (1961). The gas was thoroughly dried by passing it through two P_2O_5 towers in succession and sealed in Pyrex flasks.

Table 1. Constants of the apparatus

Volume of tracer chamber (V_1)	222.27 cm ³
Volume of other chamber (V_2)	220.47 cm ³
Diffusion length (l)	8.05 cm
Cross-sectional area of capillary stop-cock (A)	0.151 cm ²
Cross-sectional area of capillary tube connecting the chamber to manometer	0.0314 cm ²

The apparatus was immersed in a water bath, the temperature of which was controlled to within ± 0.05 degc. The constants of the apparatus (V_1 , V_2 , A , l) were checked by measurement of the self-diffusion coefficient of krypton by way of calibration.

The experiment was performed at temperatures of 30 °c and 40 °c under the following two conditions:

(a) Both chambers were filled with $N_2O_4 \rightleftharpoons 2NO_2$ gas at the same temperature and pressure, with a trace of radioactive ^{85}Kr in one chamber.

(b) One chamber was filled with nitrogen tetroxide at a desired pressure, and the other chamber was filled with krypton at the same pressure, to which a trace of ^{85}Kr was added.

The diffusion was started by opening the stop-cock linking the two chambers and a count was made every five minutes. A plot of $\log C_1^t$ against t , which was a straight line, gave the value of (relaxation time)⁻¹ = α . The diffusion coefficient D_p was calculated from α using equation (2).

4. Interpretation of data

In the present experiment the measured value of D_p corresponds to the multi-component diffusion coefficient of the tracer ^{85}Kr in the mixture of Kr, N_2O_4 and NO_2 . As an approximation, this diffusion coefficient is given by (Hirschfelder *et al.* 1954)

$$\frac{1 - x_i}{D_{iM}} = \sum_{j \neq i} \frac{x_j}{\mathcal{D}_{ij}} \quad (3)$$

where D_{iM} is the diffusion coefficient of the species i in the mixture, \mathcal{D}_{ij} the binary diffusion coefficient between species i and j , and x_j the mole fraction of the species j . When i refers to the tracer element, x_i is negligible, and equation (3) simplifies to

$$\frac{1}{D_{iM}} = \sum_{j \neq i} \frac{x_j}{\mathcal{D}_{ij}}. \quad (4)$$

Let us now consider the nature of the diffusion coefficients D_p measured in the experiment. In case (a) both the chambers as well as the bore of the stop-cock (closed) contain the reacting gas $N_2O_4 \rightleftharpoons 2NO_2$ at the same temperature and pressure, and hence are in the same state of equilibrium. When the stop-cock is opened the diffusion of ^{85}Kr , which is present only as a trace, does not affect the reaction equilibrium, and the diffusion coefficient of ^{85}Kr in the mixture should be given accurately by the Chapman-Enskog theory. In case (b) one chamber is full of krypton and the other is full of nitrogen tetroxide; thus when the stop-cock is opened, the diffusional transfer changes the spatial distribution of the reacting species and hence serves to dislocate the instantaneous chemical equilibrium from its original position. In both these cases the concentration gradient of the tracer ^{85}Kr between the two chambers is initially the same, viz. 100%, and hence D_p can be defined in the same manner, which is given approximately by D_{iM} in equation (4).

Table 2. Coefficient for the diffusion of krypton in the system $N_2O_4 \rightleftharpoons 2NO_2$

T ($^{\circ}C$)	Pressure (torr)	D (atm cm ² s ⁻¹)		D_a/D_b
		(a)	(b)	
30	23.0	0.122	0.113	1.080
	40.5	0.123	0.109	1.128
	61.0	0.128	0.119	1.076
40	25.0	0.147	0.142	1.035
	33.5	0.150	0.141	1.064
	51.0	0.140	0.133	1.053

In table 2 the measured values of the diffusion coefficient are given for each temperature and pressure, corresponding to cases (a) and (b) of the experiment. The quantities are expressed in atmospheric units, putting $D = pD_{iM}/760$, where p is the pressure in torr. It is seen that the values obtained for set (a) in each case maintain a uniform ratio to the values corresponding to set (b) over the entire pressure range for each temperature. This proves convincingly the retarding effect of chemical reaction upon diffusion when the latter disturbs the instantaneous equilibrium state of the reaction. Again, the present observations are free from the effects of relaxation of chemical energy and therefore furnish more direct proof of the effect of reaction upon diffusion than the thermal conductivity experiments can.

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