

### Heterogeneous Equilibria with Deuterium

THE heterogeneous equilibria between hydrogen and the metallic chlorides have been extensively studied, notably by Berger and Crut<sup>1</sup> using a static

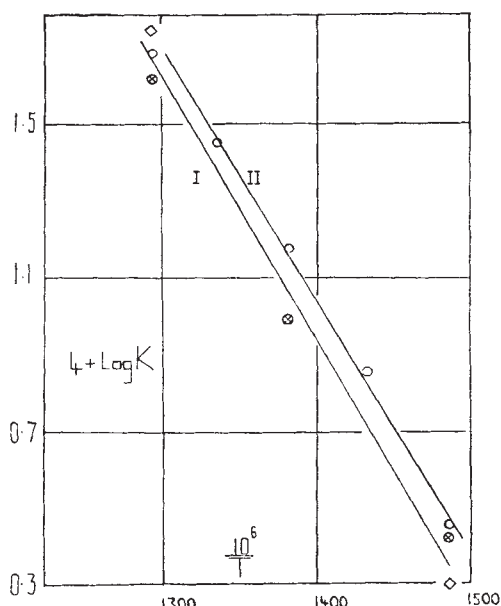


Fig. 1.

GRAPH I FOR HYDROGEN; GRAPH II FOR DEUTERIUM.

⊗, PARTINGTON AND TOWNDROW. (H<sub>2</sub>)  
O, " " " " (D<sub>2</sub>)  
◇, JELLINEK AND ULOTH. (H<sub>2</sub>)

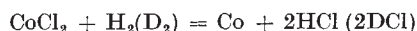
method, and by Jellinek and his collaborators<sup>2</sup> using a dynamic method. More recently, Kapustinsky<sup>3</sup> has studied the reduction of cuprous chloride with both

TABLE I.

	H <sub>2</sub> + CoCl <sub>2</sub>			D <sub>2</sub> + CoCl <sub>2</sub>				
T°	673	723	773	673	698	723	748	773
10 <sup>6</sup> /T	1486	1383	1294	1486	1433	1383	1337	1294
4 + log K	0.413 P. & T. 0.990 P. & T. 1.621 P. & T.			0.447 0.854 1.179 1.456 1.685				
	0.295 J. & U.			1.749 J. & U.				

hydrogen and deuterium, using a static method. The agreement among the results of different authors is not very satisfactory and we are engaged in further investigations of heterogeneous equilibria involving hydrogen and deuterium.

A static method has been used to study the reduction of cobalt chloride by hydrogen and deuterium. The cobalt chloride is heated with the gas at constant volume, the temperature being measured by a thermocouple, and pressure by a mercury manometer. The extent of the reaction is deduced from the increase of pressure due to the reactions:



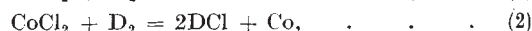
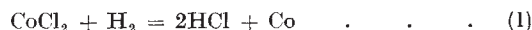
The values of the equilibrium constant

$$K = C_{\text{HCl}}^2/C_{\text{H}_2}$$

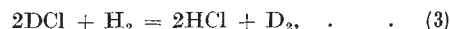
obtained for hydrogen are in good agreement with those found by Jellinek and Uloth by a different method.

Table I shows the values of the equilibrium constant for hydrogen and deuterium at various temperatures. In Fig. 1 the logarithm of  $K$  is plotted against  $1/T$ , where  $T$  is the absolute temperature at which  $K$  is measured.

If  $K_1$ ,  $K_2$  are the equilibrium constants for the reactions:



respectively, then  $K^* = K_1/K_2$  is the equilibrium constant for the homogeneous reaction:



namely,  $K^* = C_{\text{D}_2} \cdot C_{\text{HCl}}^2/C_{\text{H}_2} \cdot C_{\text{DCl}}^2$

Urey and Rittenberg<sup>4</sup> have calculated values of  $K^*$  at different temperatures on theoretical grounds. These are compared in Table II with values obtained experimentally by Kapustinsky and ourselves.

TABLE II.

	1 + log K*				
T°	769	700	690	658	575
Urey and Rittenberg	0.96	0.94	—	—	0.91
Kapustinsky	—	—	0.78	0.70	—
Partington and Towndrow	0.92	0.89	—	—	—

The heats of reaction ( $Q_p = \Delta U$ ) of reactions (1) and (2) above are deduced from graphs I and II to be  $-31,850$  gm. cal./mol and  $-30,790$  gm. cal./mol respectively, at a mean temperature of  $450^\circ\text{C}$ . The value given in the International Critical Tables for reaction (1) is  $-32,360$  gm. cal./mol at  $18^\circ\text{C}$ . (determined thermochemically).

On plotting  $\log K^*$  against  $1/T$  a straight line is obtained from which the heat of reaction (3) is deduced to be  $-1,100$  gm. cal./mol.

As would be expected from theoretical considerations, the value of  $K^*$  tends towards unity with increasing temperature, and the difference from unity may be shown to be negligibly small at  $800^\circ\text{C}$ .

The investigation is being extended to other types of reaction.

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London. June 14.

<sup>1</sup> Berger and Crut, *C. R.*, **173**, 977 (1921).

<sup>2</sup> Jellinek and Uloth, *Z. phys. Chem.*, **119**, 161 (1926); Jellinek and Rudat, *Z. phys. Chem.*, **143**, 244 (1929).

<sup>3</sup> Kapustinsky, *J. Amer. Chem. Soc.*, **53**, 460 (1936).

<sup>4</sup> Urey and Rittenberg, *J. Chem. Phys.*, **1**, 142 (1933).

### The Corona by Reflection from the Moon

THE light from the photosphere of the sun will illuminate not only the hemisphere of the moon facing the sun but also a zone five miles wide beyond the great circle bounding the hemisphere. A further zone five miles in width will be illuminated by those radiations emanating from the corona, if the height of the corona be regarded as equal to one radius of