760. *The Dissociation Pressure of Cadmium Oxide.*

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The partial pressure of cadmium over solid cadmium oxide has been determined between 880° and 1100°c by an accurate form of the entrainment method. The influence of increased oxygen pressure, and comparison with thermodynamic calculations, establish that the vapour is almost completely dissociated. The standard Gibbs free energy of the dissociation CdO (s) = Cd (g) + $\frac{1}{2}O_2$ (g) is found to be

$$\Delta G° \text{ (at 1150—1374° K) } (\pm 150°) = 86,120 (\pm 2900) - 48.84 (\pm 2.5) T \text{ (cal. mole}^{-1})$$

BREWER and MASTICK [1] have recently concluded from examination of earlier, approximate, data for the sublimation pressure of cadmium oxide that the vapour of this substance, like those of mercury(I), zinc,[2] and lead(II) oxides, is probably almost completely dissociated. The partial pressures of cadmium (free or combined) in equilibrium with solid cadmium oxide in presence of nitrogen and in pure oxygen have now been determined by an accurate form of the entrainment method.

EXPERIMENTAL

Method.—The reaction vessel is shown in Fig. 1, and is a development of that used by Kitchener and Ignatowicz,[4] the inlet tube being sealed directly in the hot zone to the tube
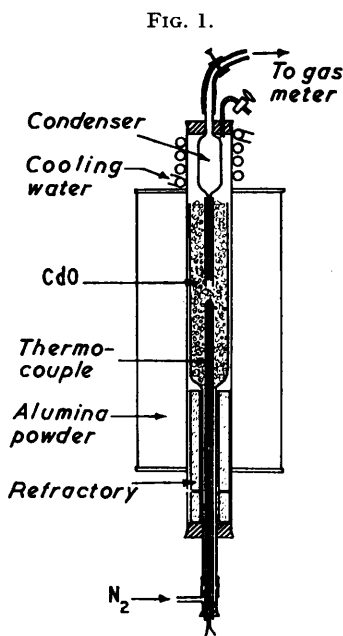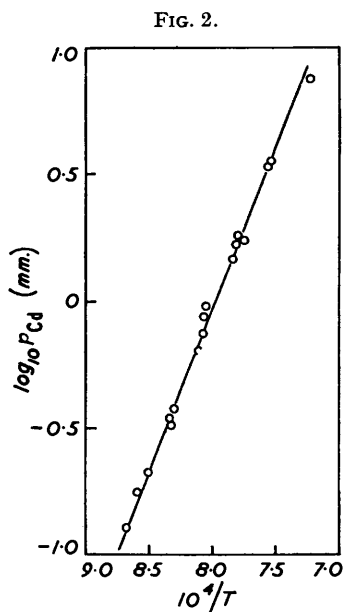
FIG. 1.

FIG. 2.

containing the cadmium oxide. The oxide (Hopkin and Williams) was previously sintered at *ca.* 1000°. Temperature was measured to $\pm 1°$ by a platinum/platinum–rhodium thermo-couple, and maintained within $\pm 1°$ by an energy-regulator.

Nitrogen from a cylinder (" oxygen-free "; <0.001% of oxygen) and oxygen, also from a cylinder, used as the entraining gases, were dried with anhydrous magnesium perchlorate.

[1] Brewer and Mastick, *J. Chem. Phys.*, 1951, **19**, 834.
[2] Pourbaix, *Bull. Soc. chim. Belg.*, 1944, **53**, 159.
[3] Richardson and Webb, *Trans. Inst. Min. Met.*, 1955, **64**, 529.
[4] Kitchener and Ignatowicz, *Trans. Faraday Soc.*, 1951, **47**, 1278.

Gas volumes were measured with a Hyde-pattern wet-test meter, calibrated to $\pm 0.2\%$ under closely similar conditions.

The quantity of cadmium carried over into the condenser was determined by slow electro-deposition from weakly alkaline cyanide solution; the method was reliable to $\pm 0.8\%$ for the small quantities collected in these experiments.

Procedure.—After the furnace had attained a steady temperature, the condenser was inserted and sealed in place with picein wax. Gas was passed through the bed of oxide (but not through the condenser) to remove air. In the actual determination, only part of the gas stream flowed through the condenser, its volume being measured by the gas-meter. This procedure was to eliminate back-diffusion. At the end of the run, the condenser was quickly removed from the furnace. The deposited cadmium was dissolved in dilute hydrochloric acid, and chloride (which interferes with the analysis) removed by evaporation with dilute nitric acid.

The quantity of cadmium diffusing into the condenser during the preparatory period was found to be negligible.

Results.—The partial pressure of cadmium (p_{Cd}, in mm. Hg,) was calculated by the ideal-gas laws, with use of the formula

$$p_{Cd} = \frac{(P + p)}{1 + (112 \cdot 4/R)[V(P - p_w)/Tw]}$$

where P (mm.) is the atmospheric pressure, p (mm.) is the (small) excess of pressure in the furnace, T(°K) the temperature of the gas meter, p_w (mm.) the parial pressure of water vapour at T °K, V (l.) the volume of permanent gas collected, and w (g.) the weight of cadmium deposited.

Temp. (c)	Press. of Cd (mm.)	Total gas flow rate (c.c./min.)	Temp. (c)	Press. of Cd (mm.)	Total gas flow rate (c.c./min.)	Temp. (c)	Press. of Cd (mm.)	Total gas flow rate (c.c./min.)
				Carrier gas : nitrogen				
880°	0·132	88	958°	0·630	30	1009°	1·72	220
890	0·179	120	963	0·740	30	1010	1·69	110
903	0·218	66	966	0·865	40	1051	3·33	150
927	0·345	125	968	0·939	50	1053	3·51	78
928	0·328	88	1001	1·42	76	1053	3·51	200
934	0·375	50	1006	1·65	140	1101	7·36	100
				Carrier gas : oxygen				
925	0·005	—	983	0·015	—			

Results.—These are shown in the Table. There is seen to be no systematic variation of p_{Cd} with flow-rate, indicating that a true equilibrium had been reached and measured.

Fig. 2 shows that, with an inert entraining gas, log p_{Cd} is linear with $1/T$ over the range 880—1100° c within experimental error. The least-squares line is given by :

$$\log_{10} p_{Cd} \text{ (mm.)} = 10 \cdot 008 - 12{,}548/T \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

The standard deviation of the points from the line is ± 0.029.

DISCUSSION

The results obtained with oxygen as the entraining gas are smaller by a factor of about 80 than those with nitrogen, demonstrating that oxygen takes part in the equilibrium studied, and that the proportion of molecular cadmium oxide in the vapour above the oxide in nitrogen is certainly very small. In fact, the observed quantities of cadmium obtained with oxygen accord, within the experimental error, with the assumption of complete dissociation.

On this basis, the equilibrium constant ($K = p_{Cd} \cdot p_{O_2}^{\frac{1}{2}}$) for the decomposition

$$\text{CdO (s)} = \text{Cd (g)} + \tfrac{1}{2}\text{O}_2 \text{ (g)}$$
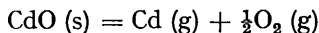
follows from equation (1), as

$$\log_{10} K \text{ (atm.}^{3/2}) = 10 \cdot 691 - 18{,}822/T \qquad . \quad . \quad . \quad . \quad (2)$$

and hence the standard Gibbs free energy of the reaction, $\Delta G°$, is given by :

$$\Delta G° \text{ (at 1150—1374° K) } (\pm 150°) = 86{,}120 \ (\pm 2900) - 48 \cdot 84 \ (\pm 2 \cdot 5) \ T \text{ (cal. mole}^{-1})$$

To confirm the conclusion that vaporization occurs only through dissociation, these results have been compared with thermodynamic calculations based on a calorimetric value of the heat of formation of CdO (s),[5] vapour-pressure data for cadmium metal, and heat content and entropy data (see Appendix). The resulting equation for log p_{Cd} was found to be (perhaps fortuitously) indistinguishable from experimental results shown in Fig. 2.

These thermodynamic data are not affected by the non-stoicheiometry of cadmium oxide which is negligible in extent under the conditions studied; even with 1 atm. of cadmium vapour, the excess of metal amounts to only 0·5%.[6]
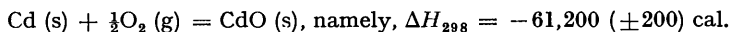
APPENDIX

Calculation, from thermodynamic data, of the free energy of the reaction :

$$CdO \text{ (s)} = Cd \text{ (g)} + \tfrac{1}{2}O_2 \text{ (g)} \quad \cdots \cdots \cdots \text{(i)}$$

The standard heat of the above reaction at 25° c (298·1° K), $\Delta H°_{298}$, is obtained from Mah's value [5] for the reaction :

$$Cd \text{ (s)} + \tfrac{1}{2}O_2 \text{ (g)} = CdO \text{ (s)}, \text{ namely, } \Delta H_{298} = -61,200 \ (\pm 200) \text{ cal.}$$

together with a value for the heat of sublimation, $\Delta H_{sub.}$ calculated from Egerton and Raleigh's vapour-pressure data.[7] Their results lead to $\Delta H_{sub.}$ at 500° K = 26,590. The specific heats of Cd (g) and Cd (s) are 4·97 and $(5·31 + 2·94 \times 10^{-3}T)$ respectively.[8] Hence, by Kirchhoff's equation, $\Delta H_{sub.}$ at 298° K is obtained as $+26,900$ cal, giving, for reaction (i)

$$\Delta H°_{298} = +88,100 \text{ cal.}$$

The standard entropy of the reaction is obtained from the following absolute entropies at 298·1° K : for Cd (g), 40·07 ± 0·01 (Sackur's equation); for CdO (s), 13·1 ± 0·3 from Millar's low-temperature specific-heat determinations;[9] for $\tfrac{1}{2}O_2$ (g), 24·31 ± 0·01 (Kelley [8]). Hence, for reaction (i)

$$\Delta S°_{298} = +51·45 \pm 0·3 \text{ cal. degree}^{-1}$$
$$\text{and} \quad \Delta G°_{298} = +72,800 \text{ cal.}$$

To obtain a free-energy equation for a range of temperatures, use is made of the following specific heats : for CdO (s), $C_p = 9·78 + 2·02 \times 10^{-3}T$ (estimated by Kelley [8]); for $\tfrac{1}{2}O_2$, $C_p = 3·58 + 0·50 \times 10^{-3}T - 0·20 \times 10^5 T^{-2}$ (Kelley [8]); for Cd (g), $C_p = 4·97$ (monatomic gas). By standard methods, the final equation is obtained as

$$\Delta G_T° = 88,465 + 1·23T \ln T + 7·6 \times 10^{-4}T^2 + 1·0 \times 10^4 T^{-1} - 59·84T$$

The uncertainty in this equation probably does not exceed 1 kcal. at 1000° K.

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[5] Mah, *J. Amer. Chem. Soc.,* 1955, **76**, 3363.
[6] Faivre, *Ann. Chim. France,* 1944, **19**, 58.
[7] Egerton and Raleigh, *J.,* 1923, **123**, 3024.
[8] Kelley, *U.S. Bur. Stand. Bull.,* 1949, No. 476; 1950, No. 477.
[9] Millar, *J. Amer. Chem. Soc.,* 1928, **50**, 2653.