much more difficult to obtain precise results in these more viscous solutions than in water. We do not yet understand the factors which cause this difficulty. In concluding, it should be noted that at these low concentrations of potassium chloride, we have avoided the difficulties which would be encountered in considering the migration of all the components in this three component system.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON]

Vapor Pressure of Chromium(II) Bromide

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The vapor pressure of $CrBr_2(s)$ has been measured over the temperature interval 837–1083°K., and thermodynamic properties of the monomeric and dimeric forms have been evaluated relative to the solid.

The vapor pressure of $CrBr_2$ has been measured between 972 and 1083°K. by the transpiration method and in the vicinity of 839°K. by the torsion effusion method.

Experimental Part

The experimental methods and apparatus have been described in earlier papers.[1,2] Argon was used as a carrier gas in transpiration experiments; flow rates between 13 and 60 ml./min. gave the same vapor pressures. The quantity of $CrBr_2$ transported was determined spectrophotometrically, after oxidation to chromate, as described in an earlier study on $CrBr_3$.[3] $CrBr_2$ was prepared in a quartz tube by reaction of HBr with powdered chromium metal at 750°. It was purified by sublimation in high vacuum; analysis gave a chromium content corresponding to 99.3% $CrBr_2$.

With the radiant heating technique employed,[2] the torsion effusion cell could be heated only to 568° at which the vapor pressure of $CrBr_2$ is near the lower limit of the sensitivity of the apparatus. Hence torsion measurements were limited to this one temperature and to a cell with moderately large orifices ($A_o = 2.60 \times 10^{-3}$ and 3.72×10^{-3} cm.^{2}). The sample was introduced into the cell (in a dry box) through the effusion orifices. Calibration of the apparatus has been described earlier.[2]

Results and Discussion

Results are shown in Fig. 1. The solid line is drawn through the calculated transpiration pressures when the monomer is assumed the only vaporizing species; the dotted line represents the same data if the dimer were the only vapor species. The monomer line is seen to be in better agreement with the absolute pressures obtained by the torsion effusion method (the points grouped at the lowest temperature). We were unable to confirm independently that the torsion pressures shown are a good approximation to equilibrium vapor pressures (steady-state pressures in effusion cells with moderately large orifices will be below equilibrium values if the condensation coefficient is small)[2,4] by repeating the measurement with a cell with smaller orifices since the latter would give a deflection at 568° too small for accurate measurement. Hence the torsion points (Fig. 1) are regarded as lower limiting values; they do correlate well with the transpiration data, however, which suggests they are close to equilibrium. The solid line may be represented by the equation

$$(837\text{–}1083°\text{K.}) \log P_{\text{mm.}} = -12050T^{-1} + 11.06$$

which, without further knowledge of the mode of vaporization, gives the standard (atm.) free energy of sublimation equation

$$\Delta F^0 = 55{,}100 - 37.4T$$

Recently Schoonmaker, Friedman and Porter[5] have carried out a mass spectrometric analysis of the vapor in equilibrium with $CrBr_2$ at 931°K. Their results indicate about 20% of the vapor to be in the form Cr_2Br_4 at this temperature. They also measured the vapor pressure at this one temperature by conventional effusion technique and report $\Delta F^0 = 17.2$ for the reaction

$$Cr_2Br_4(g) = 2CrBr_2(g) \qquad (1)$$

and, from an estimated ΔS^0 of 32 e.u., calculate ΔH^0 for (1) as 47 kcal.

Using their standard free energy and estimated entropy changes for (1), we have calculated the partial pressures of monomer and dimer for each of our measured vapor pressures ($\Delta F^0 = -RT \ln K_1 = 47{,}000 - 32\ T.$, assumed; ΔC_p for (1) neglected). Data are summarized in Table I. P_{am} represents the apparent pressure of monomer, *i.e.*, as shown in Fig. 1, the pressure calculated from the number of grams of chromium halide transported, assuming

TABLE I

°K.	$P_{am} \times 10^4$, atm.	$K_1 \times 10^4$	$P_m \times 10^5$, atm.	$P_d \times 10^5$, atm.
		Transpiration data		
972	0.603	2.67	4.5	0.76
1000	1.26	5.28	9.3	1.64
1021	2.41	8.60	17.2	3.44
1024	2.48	9.20	17.7	3.41
1024	2.46	9.20	17.8	3.44
1048	4.58	15.6	32.4	6.73
1083	12.8	32.4	84.0	21.8
		Torsion effusion data		
	($P_t \times 10^4$)			
837	0.00607	0.0528	0.055	0.0057
837	.00775	.0528	.069	.0085
838	.00538	.0546	.049	.0048
841	.00640	.0676	.059	.0050

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[4] J. H. Stern and N. W. Gregory, *J. Phys. Chem.*, **61**, 1226 (1957).

[5] R. C. Schoonmaker, A. H. Friedman and R. F. Porter, private communication; *J. Chem. Phys.* in press.

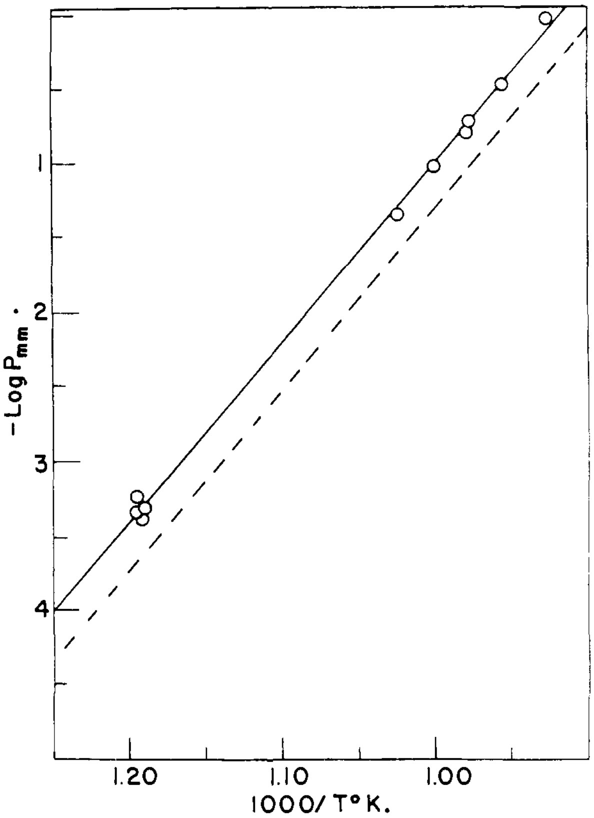

Fig. 1.—Vapor pressure of chromium(II) bromide.

the vapor to be only $CrBr_2$(g). Actually $P_{am} = k(n_m + 2n_d) = P_m + 2P_d$, where k is a proportionality constant, n_m and n_d represent the actual number of moles of monomer and dimer, respectively, in the volume of vapor taken and P_m and P_d the partial pressure of each form. We may write $K_1 = P_m^2/P_d$ and $2P_d = P_{am} - P_m$ and thus from calculated values of K_1 and P_{am} at each temperature a quadratic equation for P_m may be solved and P_d subsequently evaluated. The torsion data were treated in a similar manner, starting with actual measured total pressure, $P_t = P_m + P_d$.

The relationship of P_m and P_d and their variation with temperature is shown in Fig. 2, which also includes for comparison the single pressure measurement by Schoonmaker, Friedman and Porter. The lines drawn lead to the equations (837–1083° K.)

$$CrBr_2(s) = CrBr_2(g)\ \Delta F^0 = 52300 - 33.9T \quad (2)$$

$$2CrBr_2(s) = Cr_2Br_4(g)\ \Delta F^0 = 58000 - 36.6T \quad (3)$$

We suggest an uncertainty in ΔH^0 for (2) of ±3 kcal.; that for (3) is somewhat larger because of the small concentration of dimer and the estimations involved in the calculation of the dimer pressures.

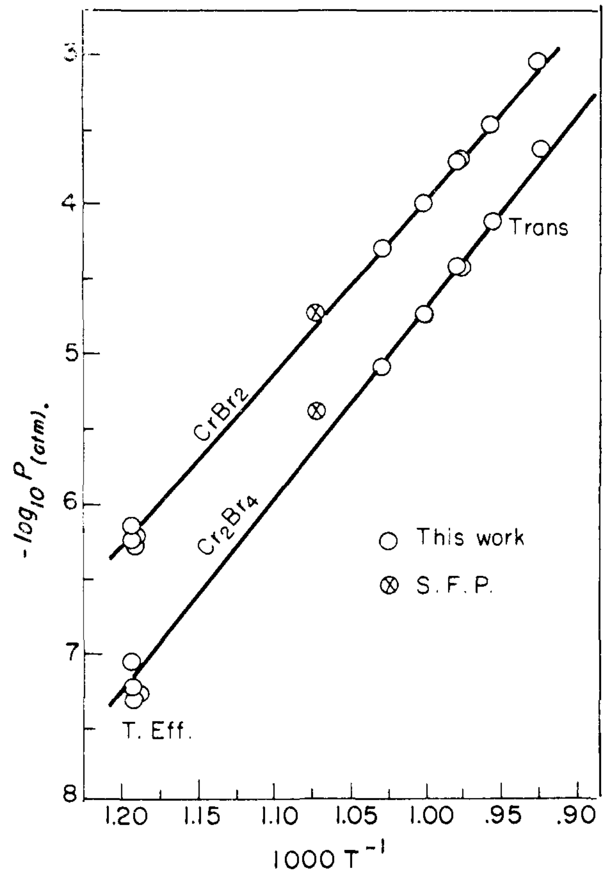

Fig. 2.—$CrBr_2$ and Cr_2Br_4 pressures over solid $CrBr_2$.

The entropy of solid $CrBr_2$ at 298°K. may be estimated from Latimer's tables[6] (32 e.u.); assuming the heat capacity of $CrBr_2$ to be about the same as $CrCl_2$[7] the entropy of solid $CrBr_2$ at 1000°K. is estimated to be 54 e.u. and the entropy of $CrBr_2$(g), from the entropy of sublimation, 88 e.u. This value seems quite reasonable from statistical thermodynamic considerations, although the vibrational contribution is so large that a quantitative estimate is difficult. Translational and rotational contributions alone, assuming $CrBr_2$(g) is linear with a Cr–Br distance of 2.2 Å., total 69 e.u., leaving 19 e.u. to be accounted for by vibrational and electronic states. Frequencies observed for somewhat similar molecules, *e.g.*, $ZnBr_2$, $CdBr_2$, $HgCl_2$, $HgBr_2$,[8] suggest that the vibrational contribution can easily be this large.

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