Cycloheptane $$\log_{10} p = 6.85271 - 1330.742/(t + 216.246) \quad (4)$$

Cycloöctane $$\log_{10} p = 6.86173 - 1437.682/(t + 210.003) \quad (5)$$

Cycloheptatriene $$\log_{10} p = 6.97032 - 1374.656/(t + 220.538) \quad (6)$$

The Antoine equations, with three empirical constants, are of a form convenient for numerical computation and are satisfactory for most purposes. However, for extrapolation outside the range of experimental measurements Cox equations, with four empirical constants, are more reliable. For calculations at 298.16°K. for cycloheptane and cycloöctane, the following Cox equations were obtained from the vapor pressure data. The units are P in atm. and T in °K.

$$\text{Cycloheptane: } \log_{10} P = \text{A}(1 - 391.953/T) \quad (7)$$

$$\text{where } \log_{10} \text{A} = 0.839609 - 6.9133 \times 10^{-4}\, T + 6.4035 \times 10^{-7}\, T^2$$

$$\text{Cycloöctane: } \log_{10} P = \text{A}(1 - 424.300/T) \quad (8)$$

$$\text{where } \log_{10} \text{A} = 0.839906 - 6.2033 \times 10^{-4}\, T + 5.1773 \times 10^{-7}\, T^2$$

The differences between the observed values of the vapor pressure and those calculated from the foregoing equations are listed in Tables X and XI.

The normal boiling points calculated from the equations are 118.79° for cycloheptane, 151.14° for cycloöctane and 115.60° for cycloheptatriene. The extrapolated value for cycloheptatriene is much less reliable than the directly measured values for the other two compounds. Other reported values for the boiling points are 118.48° for cycloheptane,[8] 150.70° for cycloöctane[8] and 115.50° for cycloheptatriene.[23]

The Heat of Vaporization.—Values of the heat of vaporization, at saturation pressure at 298.16°K., were computed by use of eq. 7, 8 and 6 and the exact form of the Clapeyron equation. The equation of state, $PV = RT + BP$, was assumed for the vapor; values of the second virial coefficient, B, were estimated from a correlation published previously[28] to be −2.7, −4.2 and −2.3 liters at 298.16°K. for cycloheptane, cycloöctane and cycloheptatriene, respectively. The values obtained for the heat of vaporization are 9210, 10360 and 9250 cal. mole^{-1} for cycloheptane, cyloöctane and cycloheptatriene, respectively, each with an estimated uncertainty of ±50 cal. mole^{-1}.

The Entropy in the Ideal Gaseous State.—The experimental and derived results given in the foregoing sections were used to compute "observed" values of the entropy in the ideal gaseous state at 1 atm. pressure. These calculations are summarized in Table XII.

[28] D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, THIS JOURNAL, **72**, 2424 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Vapor Pressure and Heat of Sublimation of Chromous Iodide. The Chromium–Iodine Bond Energy in Chromous Iodide*

BY THOMAS L. ALLEN

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The vapor pressure of CrI_2 has been determined from 943 to 1054°K. For sublimation at 298.16°K., $\Delta F° = 54.0$ kcal./mole, $\Delta H° = 71.4$ kcal./mole, and $\Delta S° = 58.4$ cal./deg. mole. The average chromium–iodine bond energy in CrI_2 has been found to be 55.7 kcal./mole. Experimental bond energies of this and other group VIa halides ($CrCl_2$, $CrCl_3$, $CrCl_4$, MoI_2 and WCl_6) are compared with bond energies calculated theoretically.

The chromium–iodine bond energy in CrI_2 may be calculated from the heat of formation of CrI_2(c), the heats of atomization of chromium and iodine, and the heat of sublimation of CrI_2. Only the latter quantity has not been measured previously. It was determined from the change in vapor pressure of CrI_2 with temperature, using the transpiration method (saturated vapor flow method).

Experimental

Chromous iodide was prepared from the elements by the method of Handy and Gregory,[1] using Fisher chromium powder (98% pure) and Mallinckrodt iodine (A.R.). Analysis for iodine by ignition to Cr_2O_3 gave 82.9% I (stoichiometric for CrI_2, 83.0% I). Operations with the CrI_2 were conducted in a dry box under a nitrogen atmosphere.

The CrI_2 was sublimed into a transpiration tube of the type described by MacLaren and Gregory.[2] Fused quartz glass was used for those parts of the apparatus within the furnace. The end of the collector tube extending into the transpiration chamber was made of 1.5 mm. bore capillary tubing to decrease diffusion of CrI_2 into the collector. Dow Corning silicone high vacuum grease was used on stopcocks and ground joints.

Measurements were made on two samples of CrI_2. The first was sublimed into the transpiration chamber from a mixture of chromous iodide and unreacted chromium. The second was sublimed from pure CrI_2. In each case the sample bulb was left attached to the transpiration chamber. During the initial state of sublimation of the second sample, a temporary leak developed in the vacuum system. Air from this source oxidized a small amount of the CrI_2. The oxidation product (green in color, probably Cr_2O_3) was not volatile at the temperature of the vapor pressure measurements.

Argon (Linde Air Products Co.) was used as the carrier gas. It was passed through a flowmeter of the capillary type which was fitted with an overflow tube. Oxygen and water vapor were removed by means of hot copper and magnesium perchlorate, respectively.

The furnace (Hevi-Duty, Type HDT-1712) was lined with a nickel tube of one-quarter inch wall thickness, and the ends were insulated with asbestos. Temperature control was provided by a chromel–alumel thermocouple, located between the nickel tube and the heating coils, and a Minneapolis–Honeywell controller. Along the last three inches of the transpiration chamber the temperature was constant to within ±1°.

A chromel–alumel thermocouple, calibrated with a National Bureau of Standards certified platinum *vs.* platinum–rhodium thermocouple, was used for temperature measurement in the first set of experiments. After that, the platinum *vs.* platinum–rhodium thermocouple was used directly. The hot junction was placed next to the transpiration chamber.

After the nitrogen in the transpiration tube was replaced with argon, the furnace was heated rapidly. When the temperature had reached 100° below the set temperature, the flow of argon was stopped. It was started again when the temperature was constant at the desired value. The experiment was stopped by shutting both stopcocks and re-

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* Presented at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

[1] L. L. Handy and N. W. Gregory, THIS JOURNAL, **72**, 5049 (1950).

[2] R. O. MacLaren and N. W. Gregory, *J. Phys. Chem.*, **59**, 184 (1955).

moving the transpiration assembly from the furnace. For different experiments the duration varied from 90 to 203 minutes.

The CrI_2 was rinsed out of the collector and oxidized with Na_2O_2. The excess peroxide was decomposed by heating the solution to boiling.[3] After adjusting the concentration of hydroxide ion to 0.05 *N*, chromate ion was determined with a Beckman DU spectrophotometer at 375 mμ.[4]

It was assumed that the CrI_2 vapor consisted of the monomer only. Since CrI_2 has a large heat of vaporization, and since the measurements were made far below the boiling point, this assumption should be valid.[5]

In some of the experiments a very small amount of a dark substance, probably CrI_3, was noted in the collector downstream from the CrI_2 sublimate. A small amount of iodine vapor was present in the argon leaving the furnace. (The iodine resulted from thermal decomposition of the chromous iodide.) The CrI_3 may have been a product of reaction of I_2 with CrI_2 as the gas stream left the furnace. If this was the source of the CrI_3, it caused no error in the vapor pressure measurements, since it did not change the amount of chromium in the collector. If the CrI_3 resulted from disproportionation of CrI_2 within the transpiration chamber, then the calculated vapor pressure is too large. However, the amount of CrI_3 in the collector was always very small compared to the amount of CrI_2.

In the experiment at 1054.2°K. the partial pressure of iodine was measured by collecting the iodine in a Dry Ice trap. The iodine was determined by thiosulfate titration. In this experiment visual inspection showed that the only sublimate in the collector was CrI_2. Confirmation of this was obtained by gravimetric determination of iodide as the silver salt. This analysis and the chromium determination gave a formula of $CrI_{1.995}$ for the sublimate.

Results and Discussion

Experimental results are summarized in Table I.

TABLE I

VAPOR PRESSURE MEASUREMENTS

T(°K.)	P_{CrI_2} (atm.)	Flow rate (ml./min.)
943.4	3.11×10^{-5}	25.8
964.1	6.79×10^{-5}	23.1
983.4	1.36×10^{-4}	22.4
999.9	2.41×10^{-4}	18.9
1021.0	4.66×10^{-4}	20.7
1038.8	8.03×10^{-4}	30.0
1038.8	8.01×10^{-4}	10.0
1038.8	8.14×10^{-4}	20.0
1038.8	8.16×10^{-4}	5.06
1054.2	1.33×10^{-3}	29.8

In the four experiments at 1038.8°K. the flow rate varied from 5 to 30 ml./min., with no appreciable change in measured vapor pressure. The average is 8.08×10^{-4} atm., and the mean deviation is 0.8%. These results show that errors from diffusion of CrI_2 vapor into the collector and failure to saturate the argon stream with CrI_2 are negligible.[6]

For each temperature, a calculation was made of the Σ function[7] for the reaction $CrI_2(c) = CrI_2(g)$, where

$$\Sigma = -R \ln f + a \ln T$$

R is the gas constant, *f* is the fugacity of CrI_2, *a* is $\Delta C_p°$ for the sublimation of CrI_2 and *T* is the absolute temperature. The fugacity was taken as equal to the vapor pressure of CrI_2. Heat capacities of PbI_2,[8] HgI_2[8] and $CrCl_2$[9] were used to obtain an estimate of −7.0 cal./deg. mole for *a*.

Figure 1 shows a plot of Σ *vs.* 1000/*T*. The experimental points lie very near a straight line, with good agreement for the two different samples of CrI_2. The slope of this line is $\Delta H_0°$ and the intercept on the Σ axis is *I*. Both graphical and least squares methods give $\Delta H_0° = 73.5$ kcal./mole and $I = -105.3$ cal./deg. mole. From these the following thermodynamic properties are obtained for the sublimation of CrI_2

$$\Delta F°_{298.16} = 54.0 \text{ kcal./mole}$$
$$\Delta H°_{298.16} = 71.4 \text{ kcal./mole}$$
$$\Delta S°_{298.16} = 58.4 \text{ cal./deg. mole}$$

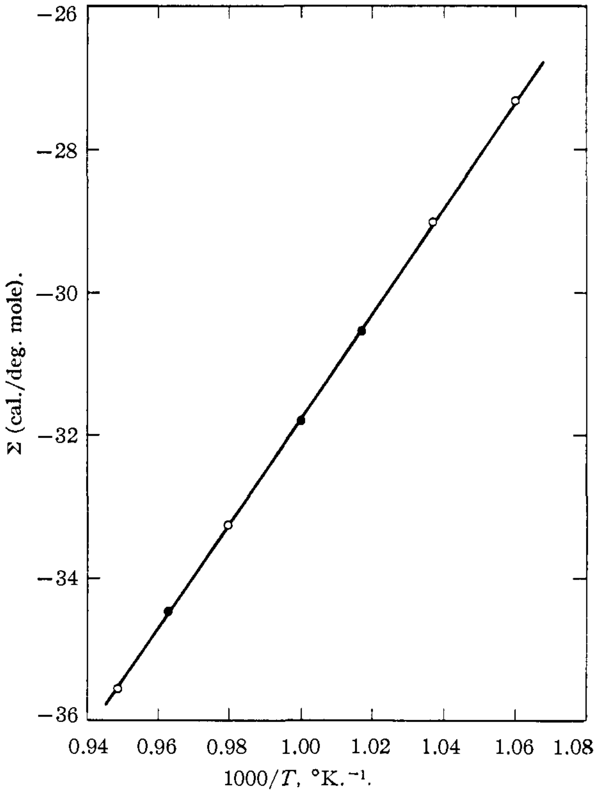

Fig. 1.—The dependence of $\Sigma = -R \ln f + a \ln T$ on the reciprocal of the absolute temperature. Open and closed circles represent results with different samples of CrI_2.

In the experiment at 1054.2°K., the partial pressure of I_2 in the exit gas stream was found to be 1.95×10^{-4} atm. From thermodynamic data for the dissociation of iodine,[10] the partial pressures of iodine atoms and iodine molecules in the transpiration chamber were calculated

$$P_I = 3{,}58 \times 10^{-4} \text{ atm.}$$
$$P_{I_2} = 0.16 \times 10^{-4} \text{ atm.}$$

The former value may be used to calculate the free

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[3] In the first experiment there was a small amount of ferric hydroxide from an impurity of ferrous iodide in the chromous iodide. It was removed by filtration through a sintered glass crucible.

[4] G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

[5] L. Brewer in "The Chemistry and Metallurgy of Miscellaneous Materials," edited by L. L. Quill, McGraw-Hill Book Co., Inc., New York, N. Y., 1950 (Natl. Nuclear Energy Ser., Div. IV, **19B**, p. 262.)

[6] J. V. Lepore and J. R. Van Wazer, U. S. Atomic Energy Comm. Rept., MDDC-1188 (1948).

[7] L. Brewer and A. W. Searcy, *J. Chem. Ed.*, **26**, 548 (1949).

[8] K. K. Kelley, *U. S. Bur. Mines Bull.*, No. 383 (1935).

[9] C. G. Maier, *ibid.*, No. 436 (1942).

[10] Reference 5, pp. 65–66.

energy change in the thermal decomposition $CrI_2(c) = Cr(c) + 2I(g)$

$$\Delta F^\circ_{1054.2} = 33.2 \text{ kcal./mole}$$

The heat of this reaction was calculated from the heat of formation of $CrI_2(c)$,[11] the heat of atomization of $I_2(c)$,[12] and the changes in heat content between 298.16 and 1054.2°K. for the substances entering into this reaction.[13] This calculation gave $\Delta H^\circ_{1054.2} = 86.6$ kcal./mole. Thus $\Delta S^\circ_{1054.2} = 50.7$ cal./deg. mole. This was converted to normal temperature by means of the entropy increments between 298.16 and 1054.2°K. for Cr(c), $CrI_2(c)$ and I(g),[13] giving $\Delta S^\circ_{298.16} = 55.2$ cal./deg. mole.

From the entropies of Cr(c) and I(g) at this temperature[13]

$$S^\circ_{298.16}(CrI_2,c) = 36.9 \text{ cal./deg. mole.}$$

This value may be compared with an estimate of 37.4 cal./deg. mole obtained from Latimer's entropy tables.[14] The agreement is excellent. Combination of the entropy of crystalline chromous iodide with the entropy of sublimation yields 95.3 cal./deg. mole for the entropy of chromous iodide vapor at 298.16°K.

From the heat of sublimation of CrI_2 determined in this investigation, the heat of formation of CrI_2 (c),[11] and the heats of atomization of iodine and chromium,[12] one may calculate the heat of atomization of chromous iodide

$$CrI_2(g) = Cr(g) + 2I(g)$$
$$\Delta H^\circ_{298.16} = 111.4 \text{ kcal./mole}$$

Thus the average chromium–iodide bond energy[15] in CrI_2 is 55.7 kcal./mole.

Table II summarizes average bond energies of Group VIa halides for which experimental data are available. Heats of formation are those given by NBS 500.[16] Heats of atomization of the elements are from Cottrell,[12] except for tungsten, for which the value 192.3 kcal./mole is taken from a recent review by Brewer.[17] Other references are given at the end of the table.

TABLE II

BOND ENERGIES FOR GROUP VIa HALIDES

Substance	Exptl. bond energy (kcal./mole)	Electro-negativity of metal	Calcd. bond energy (kcal./mole)
$CrCl_2$[a]	91.3	1.4	96
$CrCl_3$[a]	84.5	1.6	82
$CrCl_4$	78.4	1.7	76
CrI_2	55.7	1.4	56
MoI_2[b]	89.4	1.2	73
WCl_6[c]	73.7	2.0	68

[a] Heats of sublimation at 298.16°K. are calculated from the data of reference 9. [b] T. L. Allen and D. M. Yost, *J. Chem. Phys.*, **22**, 855 (1954). For the atomization of $MoI_2(g)$, ΔC_p° was estimated as zero. [c] Heat of sublimation from J. A. A. Ketelaar, G. W. van Oosterhout and P. B. Braun, *Rec. trav. chim.*, **62**, 597 (1943), converted to normal temperature with an estimate of $\Delta C_p^\circ = -10$ cal./deg. mole.

Also included in Table II are bond energies calculated by means of the equation of Pauling.[18] In the calculations, metal–metal single bond energies are taken as one-sixth of the heats of atomization of the metals.[19] The electronegativities (listed in column 3) are those selected by Gordy and Thomas,[20] except for Cr^{IV} and Mo^{II}. Values given in reference 20 for Cr^{IV} should belong to Cr^{VI}, and no value is given for Mo^{II}. Electronegativities of quadrivalent chromium and bivalent molybdenum have been calculated by means of eq. 6 of reference 20.

Satisfactory agreement between experimental and calculated bond energies is obtained for the chromium halides. The other experimental bond energies have been used to calculate the electronegativities of the metals. The results are: Mo^{II}, 1.0; W^{VI}, 1.9.

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(11) N. W. Gregory and T. R. Burton, THIS JOURNAL, **75**, 6054 (1953).

(12) T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954, pp. 154–155.

(13) Reference 5, Papers 3, 5 and 6.

(14) W. M. Latimer, THIS JOURNAL, **73**, 1480 (1951).

(15) As defined in reference 12, p. 119.

(16) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Standards Circular 500, 1952.

(17) L. Brewer, Univ. of Calif. Rept. UCRL-2854 (rev.), November, 1955.

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(19) D. D. Eley, *Disc. Faraday Soc.*, **8**, 34 (1950).

(20) W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).