in which Q_e is the electronic partition function,[7] m is the mass of the atom in grams, and the other symbols have their usual significance.[8]

The results of these calculations are presented in Table II, the average value of ΔH_0^0 being 121.95 kcal. per mole, with a standard deviation from the mean of 0.14 kcal. The absence of a trend in the calculated values of ΔH_0^0 indicates that α is unity.

Using equation (2), in conjunction with a linear equation in T for the difference in the free energy functions, and an average value of 121.95 kcal. for ΔH_0^0, we obtain the vapor pressure equation

$$R \ln p = \frac{-121.95 \times 10^3}{T} - 5.123 \times 10^{-4}T + 36.29 \quad (4)$$

where p is the pressure in atmospheres and R is the gas constant in cal. mole^{-1} deg.$^{-1}$.

COLUMBUS 10, OHIO RECEIVED APRIL 4, 1951

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[7] Term designations and values were taken from Charlotte E. Moore, "Term Designations for Excitation Potentials," Princeton Observatory, Princeton, N. J., 1934.

[8] Values of physical constants used were taken from Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research, Natl. Bur. Standards*, **34**, 143 (1945); also designated as Research Paper RP 1634.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vapor Pressures of Inorganic Substances. VII. Iron Between 1356°K. and 1519°K. and Cobalt Between 1363°K. and 1522°K.[1]

BY JAMES W. EDWARDS, HERRICK L. JOHNSTON AND WALTER E. DITMARS

The vapor pressures of iron and cobalt have been determined by the vacuum evaporation method introduced by Langmuir. Heats of sublimation at the absolute zero have been calculated and equations formulated for vapor pressure as a function of temperature. The condensation (accommodation) coefficient has been found to be unity.

Introduction

The vapor pressures of iron and cobalt have been determined in this Laboratory by the method of vacuum evaporation[2] from cylinders heated inductively. Our data constitute the first measurements reported for cobalt, but measurements on iron were carried out previously by Jones, Langmuir and Mackay,[3a] and by Marshall, Dornte and Norton.[3b]

Experimental Method

Apparatus and Procedure.—Techniques and apparatus used were essentially similar to those described in earlier papers from this Laboratory[4] although a new Pyrex apparatus was built for these runs with some modification from the previous design. The most marked modification was use of a suspension wire (0.020 inch tantalum) to support the iron and cobalt cylinders from above. The disk shaped iron sample was supported from below on the tips of three wolfram rods.

The Pyrex cell was baked out at about 400° with the sample in place for at least two hours before each run, by placing a removable oven around it. During a preliminary evacuation, prior to the bakeout, a charcoal trap in communication with the cell was heated to about 300° under vacuum to drive off most of the gases, and then the entire system was flushed three times with C.P. hydrogen. As a check of experimental results, C.P. hydrogen to a pressure of 20 mm. was also admitted during the bakeout of the Pyrex cell in one run (No. 9). With this preliminary heat treatment we were able to maintain pressures in the neighborhood of 5×10^{-7} mm. during evaporation runs, with liquid air around the charcoal trap.

The apparatus was opened after each run by cutting the upper portion of the Pyrex cell with a hot wire glass cutter. When it was then closed by fusion, some components of the Pyrex glass were volatilized and condensed on the optical window forming a barely visible white coating. Experiment showed that in one instance this coating required a temperature correction of 3.5°. The correction could not be expected to be constant, however, and so it was determined for each run individually by calibrating the optical pyrometer used for temperature measurement against a standard lamp with the window in the line of sighting. The correction was essentially independent of the time and temperature of the run.

Independent checks of the pyrometer calibration were obtained by: (1) observing the temperature of a black body immersed in freezing copper (an N. B. S. standard freezing point sample); and (2) intercomparing the standard lamp and another optical pyrometer that had been calibrated at the National Bureau of Standards. The three temperature scales were in agreement within the experimental error.

Samples.—The iron was an especially pure sample prepared for us by the Philips Research Laboratory of Eindhoven, Holland. The cobalt was produced by the Kulite Tungsten Company, New Jersey.

One iron sample was in the form of a solid cylinder of 1.3400-in. height and 0.8110-in. diam.; the other was a solid disk of 0.5354-in. height and 1.0010-in. diam. A black body hole was drilled into each sample near the edge; in the cylinder it had a 0.05-in. diam. and 0.70-in. depth and in the disk a 0.040-in. diam. and 0.30-in. depth.

Spectroscopic analysis[5] of the vacuum cast iron gave the following percentages:

Co — Not detected
Mo — Not detected
Si — From 0.001 to 0.01
Ni — < 0.001
Cu — From 0.001 to 0.01
Al — From 0.001 to 0.01
Mn — Not detected
Ca — < 0.001
Fe (by difference) — 99.97.

The cobalt sample was in the form of a solid cylinder of 1.1048-in. height and 0.6970-in. diam. A 0.050-in. black body hole was drilled near the edge, to a depth of about 0.51 in. We found that putting a few very small metal turnings from the sample material into the hole broke up reflectivity from the bottom and produced a nearly perfect black body condition. Spectroscopic analysis[5] of the cobalt showed the percentages

Fe — From 0.01 to 0.1
Mo — Not detected
Si — From 0.005 to 0.05
Ni — From 0.05 to 0.5
Cu — From 0.005 to 0.05
Al — From 0.001 to 0.01
Mn — From 0.005 to 0.05
Ca — < 0.001
Co (by difference) — 99.25.

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] *Cf.* references (1) and (2) of paper No. VI in this series.

[3] (a) H. A. Jones, I. Langmuir and G. M. J. Mackay, *Phys. Rev.*, **30**, 201 (1927); (b) A. L. Marshall, R. W. Dornte and F. J. Norton, THIS JOURNAL, **59**, 1161 (1937).

[4] *Cf.* reference 3 of paper No. VI of this series.

[5] The authors wish to express their appreciation to Mr. John Center, Chief Analyst, Battelle Memorial Institute, Columbus, Ohio, for carrying out these analyses.

TABLE I

VAPOR PRESSURE DATA FOR IRON

Run	Temp., °K.	Effective time, sec.	Total wt. loss, g.	Effective area, cm.^{2}	Evap. rate, g. cm.$^{-2}$ sec.$^{-1}$ $\times 10^7$	Pressure, atm. $\times 10^8$
2 disk	1356	24842	0.02158	20.7896	0.4178	0.465
7 cylinder	1389	7685	.01950	28.5840	0.8877	0.999
5 cylinder	1438	4217	.03261	28.5857	2.705	3.10
4 cylinder	1452	2534	.02780	28.9285	3.792	4.42
6 cylinder	1460	5266	.06985	29.2632	4.533	5.23
9 cylinder	1463	3356	.04750	28.9638	4.887	5.64
2 cylinder	1485	3630	.07852	28.6625	7.547	8.78
8 cylinder	1489	3106	.07558	28.6357	8.498	9.90
3 cylinder	1492	3846	.10552	29.1017	9.428	10.99
1 disk	1519	1415	.04762	20.6367	16.31	19.19

TABLE II

HEAT OF EVAPORATION OF IRON

Run	Temp., °K.	$-R \ln P$ cal. deg.$^{-1}$mole^{-1}	$-((F^0 - H_0^0)/T)_c$, cal. deg.$^{-1}$mole^{-1}	$-((F^0 - H_0^0/)/T)_g$, cal. deg.$^{-1}$mole^{-1}	ΔH_0^0, cal.
2 disk	1356	38.1362	11.301	46.214	99055
7 cylinder	1389	36.5191	11.508	46.350	99121
5 cylinder	1438	34.2752	11.800	46.550	99258
4 cylinder	1452	33.5709	11.900	46.615	99151
6 cylinder	1460	33.3244	11.922	46.637	99338
9 cylinder	1463	33.0861	11.940	46.646	99180
2 cylinder	1485	32.2101	12.070	46.730	99302
8 cylinder	1489	32.0558	12.090	46.747	99335
3 cylinder	1492	31.7642	12.110	46.755	99083
1 disk	1519	30.7405	12.255	46.854	99251
				Mean ΔH_0^0	99,207 cal./mole
				Standard deviation	98 cal./mole

TABLE III

VAPOR PRESSURE DATA FOR COBALT

Run	Temp., °K.	Effective time, sec.	Total wt. loss, g.	Effective area, cm.^{2}	Evap. rate, g. cm.$^{-2}$sec.$^{-1}$ $\times 10^7$	Press., atm. $\times 10^8$
10	1363	25200	0.01053	20.949	0.1995	0.216
7	1382	10379	.00729	20.985	.3347	.366
6	1414	8076	.01355	21.112	.7947	.878
5	1432	4624	.01092	21.066	1.121	1.25
2	1443	8638	.02762	20.897	1.530	1.71
3	1453	4868	.02010	21.083	1.958	2.19
8	1470	2687	.01630	21.093	2.876	3.24
4	1490	3278	.02999	21.070	4.342	4.92
9	1522	2734	.04804	21.080	8.336	9.55

TABLE IV

HEAT OF EVAPORATION OF COBALT

Run	Temp., °K.	$-R \ln P$	$-((F^0 - H_0^0)T)_c$, cal. deg.$^{-1}$mole^{-1}	$-((F^0 - H_0^0)/T)_g$, cal. deg.$^{-1}$mole^{-1}	ΔH_0^0, cal.
10	1363	39.6540	11.280	46.183	101621
7	1382	38.6124	11.380	46.274	101586
6	1414	36.8706	11.544	46.421	101451
5	1432	36.1736	11.630	46.500	101734
2	1443	35.5484	11.690	46.549	101598
3	1453	35.0514	11.744	46.596	101570
8	1470	34.2757	11.820	46.660	101600
4	1490	33.4432	11.920	46.740	101712
9	1522	32.1261	12.080	46.862	101834
			Mean ΔH_0^0		101,634 cal./mole
			Standard deviation		105 cal./mole

Calculations

Vapor pressures were calculated according to procedures previously described.[4] Free energy functions for the solid state were calculated from data given by Kelley.[6] Moore's values[7] were used for calculation of the electronic partition functions of the gaseous metals.

Experimental Results

The data are presented in Tables I, II, III and IV, and plotted in Figs. 1 and 2. In Fig. 1 (for iron) the curve has been drawn from

$$\log p = \frac{-21677}{T} + 0.00044438T - 0.0000003157T^2 + 7.5918 \quad (1)$$

in Fig. 2 (for cobalt) it has been drawn from

$$\log p = \frac{-22209}{T} - 0.000223T + 7.9366 \quad (2)$$

The coefficient of the term in $1/T$ is $\Delta H_0^0/2.303\ R$, and the other constants have been obtained by expressing the difference in the free energy functions as a polynomial in T and substituting in the equation

$$R \ln p = \left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{gas}} - \frac{\Delta H_0^0}{T} \quad (3)$$

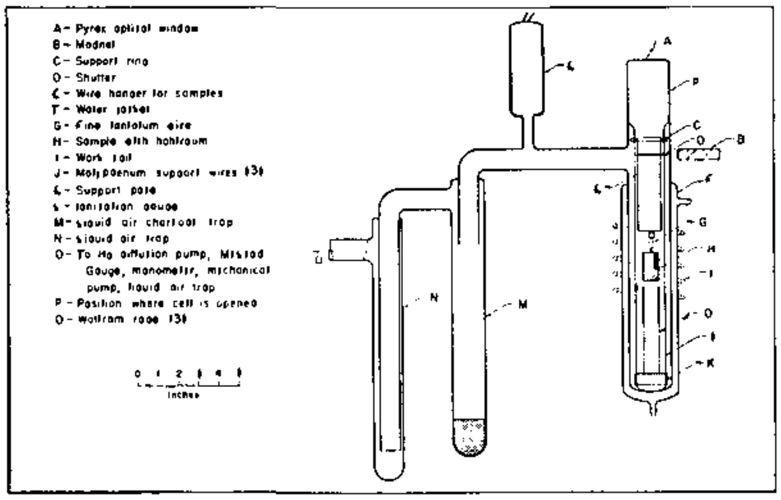

Fig. 1.—Vapor pressure apparatus.

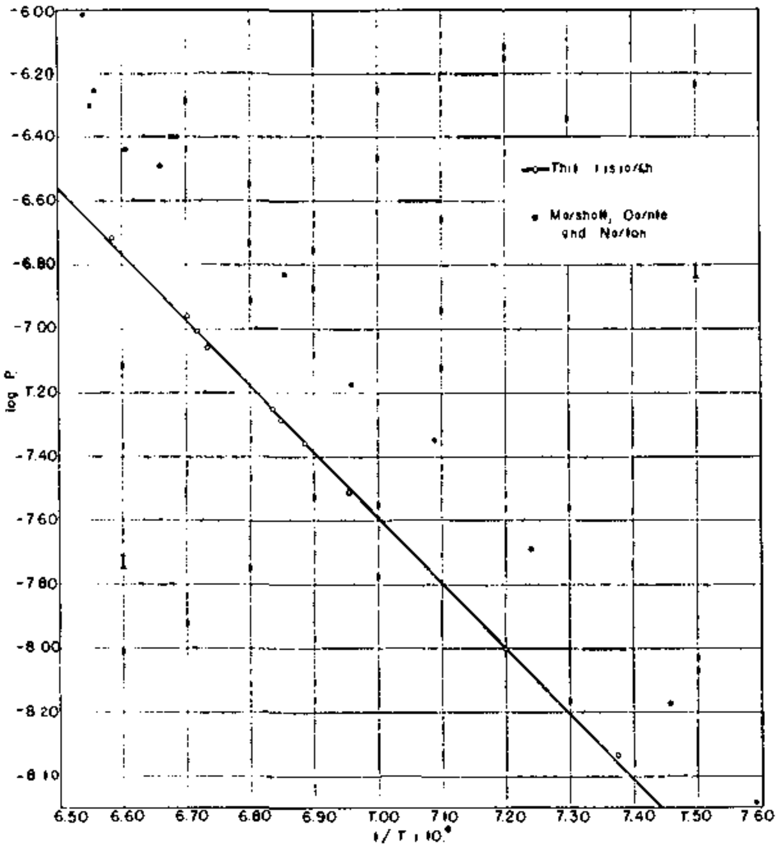

Fig. 2.—Vapor pressure of iron.

Experimental Errors

For a single calculation of ΔH_0^0, the standard deviations of the various measurements were determined as

Temperature ±1.5°
Effective time ±5 sec.
Weight loss ±0.0001 g.
Sample dimensions ±0.0025 cm.

As calculated by propagation of these observational errors, the standard deviation for an individual value of ΔH_0^0 amounts to about 47 cal. for Fe and 52 cal. for Co. The over-all accuracy of our data, however, depends on the accuracy of the temperature scale of the standard lamp we used.[8] Taking its maximum uncertainty into account, the standard deviation for an individual value of ΔH_0^0 amounts to 141 cal. for Fe and 146 cal. for Co.

As shown in Tables II and IV, the standard deviations of ΔH_0^0 calculated from the mean of our experimental values are in reasonably good agreement with the values calculated by propagation of observational errors. This agreement suggests that the deviations from the mean do not represent a temperature trend but are merely the scatter to be expected from observational errors, and it supports our assumption that the accommodation coefficient, α, in equation (1) is unity within experimental error.

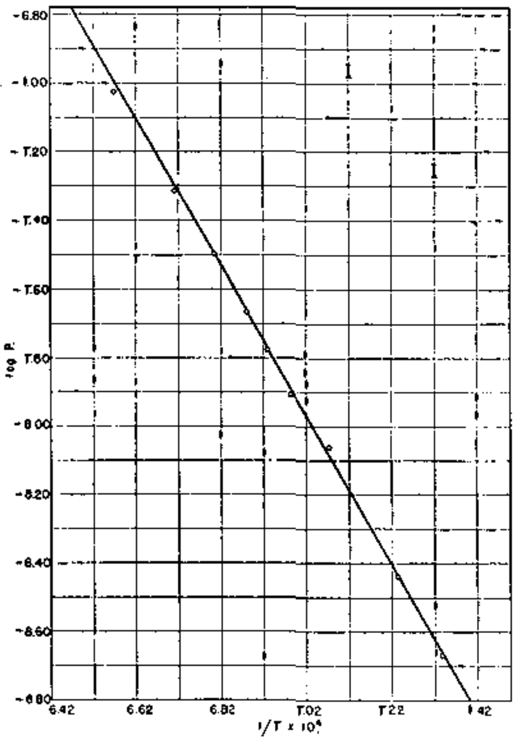

Fig. 3.—Vapor pressure of cobalt.

Comparison with Earlier Data

The earlier work on iron by Marshall, Dornte and Norton[3] differs somewhat from ours. Their value of ΔH_0^0 was 96.033 ± 0.310 kcal. per mole, as compared with our value of 99.207 ± 0.098 kcal. per

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(6) K. K. Kelley, "Contributions to Data on Theoretical Metallurgy: X. High Temperature Heat Content, Heat Capacity, and Entropy Data for Inorganic Compounds," and "XI. Entropies of Data and Methods of Calculation," Bulletins 476 (1949) and 477 (1950), Bureau of Mines.

(7) Charlotte E. Moore, "Term Designation for Excitation Potentials," Princeton University Observatory, Princeton, N. J., 1934.

(8) The National Bureau of Standards, in calibrating the lamp, set its maximum uncertainty as 5 deg. at 800°, 3 deg. at 1063°, and 7 deg. at 2300°.

mole. Some of this disagreement can be accounted for by the fact that they used a shallower black body hole, 1 mm. in diam. and 3 mm. deep; we found, by a comparison of brightness temperatures for holes of different depths and diameters, that at 1100° a cavity of these dimensions gives temperatures 11 deg. lower than the black body we used. This error is in the right direction to account for the disagreement but is not of sufficient magnitude. In general, the Marshall, Dornte and Norton values of vapor pressure are double or slightly more than double our own. This corresponds to a temperature difference of about 35 deg., which still leaves more than 20 deg. in temperature, or 50% in vapor pressure, to be accounted for. Possibly their "electrolytic" iron contained some volatile impurity that contributed significantly to the vapor pressures.

The vapor pressures obtained by Jones, Langmuir and Mackay,[2] who measured the evaporation loss from a heated filament, are also about double our own. No information is given on the source or purity of their iron.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. LIV. The Conductance and Molecular Weight of Some Salts in Benzene at Higher Concentrations[1]

BY HOWARD S. YOUNG[2] AND CHARLES A. KRAUS

Cryoscopic measurements were carried out with solutions of octadecyltri-*n*-amyl-, octadecyltri-*n*-butylammonium thiocyanate and tri-*n*-butylammonium iodide. Association numbers for the first two salts are the same within the limit of experimental error. The association of the iodide is much smaller than that of the two thiocyanates. The conductances of solutions of the three salts were also measured at 25°. The two thiocyanates have complex conductance curves resembling those of other similar quaternary ammonium salts. The conductance of the iodide is much lower than that of the other two salts at low concentrations and is higher at high concentrations. The results are discussed.

I. Introduction

Cryoscopic[3] and conductance measurements[4] with dilute solutions of 1–1 salts in benzene, combined with molecular polarization values derived from dielectric constant measurements[5,6] have demonstrated that the association of ion dipoles is greatly dependent upon the size and symmetry of their ions. All measured properties are in accord with the view that interactions are governed, chiefly, by electrical forces. Recently, these measurements have been extended to considerably higher salt concentrations by Strong[6] and Copenhafer.[7] It was found that salts, exhibiting high association cryoscopically, yield complex curves of conductance *vs.* concentration; less strongly associated salts on the other hand, yield much simpler curves. In general, salts of large, symmetrical cations and small anions were found to be the more highly associated.

The most highly associated salt measured cryoscopically by Copenhafer was *n*-octadecyltri-*n*-butylammonium formate. In view of the low solubility of this salt, it was thought worthwhile to investigate more soluble salts of the same cation type. Accordingly, we have studied solutions of *n*-octadecyltri-*n*-butyl- and *n*-octadecyltri-*n*-amylammonium thiocyanate with regard to their cryoscopic as well as their electrical behavior. In addition, we have investigated the less strongly associated salt, tri-*n*-butylammonium iodide, over a considerable range of concentration.

II. Experimental

1. **Materials.**—Benzene was purified by the method of Batson and Kraus.[3b]

Tri-*n*-butylammonium iodide was furnished us by Dr. H. L. Pickering who prepared it by treating the purified amine with gaseous hydrogen iodide; it was recrystallized from anhydrous ethyl acetate, m.p. 101.2–101.7° (cor.). *n*-Octadecyltri-*n*-butylammonium thiocyanate was prepared from the nitrate by metathesis with potassium thiocyanate in absolute alcohol according to the procedure described by Strobel.[8] The product was recrystallized from hexane to which had been added a small quantity of isopropyl alcohol, m.p. 66.5–67.2° (cor.). *n*-Octadecyltri-*n*-butylammonium nitrate, m.p. 89.2–90.0° (cor.), was prepared from the iodide by metathesis with silver nitrate, m.p. 101.0–101.3° (cor.). *n*-Octadecyltri-*n*-amylammonium thiocyanate was prepared by Mr. C. H. Keith, using a procedure paralleling that employed for the butyl compound, m.p. 55.8–58.0°. This thiocyanate was found to be approximately 60% more soluble in benzene at its freezing point than is the corresponding butyl derivative.

2. **Apparatus and Procedure.**—Conductance measurements were carried out at 25° using the apparatus and procedure described by Strong.[6] Densities of the more concentrated solutions were determined by means of a Weld specific gravity bottle; the results are given in Table I, where *m* is the molal concentration and *d* is the density.

The apparatus employed in freezing point measurements was that described in earlier papers[3,9]; the thermel was constructed by Dr. H. L. Pickering. A value of 5.088° was employed for the cryoscopic constant of benzene.

Difficulty was experienced in determining the concentration of solutions of the long chain salts by means of the analytical method described by Barton,[9] owing to their tendency to retain traces of solvent. Although this difficulty

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[1] Taken in part from the dissertation of Howard S. Young presented in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1948.

[2] University Fellow in Brown University, 1947-1948.

[3] (a) C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934); (b) F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934); (c) D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **59**, 1699 (1937).

[4] (a) C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933); (b) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 3614 (1943); (c) W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, *ibid.*, **58**, 255 (1936).

[5] (a) G. S. Hooper and C. A. Kraus, *ibid.*, **56**, 2265 (1934); (b) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936); (c) C. A. Kraus and G. S. Hooper, *Proc. Nat. Acad. Sci.*, **19**, 939 (1933).

[6] L. S. Strong and C. A. Kraus, THIS JOURNAL, **72**, 166 (1950).

[7] (LIII) D. T. Copenhafer and C. A. Kraus, THIS JOURNAL, **73**, 4557 (1951).

[8] H. A. Strobel and H. C. Eckstrom, *J. Chem. Phys.*, **16**, 817 (1948).

[9] B. C. Barton Thesis, Brown University, 1939.