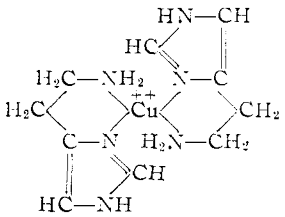
mine chelate is reduced by log 2, the statistical correction if only a *trans* species were formed, then log k_1 minus log k_2 becomes 2.90. This compares to 3.07 as observed for the histamine–copper system. The large difference between constants suggests that, in bis-histamine–Cu(II), the imidazole groups are *trans* to one another.



In contrast to copper, differences between constants are small for the tetracovalent nickel and cobaltous chelates. These intermediate complexes must exist in an ionic bonding configuration.

The contributions to chelate stability of ring and side-chain nitrogen atoms were estimated in terms of the corresponding metal ammines and imidazole complexes. The stabilities of the methylamine–cadmium complexes and the cadmium ammines are nearly identical.[8] The same relationship has been observed in the case of silver–ethylamine.[9] Formation constants for the metal ammines[6] were used in estimating the binding energy of histamine side-chain nitrogen. The gain in stability through formation of the n^{th} chelate ring, $\Delta(\Delta F)_n$, was calculated as

$$\Delta(\Delta F)_1 = \Delta F_1^{\text{hn}} - [\Delta F_1^{\text{im}} + \Delta F_2^{\text{NH}_3}] \qquad (1)$$

$$\Delta(\Delta F)_2 = \Delta F_2^{\text{hn}} - [\Delta F_3^{\text{im}} + \Delta F_4^{\text{NH}_3}] \qquad (2)$$

In the above, hn and im designate the energies of formation of the n^{th} histamine or imidazole species. The free energy values for imidazole and ammonia were chosen such that $\Delta(\Delta F)_n$ was minimized. For copper–histamine at 25°, $\Delta(\Delta F)_1$ is -2.7 kcal. mole^{-1}, and $\Delta(\Delta F)_2$ is -2.3 kcal. Corresponding values for nickel–histamine are -2.5 and -2.7 kcal. mole^{-1}.

Thermodynamic quantities, calculated from temperature data, may be of principal significance in a comparative sense. The increased stability of the histamine chelates is indicated to be in consequence of the more positive entropy term. Average values of -7 kcal. mole^{-1} and 12 e.u. were calculated for the heats and entropies in the stepwise formation of $Cu^{++}(hn)_2$; these quantities are -4 kcal. and 10 e.u. for $Ni^{++}(hn)_3$. Under the same conditions, the averages for $Cu^{++}(im)_4$ were -6 kcal. and about -7 e.u. Corresponding values for $Ni^{++}(im)_4$ were -4 kcal. and -4 e.u. In general, small negative entropies of formation are reported for the various metal ammines.

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[8] C. G. Spike and R. W. Parry, THIS JOURNAL, **75**, 2726, 3770 (1953).

[9] G. A. Carlson, J. P. McReynolds and F. H. Verhoek, *ibid.*, **67**, 1334 (1945).

The Magnetic Susceptibilities of Chlorine Trifluoride, Bromine Trifluoride, Bromine Pentafluoride and Iodine Pentafluoride[1]

BY MAX T. ROGERS, MORTON B. PANISH AND JOHN L. SPEIRS

RECEIVED APRIL 14, 1955

As part of a general study of the physical properties of the halogen fluorides we have determined the magnetic susceptibilities of chlorine trifluoride, bromine trifluoride, bromine pentafluoride and iodine pentafluoride. These substances were investigated in the liquid phase at room temperature using the Gouy method. They are all diamagnetic and the measured gram susceptibilities are shown in Table I at several field strengths. The average value, expressed as a molar susceptibility, is shown for each compound along with the molar susceptibility calculated from the theoretical ionic susceptibilities of Angus.[2] The compounds are somewhat less diamagnetic than calculated, as noted also for other polyfluorides which have been investigated.[3] The differences may result from the fact that the bonds are partly covalent in character and the paramagnetic term of the Van Vleck equation for the diamagnetic susceptibility of a polyatomic molecule[4] has become significantly large in these molecules.

TABLE I

SPECIFIC AND MOLAR SUSCEPTIBILITIES OF SOME HALOGEN FLUORIDES AT ROOM TEMPERATURE

H, oersteds	$X \times 10^6$			
	ClF_3	BrF_3	BrF_5	IF_5
4,770	......	-0.267	-0.256	-0.266
7,360	-0.289	.250	.257	.262
9,070	.284	.246	.259	.265
10,500	.286	.236	.258	.261
11,600	.287	.240	.260	.257
X_{gm} (av.)	-0.287	-0.248	-0.258	-0.262
X_{M} (obsd.)	-26.5	-33.9	-45.1	-58.1
X_{M} (calcd.[2])	-30.1	-39.4	-48.1	-58.4

Experimental

Apparatus.—The Gouy balance, the electromagnet and the technique used have been described.[5] A susceptibility tube of the compensated type was constructed of Vycor, which resists the corrosive action of the halogen fluorides fairly well for short periods. Fluorothene tubes were unsuccessful since they absorbed halogen fluorides to too great an extent. The compounds were distilled directly into the susceptibility tube by use of auxiliary apparatus also constructed of Vycor. The tube was closed with a Vycor ground joint while measurements were made. The distillation in Vycor apparatus was found to be necessary in order to eliminate ferromagnetic impurities. All measurements were made at room temperature (25–30°).

Materials.—The apparatus used for purification and handling of halogen fluorides has been described and the purity of the bromine pentafluoride and iodine pentafluoride

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[1] Physical properties of the halogen fluorides. III. For preceding article see M. T. Rogers, H. B. Thompson, Jr., and J. L. Speirs, THIS JOURNAL, **76**, 4841 (1954).

[2] W. R. Angus, *Proc. Roy. Soc.* (*London*), **A136**, 569 (1932).

[3] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 45.

[4] J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932, p. 275.

[5] M. T. Rogers and R. Vander Vennen, THIS JOURNAL, **75**, 1751 (1953).

established by freezing point measurements.[6] The chlorine trifluoride and bromine trifluoride probably contained less than one mole per cent. impurity. In any case, diamagnetic impurities should introduce only a small error into the results which are assigned a probable error of about two per cent.

Acknowledgment.—The authors are grateful to the Atomic Energy Commission for support of this work through contract AT(11-1)-151.

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[6] M. T. Rogers, J. L. Speirs, H. B. Thompson, Jr., and M. B. Panish, THIS JOURNAL, **76**, 4843 (1954); M. T. Rogers and J. L. Speirs, unpublished results.

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The Enthalpy and Heat Capacity of Magnesium and of Type 430 Stainless Steel from 700 to 1100°K.

BY DANIEL R. STULL AND RICHARD A. MCDONALD

RECEIVED MARCH 24, 1955

Kelley[1] has reviewed the literature on the heat of melting of magnesium. All of the data have been derived from temperature–composition studies of binary alloys. Since the values range from 1,160 to 2,480 cal./gram atom, it was desirable to make a direct measurement of this quantity.

Measurements were made in a dropping calorimeter similar to that described by Southard.[2] Approximately 0.44 mole of double sublimed magnesium (99.95 to 99.98% pure) was sealed in a thin-walled container of type 430 Stainless Steel by welding in an atmosphere of argon. A duplicate container was used in determining the enthalpy of the stainless steel.

The experimental data were treated as recommended by Shomate.[3] Enthalpy is expressed by the relationship

$$H_T - H_{298.16} = aT + bT^2 + cT^{-1} + d \qquad (1)$$

The constants representing the experimental data are given in Table I. Enthalpy is expressed in cal./gram and T in degrees Kelvin.

TABLE I

VALUES FOR THE CONSTANTS IN EQUATION 1 FROM 700 TO 1100°K.

Material	Constants a	b	c	d
Type 430 Stainless steel	−0.05709	0.000141	−7380.6	29.236
Solid magnesium	.1835	.0000760	−1360.5	−56.916
Liquid magnesium	.2176	.0000535	484.63	16.851

The solid line in Fig. 1 shows the enthalpy of magnesium calculated from equation 1. The spread of the experimental error of the observed values also is shown. The maximum deviation of the observations from the line is ±0.7%. Two or three measurements were made at each temperature.

The heat of melting of magnesium was found to be 88 ± 2 cal./gram or 2,140 ± 50 cal./gram atom (1953, at. wt. Mg = 24.32).

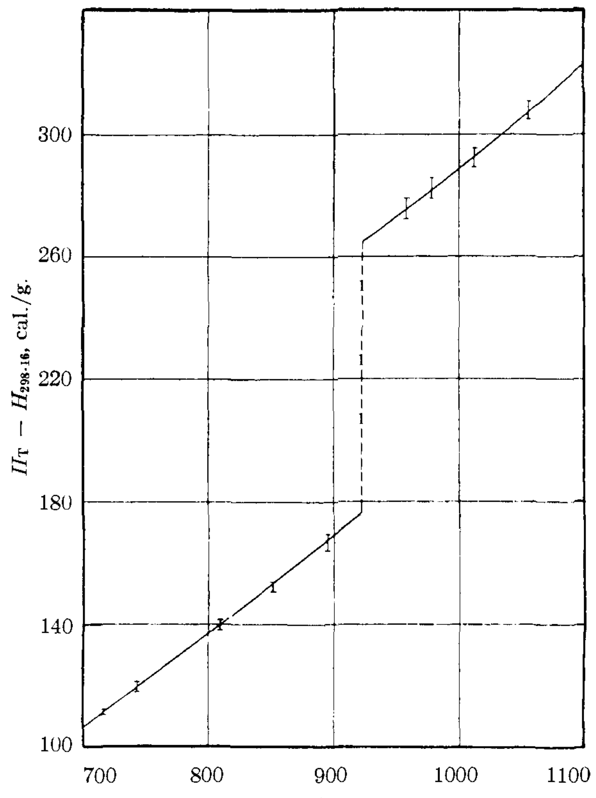

Fig. 1.—Enthalpy of magnesium; m.p. 923°K., heat of fusion = 88 cal./g.; line drawn through smoothed values. I indicates spread of experimental error of 2 or 3 observed values.

Differentiation of equation 1 gives the heat capacity

$$C_p = a + 2bT - cT^{-2} \qquad (2)$$

Heat capacities calculated from this equation are listed in Table II.

TABLE II

HEAT CAPACITY OF MAGNESIUM AND OF TYPE 430 STAINLESS STEEL FROM 700 TO 1100°K.

Temp., °K.	Heat capacity Magnesium, cal./g. atom/deg.	Magnesium, cal./g./deg.	430 stainless steel, cal./g./deg.
700	7.09	0.292	0.155
750	7.24	.298	.168
800	7.42	.305	.180
850	7.61	.313	.193
900	7.81	.321	.206
923	Melting point		
950	7.75	.319	.219
1000	7.88	.324	.232
1050	8.01	.329	.246
1100	8.14	.335	.259

Caution is urged in extrapolating beyond the limits of the observations.

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(1) K. K. Kelley, U. S. Bur. Mines Bull., 393 (1936).

(2) J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

(3) C. H. Shomate, *J. Phys. Chem.*, **58**, 368 (1954).