

reproducible, and the most intense and characteristic lines occur from  $9.35^\circ$  to  $20.5^\circ$  ( $d = 9.458\text{--}4.332 \text{ \AA}$ ). The rest of the lines show the usual line broadening of organic crystalline material.

In conclusion, the data presented show no fundamental discrepancies in the  $d$  spacings. Variations in intensities of the strongest line in the diffraction pattern have been explained. Moreover, by employing two different methods of loading the samples, preferred orientation effects were reduced to a minimum. Several runs of different sample loadings have shown that the results are both reproducible and reliable.

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**Registry No.** Acetazolamide, 59-66-5; althiazide, 5588-16-9; chlor-thaldone, 77-36-1; dichlorophenamide, 120-97-8; ethacrynic acid, 58-54-8;

furosemide, 54-31-9; hydrochlorothiazide, 58-93-5; hydroflumethiazide, 135-09-1; mersalyl acid, 486-67-9; spironolactone, 52-01-7; triamterene, 396-01-0; trichlormethiazide, 133-67-5.

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## Dissociation Constants of Picric Acid in Mixtures of *N,N*-Dimethylformamide + Ethane-1,2-diol

Fulvio Corradini, Andrea Marchetti, Mara Tagliacucchi, Lorenzo Tassi, and Giuseppe Tosi\*

Department of Chemistry, University of Modena, via G. Campi, 183, 41100 Modena, Italy

The acid dissociation constants of 2,4,6-trinitrophenol (picric acid) were determined in *N,N*-dimethylformamide and ethane-1,2-diol from  $-10$  to  $+80^\circ\text{C}$  and in two *N,N*-dimethylformamide + ethane-1,2-diol mixtures from  $+20$  to  $+80^\circ\text{C}$  using the conductometric method. The experimental conductivity data were analyzed by means of the Fuoss-Hsia equation, and the dissociation constants were fitted by the integrated Van't Hoff equation.

#### Introduction

In a series of papers (1) we have studied binary solvent systems and the acid-base properties that are characteristic of some solutes under certain conditions. In particular, we are interested in developing a model for predicting acid-base conductometric titration curves in nonaqueous media, such as monoprotic and diprotic acids, phenols, and aromatic nitroderivatives, either in binary mixtures or as mixtures with water.

This work is part of a systematic study of the influence of the solvents and the temperature on the dissociation constant of picric acid, chosen as a typical weak electrolyte (2, 3). This work reports conductivity measurements and derived acid dissociation constants for picric acid in the *N,N*-dimethylformamide (1) + ethane-1,2-diol (2) solvent system, at 19 temperatures from  $-10$  to  $+80^\circ\text{C}$ .

*N,N*-Dimethylformamide is regarded as a dipolar aprotic, protophilic, and a potentially basic solvent, while ethane-1,2-diol is regarded as a dipolar amphiprotic and a potentially acidic solvent. Measurements of dissociation constants of a weak acid in these solvents and their mixtures would provide a better understanding of solvent-cosolvent interactions, of the formation of stable adducts in solution, and of solute-solvent interactions.

*N,N*-Dimethylformamide and ethane-1,2-diol were chosen because they have very similar dielectric constants ( $\epsilon_1 = 37.51$  and  $\epsilon_2 = 37.70$  at  $25^\circ\text{C}$ ). By varying the composition of the binary mixtures, one would expect a gradual variation in the

acid-base character of the solvent system, since *N,N*-dimethylformamide and ethane-1,2-diol are almost isodielectric over the temperature range studied.

#### Experimental Section

**Materials.** The 2,4,6-trinitrophenol (picric acid), supplied by BDH (purity ca. 95%), was twice purified by recrystallization from hot ethanol and diethyl ether (mp  $122^\circ\text{C}$ ; lit.  $122\text{--}3^\circ\text{C}$  (4)). The purity of the final sample used (99.5%) was estimated by acid-base titrimetry by using standard 0.1 N sodium hydroxide solutions supplied by Aldrich. The solvents *N,N*-dimethylformamide and ethane-1,2-diol (containing both  $<0.10\%$  by mass of water, as determined by Karl-Fischer titration) were Carlo Erba high-purity grade. The *N,N*-dimethylformamide was purified by passage through a neutral alumina column before use (final purity 99.6% gas chromatographically determined). The ethane-1,2-diol (purity 99.5% gas chromatographically checked) was used without further purification.

**Apparatus.** Conductances of the solutions were measured with an Amel Model 134 digital conductivity bridge operating in the  $0.1 \times 10^{-6} \leq G/S \leq 0.3$  (scale-end) range, with a sensitivity of  $\pm 1.0\%$ , and using platinumized platinum electrodes (cell constant 0.98 cm). Temperature control was provided by a Lauda K2R thermostatic bath maintained to  $\pm 0.02^\circ\text{C}$ . Viscosity measurements were performed using a Schott-Geräte AVS 400 viscosity measuring system, equipped with a series of Ubbelohde viscometers. The densities were determined with a digital density meter, Anton Paar Model DMA 60 equipped with a density measuring cell, Model DMA 602, with a sensitivity up to  $0.000001 \text{ g cm}^{-3}$ . The dielectric constants were measured by the heterodyne beat method using a WTW-DM01 dipolemeter equipped with a stainless steel cylindrical cell, MFL3 ( $21 < \epsilon < 90$ ), that was calibrated with ethanol ( $\epsilon = 24.30$  at  $25^\circ\text{C}$ ), methanol ( $\epsilon = 32.63$  at  $25^\circ\text{C}$ ), glycerol ( $\epsilon = 42.50$  at  $25^\circ\text{C}$ ), and water ( $\epsilon = 80.37$  at  $20^\circ\text{C}$ ) (5). A frequency of 2.0 MHz was used. Karl-Fischer titrations were performed for the water content of solvents with an automatic titration system

(Crison Model KF431) equipped with a digital buret (Crison Model 738).

**Procedure.** The solvent mixtures were prepared by mass. The solutions of picric acid at different concentrations were obtained by successive dilution of stock solutions, freshly prepared by weight; concentrations in volume were then calculated from weight concentrations and densities. Conductance readings were recorded when they became invariant with time; this took about 30 min for each measurement. Solvent conductance corrections were applied to all the measured conductances.

## Results and Discussion

Measurements were made with the two pure solvents and six binary mixtures of *N,N*-dimethylformamide ( $x_1$ ) + ethane-1,2-diol ( $x_2$ ). Only for the pure solvents and two mixtures ( $x_1 = 0.8848$  and  $0.7734$ ) it was possible to determine the dielectric constant values over the entire temperature range; the impossibility to measure this property for the other four mixtures ( $0.5609 \geq x_1 \geq 0.0864$ ) probably arises from the great sensitivity of the specific conductance of the solvents on temperature and on mixture composition ( $\delta$ ). In fact the dielectric constant in its complete form  $\epsilon = \epsilon' - i\epsilon''$  contains a real ( $\epsilon'$ ) and an imaginary ( $\epsilon''$ ) contribution; in the case of the above four mixtures the  $\epsilon''$  contribution is always greater than that of  $\epsilon'$ , making impossible the experimental determination of the dielectric constant by the heterodyne beat method (7). However density and viscosity have been determined over the temperature range for all mixtures ( $\delta$ ).

The experimental dissociation constants of picric acid in solvents were determined from conductance measurements on at least six picric acid concentrations. The conductances of the solvents at each temperature were measured, and the experimental conductances reported as supplementary material are the corrected values. The corrected values were analyzed by the method of Fuoss-Hsia (9)

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log(C\gamma) + J_1C\gamma - J_2(C\gamma)^{3/2} - K_A C\gamma f_{\pm}^2 \Lambda \quad (1)$$

where the symbols have the following significance (10):

$$S = \alpha\Lambda_0 + \beta$$

$$\alpha = 8.204 \times 10^5 / (\epsilon T)^{3/2}$$

$$\beta = 82.43 / \eta(\epsilon T)^{1/2}$$

$$E = E_1\Lambda_0 - 2E_2$$

$$E_1 = 2.303k^2 a^2 b^2 / 24C$$

$$E_2 = 2.303kab\beta / 16C^{1/2}$$

$$b = e^2 / a\epsilon k_B T$$

$$k = (8\pi N z^2 e^2 C / 1000\epsilon k_B T)^{1/2}$$

$$J_1 = \sigma_1\Lambda_0 + \sigma_2$$

$$J_2 = \sigma_3\Lambda_0 + \sigma_4$$

$$\sigma_1 = [(kab)^2 / 24C] [1.8147 + 2 \ln(ka/C^{1/2}) + (2/b^3)(2b^2 + 2b - 1)]$$

$$\sigma_2 = \alpha\beta + \beta(ka/C^{1/2}) - \beta[(kab) / 16C^{1/2}] [1.5337 + (4/3b) + 2 \ln(ka/C^{1/2})]$$

$$\sigma_3 = [b^2(ka)^3 / 24C^{3/2}] [0.6094 + (4.4748/b) + (3.8284/b^2)]$$

$$\sigma_4 = [\beta(kab)^2 / 24C] [(2/b^3)(2b^2 + 2b - 1) - 1.9384] + \alpha\beta(ka/C^{1/2}) + [\beta(ka)^2 / C] - [\beta b(ka)^2 / 16C] [1.5405 + (2.2761/b)] - (\beta^2 kab / 16\Lambda_0 C^{1/2}) [(4/3b) - 2.2194]$$

**Table I. Experimental Dissociation Constant  $K$  Values<sup>a</sup> for Picric Acid in *N,N*-Dimethylformamide ( $x_1$ ) + Ethane-1,2-diol ( $x_2$ ) at Various Temperatures**

$t/^\circ\text{C}$	$K \times 10^2$			$K \times 10^3$
	$x_1 = 1.0000$	$x_1 = 0.8848$	$x_1 = 0.7734$	$x_1 = 0.0000$
-10	5.50 ± 0.09			1.81 ± 0.02
-5	5.73 ± 0.11			1.91 ± 0.02
0	5.90 ± 0.11			2.06 ± 0.02
5	6.04 ± 0.12			2.08 ± 0.02
10	6.14 ± 0.12			2.18 ± 0.02
15	6.17 ± 0.12			2.26 ± 0.02
20	6.18 ± 0.13	4.59 ± 0.67	4.47 ± 0.88	2.31 ± 0.02
25	6.18 ± 0.13	3.62 ± 0.41	3.32 ± 0.89	2.40 ± 0.02
30	6.05 ± 0.12	3.08 ± 0.35	2.63 ± 0.51	2.43 ± 0.02
35	5.68 ± 0.11	2.65 ± 0.21	2.08 ± 0.30	2.45 ± 0.02
40	5.26 ± 0.09	2.20 ± 0.14	1.59 ± 0.16	2.43 ± 0.02
45	5.01 ± 0.09	1.86 ± 0.10	1.19 ± 0.09	2.41 ± 0.01
50	4.60 ± 0.08	1.64 ± 0.08	1.00 ± 0.06	2.36 ± 0.01
55	4.32 ± 0.07	1.49 ± 0.06	0.862 ± 0.043	2.31 ± 0.02
60	3.91 ± 0.06	1.44 ± 0.06	0.795 ± 0.045	2.28 ± 0.01
65	3.50 ± 0.05	1.37 ± 0.05	0.741 ± 0.029	2.21 ± 0.02
70	3.14 ± 0.04	1.29 ± 0.05	0.690 ± 0.024	2.13 ± 0.02
75	2.90 ± 0.04	1.29 ± 0.05	0.646 ± 0.020	2.04 ± 0.01
80	2.65 ± 0.03	1.23 ± 0.05	0.621 ± 0.018	1.97 ± 0.02

<sup>a</sup>All  $K$  values are reported in the molar scale.

**Table II. Limiting Molar Conductance  $\Lambda_0$  Values for Picric Acid in *N,N*-Dimethylformamide ( $x_1$ ) + Ethane-1,2-diol ( $x_2$ )**

$t/^\circ\text{C}$	$\Lambda_0 / (\text{cm}^2 \text{S mol}^{-1})$			
	$x_1 = 1.0000$	$x_1 = 0.8848$	$x_1 = 0.7734$	$x_1 = 0.0000$
-10	48.2 ± 0.5			7.1 ± 0.1
-5	51.7 ± 0.6			8.1 ± 0.1
0	56.8 ± 0.6			9.0 ± 0.1
5	60.9 ± 0.7			11.0 ± 0.1
10	65.5 ± 0.7			13.0 ± 0.2
15	70.1 ± 0.8			15.6 ± 0.2
20	74.8 ± 0.8	56.3 ± 0.6	38.0 ± 0.5	18.3 ± 0.2
25	79.5 ± 0.8	60.9 ± 0.6	41.6 ± 0.5	21.2 ± 0.2
30	84.3 ± 0.9	65.6 ± 0.7	45.5 ± 0.5	24.8 ± 0.3
35	89.4 ± 1.0	70.3 ± 0.7	49.7 ± 0.6	28.5 ± 0.3
40	94.9 ± 1.0	75.1 ± 0.8	54.1 ± 0.6	32.6 ± 0.4
45	100.0 ± 1.1	80.4 ± 0.8	58.9 ± 0.7	37.0 ± 0.4
50	106.5 ± 1.1	86.1 ± 0.9	64.0 ± 0.7	41.6 ± 0.5
55	113.0 ± 1.2	92.7 ± 1.0	69.6 ± 0.8	46.5 ± 0.5
60	119.9 ± 1.3	99.2 ± 1.0	75.2 ± 0.8	51.6 ± 0.6
65	128.1 ± 1.4	106.5 ± 1.1	81.3 ± 0.9	56.7 ± 0.6
70	136.8 ± 1.5	115.4 ± 1.2	87.8 ± 1.0	62.0 ± 0.7
75	147.3 ± 1.6	124.8 ± 1.3	95.1 ± 1.0	67.9 ± 0.9
80	157.9 ± 1.7	136.3 ± 1.4	102.5 ± 1.1	74.5 ± 0.9

and where  $C$  = concentration (equiv  $\text{dm}^{-3}$ ),  $T$  = absolute temperature,  $\epsilon$  = dielectric constant of the solvent,  $\eta$  = solvent viscosity,  $z$  = valencies of the ions,  $N$  = Avogadro's number,  $k_B$  = Boltzmann constant,  $e$  = electronic charge,  $K_A$  = the association constant,  $\gamma$  = the degree of association,  $f_{\pm}$  = mean ionic activity coefficient, and  $a = \hat{a}$  = interionic distance parameter.

An initial value of  $\Lambda_0$  was estimated from an Onsager plot; then a few iterations were used to obtain the experimental dissociation constant  $K$  ( $K = 1/K_A$ ), the limiting ionic conductivity  $\Lambda_0$ , and the interionic distance parameter  $\hat{a}$  (given in Tables I-III, respectively).

Although the Fuoss-Hsia analysis does not usually involve excessive difficulties, for the two mixtures the calculation procedure gives results unacceptable in the -10 to +15 °C range.

**Dissociation Constant.** Each set of  $K$  values for a solvent system was fitted by the integrated Van't Hoff equation

$$\ln K = a_0 + a_1(T/K) + a_2(K/T) + a_3 \ln(T/K) \quad (2)$$

The coefficients  $a_i$ , reported in Table IV, were determined by a least-squares method (11) and reproduce the dissociation constants to within  $\pm 1.59\%$ .

**Table III. Interionic Center-to-Center Distance  $\bar{a}$  for Picric Acid in  $N,N$ -Dimethylformamide ( $x_1$ ) + Ethane-1,2-diol ( $x_2$ )**

$t/^\circ\text{C}$	$\bar{a}/(10^{-10} \text{ m})$			
	$x_1 = 1.0000$	$x_1 = 0.8848$	$x_1 = 0.7734$	$x_1 = 0.0000$
-10	3.70 ± 0.05			1.12 ± 0.01
-5	3.87 ± 0.06			1.13 ± 0.01
0	4.02 ± 0.06			1.16 ± 0.01
5	4.16 ± 0.06			1.17 ± 0.01
10	4.29 ± 0.07			1.19 ± 0.01
15	4.39 ± 0.07			1.21 ± 0.01
20	4.48 ± 0.07	9.88 ± 0.19	9.34 ± 0.47	1.23 ± 0.01
25	4.57 ± 0.07	9.59 ± 0.18	8.90 ± 0.44	1.25 ± 0.01
30	4.59 ± 0.07	9.39 ± 0.18	8.49 ± 0.41	1.27 ± 0.01
35	4.47 ± 0.07	9.17 ± 0.17	7.98 ± 0.37	1.28 ± 0.01
40	4.31 ± 0.06	8.82 ± 0.16	7.24 ± 0.33	1.30 ± 0.01
45	4.25 ± 0.06	8.48 ± 0.16	6.32 ± 0.27	1.32 ± 0.01
50	4.08 ± 0.05	8.24 ± 0.15	5.80 ± 0.24	1.33 ± 0.01
55	3.99 ± 0.05	8.05 ± 0.14	5.35 ± 0.19	1.35 ± 0.01
60	3.81 ± 0.04	8.07 ± 0.14	5.18 ± 0.17	1.36 ± 0.01
65	3.61 ± 0.04	8.06 ± 0.14	5.05 ± 0.15	1.38 ± 0.01
70	3.45 ± 0.03	8.00 ± 0.13	4.92 ± 0.13	1.39 ± 0.01
75	3.36 ± 0.03	8.17 ± 0.13	4.82 ± 0.12	1.41 ± 0.01
80	3.26 ± 0.02	8.18 ± 0.13	4.83 ± 0.11	1.40 ± 0.01

**Table IV.  $a_i$  Coefficients of Equation 2 for Picric Acid in  $N,N$ -Dimethylformamide ( $x_1$ ) + Ethane-1,2-diol ( $x_2$ )**

$x_1$	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
1.0000	117.08	-0.047 344	-7869.4	-13.932	±0.018
0.8848	1357.1	0.490 12	-26 786	-248.24	±0.025
0.7734	4169.9	1.2896	-100 922	-740.14	±0.041
0.0000	-279.43	-0.122 19	4310.9	51.839	±0.010

**Table V.  $\lambda_i^\circ$  Coefficients of Equation 3 for  $N,N$ -Dimethylformamide ( $x_1$ ) + Ethane-1,2-diol ( $x_2$ )**

$x_1$	$\lambda_0^\circ$	$\lambda_1^\circ$	$\lambda_2^\circ \times 10^{-2}$	$\lambda_3^\circ$	$\sigma/(\text{cm}^2 \text{ S mol}^{-1})$
1.0000	56.92	0.9154	-0.3252	0.9404	±0.45
0.8848	33.72	1.347	-1.460	1.718	±0.24
0.7734	25.22	0.5733	0.2593	0.2890	±0.10
0.0000	9.28	0.3018	0.7673	-0.1642	±0.19

Many difficulties may arise in explaining the reason why the  $K$  values of the two mixtures are generally greater (almost of 1 order of magnitude) than those observed in pure  $N,N$ -dimethylformamide. The formation of a solvent-cosolvent adduct (or different adducts of various stoichiometric ratios) is probable and quite coherent with the observations reported about the preliminary characterization of the solvent system ( $\beta$ ). On the other hand, the simplest conclusion is that these two solvents exhibit an effect of synergy toward the ionization and dissociation processes of the acidic solute.

**Limiting Ionic Conductivity.** The  $\Lambda_0$  values provided by the Fuoss-Hsia equation for each solvent system, and reported in Table II, were fitted as a polynomial in temperature (12)

$$\Lambda_0/(\text{cm}^2 \text{ S mol}^{-1}) = \sum_{i=0}^3 \lambda_i^\circ (t/^\circ\text{C})^i \quad (3)$$

The coefficients are given in the Table V; eq 3 reproduces the experimental  $\Lambda_0$  values to within ±0.35%.

A further difference between the pure solvents and their two mixtures is observed for the relation between  $\Lambda_0$  and viscosity. The Walden product is reported in Table VI. For  $N,N$ -dimethylformamide and for  $x_1 = 0.8848$ , the Walden product  $\Lambda_0\eta$  is approximately constant over the temperature range. For  $x_1 = 0.7734$  the Walden product increases with temperature. For ethane-1,2-diol the Walden product dramatically decreases with an increase in temperature; this behavior, also described by Fuoss for other solute-solvent systems (13), has been attributed to a decrease of the dielectric constant of the solvent with temperature. Stokes and Stokes (14) suggested, for high-

**Table VI. Walden Rule  $\Lambda_0\eta$  Values for Picric Acid in  $N,N$ -Dimethylformamide ( $x_1$ ) + Ethane-1,2-diol ( $x_2$ )**

$t/^\circ\text{C}$	$\Lambda_0\eta/(\text{cm}^{-1} \text{ s}^2 \text{ A}^2 \text{ mol}^{-1})$			
	$x_1 = 1.0000$	$x_1 = 0.8848$	$x_1 = 0.7734$	$x_1 = 0.0000$
-10	0.66			7.97
-5	0.65			6.52
0	0.66			5.33
5	0.65			4.90
10	0.65			4.45
15	0.65			4.18
20	0.65	0.67	0.63	3.90
25	0.65	0.67	0.62	3.64
30	0.65	0.67	0.62	3.49
35	0.65	0.67	0.62	3.32
40	0.65	0.67	0.62	3.18
45	0.65	0.68	0.63	3.05
50	0.65	0.68	0.64	2.92
55	0.66	0.69	0.66	2.81
60	0.67	0.70	0.68	2.70
65	0.68	0.71	0.71	2.58
70	0.69	0.73	0.75	2.48
75	0.71	0.75	0.79	2.39
80	0.73	0.78	0.85	2.33

**Table VII. Modified Walden Rule  $\Lambda_0\eta^x$  Values for Picric Acid in  $N,N$ -Dimethylformamide ( $x_1$ ) + Ethane-1,2-diol ( $x_2$ ), Where  $x = 0.7$** 

$t/^\circ\text{C}$	$\Lambda_0\eta^x/(\text{cm}^{-1} \text{ s}^2 \text{ A}^2 \text{ mol}^{-1})$			
	$x_1 = 1.0000$	$x_1 = 0.8848$	$x_1 = 0.7734$	$x_1 = 0.0000$
-10	0.50			7.69
-5	0.49			6.97
0	0.49			6.27
5	0.48			6.30
10	0.48			6.21
15	0.48			6.29
20	0.47	0.31	0.16	6.31
25	0.47	0.31	0.15	6.30
30	0.47	0.30	0.15	6.42
35	0.47	0.30	0.14	6.48
40	0.47	0.30	0.14	6.55
45	0.46	0.29	0.14	6.62
50	0.47	0.29	0.14	6.67
55	0.47	0.29	0.14	6.72
60	0.47	0.29	0.14	6.75
65	0.48	0.30	0.14	6.75
70	0.49	0.30	0.15	6.74
75	0.50	0.31	0.16	6.77
80	0.51	0.32	0.17	6.83

density aqueous solutions, a modified Walden rule  $\Lambda_0\eta^x = \text{constant}$ , where  $x$  is always less than unity and with a best result of  $x \approx 0.7$ .

For the ethane-1,2-diol ( $x_1 = 0.0000$ ) the best value was  $x = 0.689$ . For  $x_1 = 1.0000$ , 0.8848, and 0.7734, the optimized values of  $x$  were 1.066, 1.175, and 1.335, respectively (Table VII). For pure  $N,N$ -dimethylformamide,  $x \approx 1$ , confirming the validity of the Walden rule; for  $x_1 = 0.8848$  and 0.7734, the exponents greater than unity may be attributable to a greater weight of the viscosity term in the rule. A possible explanation could be related to negative deviations in the rehocor compared to the pure solvents ( $\beta$ ). An  $x$  exponent greater than unity in the modified Walden rule corrects for the negative deviations with temperature for the viscous properties of the binary solvent systems.

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**Supplementary Material Available:** Tables of molar concentrations and molar conductances of picric acid solutions in *N,N*-dimethylformamide, *N,N*-dimethylformamide + ethane-1,2-diol, and ethane-1,2-diol (4 pages). Ordering information is given on any current masthead page.

## Thermochemistry of Inorganic Solids. 10. Empirical Relations between the Enthalpies of Formation of Solid Halides and the Corresponding Gas-Phase Halide Anions

Mohamed W. M. Hisham<sup>†</sup> and Sidney W. Benson\*

Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Equation 4,  $\Delta(\text{MX}_n) = a\Delta(\text{M}'\text{X}_n) + b$ , where M and M' are two different metals, both with formal valence  $n$ ,  $\Delta(\text{MX}_n)$  is defined by eq 3,  $\Delta(\text{MX}_n) = \Delta_f H^\circ(\text{MX}_n, \text{cr}) - \Delta_f H^\circ(\text{X}^-, \text{g})$ , and for a selected pair of metals, M and M', X can be any of the halogens, has been found to correlate the standard enthalpies of formation,  $\Delta_f H^\circ$ , at 298 K for any solid halides with the corresponding gas-phase halide ions. While values of  $b$  vary over a broad range, values of  $a$  are usually close to unity. The deviations from these relations are always within the claimed accuracy of the  $\Delta_f H^\circ$  reported. For 40 monovalent halides, the average deviation is 0.7 kcal/mol with a maximum deviation of 2.0 kcal/mol. For 82 divalent halides, the average deviation is 1.2 kcal/mol with a maximum of 5.0 kcal/mol. For 68 trivalent halides, the average deviation is 2 kcal/mol with a maximum of 6.5 kcal/mol. For 16 tetravalent halides, the average deviation is 0.9 kcal/mol with a maximum of 1.8 kcal/mol. For six pentavalent halides, the average deviation is 0.9 kcal/mol with a maximum of 1.5 kcal/mol.

### Introduction

In a recent paper (1), we have presented evidence that a quantitative, linear relationship exists among the standard enthalpies of formation,  $\Delta_f H^\circ$ , of any three classes of crystalline halides. We have noted that there is no simple relationship between any pair of classes of compounds. However, when the differences in the values of  $\Delta_f H^\circ_{298}$  between two classes of compounds are considered, a two-parameter linear relationship is found.

A typical example is provided by

$$\Delta_f H^\circ(\text{MX}_n) - \Delta_f H^\circ(\text{MY}_n) = a[\Delta_f H^\circ(\text{MZ}_n) - \Delta_f H^\circ(\text{MY}_n)] + b \quad (1)$$

where M is any metal of formal valence  $n$  in a group of the

periodic table. Such relations lead to equations of the form  $\Delta_f H^\circ(\text{MX}_n) = a\Delta_f H^\circ(\text{MZ}_n) - (a-1)\Delta_f H^\circ(\text{MY}_n) + b$  (2)

When the values of  $a$  and  $b$  are known for a particular group of metals, then it is possible to estimate  $\Delta_f H^\circ(\text{MX}_n)$  for unknown members of the class. Using oxides and chlorides of metals as prime data, it is now possible to estimate  $\Delta_f H^\circ$  for almost all crystalline salts (4).

An examination of the available data on the halides of various metals with  $\Delta_f H^\circ_{298}$  of the corresponding gas-phase halide ion reveals another quantitative relation which can also be expressed by a set of two-parameter linear equations. Unless otherwise stated, thermochemical data used here are taken from National Bureau of Standards (NBS) tables (2), and values are given for  $\Delta_f H^\circ_{298}$  per mole of metal atom and at 298 K in kilocalories.

We define  $\Delta(\text{MX}_n)$  for a metal M with valence  $n$  by following eq 3. X (F, Cl, Br, or I) is a halide atom, M is a metal atom, and  $n$  is its valence state.  $\Delta_f H^\circ(\text{MX}_n, \text{cr})$  is the enthalpy of formation of solid metal halide  $\text{MX}_n$ , and  $\Delta_f H^\circ(\text{X}^-, \text{g})$  is the enthalpy of formation of the corresponding gas-phase monovalent halogen anion. The latter are known accurately.

$$\Delta(\text{MX}_n) = \Delta_f H^\circ(\text{MX}_n, \text{cr}) - \Delta_f H^\circ(\text{X}^-, \text{g}) \quad (3)$$

The values used for  $\Delta(\text{MX}_n)$  where the data for at least three halides are available for a metal M with a valence  $n$  are listed in Table I. It is interesting to note that, for any given valence state  $n$  from 1 to 5, the values of  $\Delta(\text{MX}_n)$  for any two metals within that particular valence group are linearly related, and the relation is given by the following two-parameter, linear equation (eq 4).

$$\Delta(\text{MX}_n) = a\Delta(\text{M}'\text{X}_n) + b \quad (4)$$

For monovalent ( $n = 1$ ) halides, we have chosen to relate all metal halides to the halides of sodium. The typical plots obtained for some metals to illustrate the relations are shown in Figure 1, and the values for coefficients  $a$  and  $b$  obtained in eq 4 for the metals examined are summarized in Table II. The comparison between the calculated values using eq 4 and the

<sup>†</sup> Present address: Occidental Chemical Corp., 2801 Long Rd, Grand Island, NY 14072.