

The benzene-chloroform-methanol-methyl acetate system at 1-atm. pressure does not contain a quaternary azeotrope. The Wilson equation predicts the quaternary vapor mole fractions and bubble-point temperatures with an average error of $\Delta y_{av} = \pm 0.005$ and $\Delta T_{av} = \pm 0.25^\circ\text{C}$., respectively. In the benzene-chloroform-methanol-methyl acetate-acetone quinary system at 1 atm., the average calculation errors were $\Delta y_{av} = \pm 0.006$ and $\Delta T_{av} = \pm 0.39^\circ\text{C}$.

These results indicate that the Wilson equation yields sufficient accuracy on multicomponent systems containing mixed positive and negative deviations using only binary parameters for practical application in design of separation process equipment. The average vapor composition errors are only slightly larger than the inherent analytical uncertainty. Such accuracy is obtained in spite of the assumption of vapor phase ideality. Since some components used in this work may associate in the vapor phase (i.e., chloroform-acetone), the assumption is arduously tested. The results indicate that little accuracy may be gained in systems up to 1-atm. pressure from the laborious calculations required to obtain vapor phase fugacity coefficients.

NOMENCLATURE

- β = minimization function
 k = number of components in the system
 n = number of data points
 P = pressure, mm. of Hg
 P_i^* = vapor pressure of component i , mm. of Hg
 R = gas constant, cal./gram mole, $^\circ\text{K}$.
 T = temperature, $^\circ\text{K}$.
 t = temperature, $^\circ\text{C}$.
 v_i = molar volume of component i , cc./gram mole
 x_i = liquid mole fraction of component i
 y_i = vapor mole fraction of component i
 γ_i = liquid phase activity coefficient of component i
 $(\lambda_{ij} - \lambda_{ji})$ = Wilson parameters, cal./gram mole

LITERATURE CITED

- (1) Amer, H.H., Paxton, R.R., Van Winkle, M., *Ind. Eng. Chem.* **48**, 142 (1956).
- (2) Belknap, R.C., Weber, J.H., *J. CHEM. ENG. DATA* **6**, 485 (1961).
- (3) Bushmakina, Y.N., Kish, Y.N., *Zh. Prikl. Khim.* **30**, 200 (1957).
- (4) Driesbach, R.R., *Advan. Chem. Ser.* **15**, 11 (1955).
- (5) Driesbach, R.R., Martin, R.A., *Ind. Eng. Chem.* **41**, 2875 (1949).
- (6) Free, K.W., Hutchinson, H.P., *J. CHEM. ENG. DATA* **4**, 193 (1959).
- (7) Fritzweiler, R., Dietrich, K.R., *Angew. Chem.* **46**, 2347 (1933).
- (8) Holmes, M.J., M.S. thesis, The University of Texas, Austin, Tex., 1969.
- (9) Kaes, G.L., Weber, J.H., *J. CHEM. ENG. DATA* **7**, 345 (1962).
- (10) Karr, A.E., Scheibel, E.G., Towers, W.H., Othmers, D.F., *Ind. Eng. Chem.* **43**, 961 (1951).
- (11) Nagata, I., *J. CHEM. ENG. DATA*, **1**, 360 (1962).
- (12) *Ibid.*, **7**, 367 (1962).
- (13) Nagata, I., *Mem. Fac. Tech., Kanazawa Univ.* **3**, 1 (1963).
- (14) Neretniek, I., *Ind. Eng. Chem., Process Design Develop.* **7**, 335 (1968).
- (15) Ocón, J., Espantoso, J., *An. Real Soc. Espan. Fis. Quim.* **54B**, 421 (1958).
- (16) Orye, R.V., Prausnitz, J.M., *Ind. Eng. Chem.* **57**, 18 (1965).
- (17) Sinor, J.E., Weber, J.H., *J. CHEM. ENG. DATA* **5**, 243 (1960).
- (18) Stephenson, R.W., Ph.D. dissertation, The University of Texas, Austin, Tex., 1962.
- (19) Williams, G.C., Rosenberg, S., Rothenberg, H.A., *Ind. Eng. Chem.* **40**, 1273 (1948).
- (20) Wilson, G.M., *J. Am. Chem. Soc.* **86**, 127 (1964).

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Activity of NaNO_3 in Molten CdCl_2 - NaNO_3 Mixtures

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Freezing point depressions are reported for the system CdCl_2 - NaNO_3 over the range 0 to 0.16 mole fraction of CdCl_2 . The freezing point depression of NaNO_3 indicates that the dominant factor at these temperatures is the presence of the cadmium species, CdCl_4^{2-} , CdCl_2 , and Cd^{2+} .

A FREEZING POINT depression study of the system CdCl_2 - NaNO_3 has been reported by Van Artsdalen (15), and similar studies of CdSO_4 - LiNO_3 and CdF_2 - LiNO_3 have been described by Isbell *et al.* (6). The studies were confined to the region dilute in the cadmium salt, to a maximum concentration of about 0.10 to 0.15*m*. The maximum freezing point depression of the solvent was about 2° to 3.5°K . Assuming dilute solution behavior, the results were taken to indicate that CdSO_4 and CdCl_2 dissociate incompletely into the simple ions, and also form the complexes $\text{Cd}(\text{SO}_4)_2^{2-}$ and CdCl_4^{2-} , while CdF_2 dissociates completely.

The present work extends Van Artsdalen's study to higher concentrations of CdCl_2 for the purpose of determining

if the behavior there is consistent with the concept of incomplete dissociation and complexation, or is better represented by models assuming complete dissociation. This is accomplished by calculating NaNO_3 activity from freezing point depressions to the eutectic composition, 0.95*m* CdCl_2 , and comparing the experimental values with those predicted with models of energy and entropy behavior.

EXPERIMENTAL

Materials. All chemicals were reagent grade, used without further purification. The sodium nitrate was dried and stored in sealed bottles. The freezing point of the sodium nitrate, 579.2°K . [lit., 579.0° (15) and 579.2°K . (7)],

indicated high purity. Cadmium chloride was dried to constant weight at 120°C. and stored in desiccators. Freezing point determination on cadmium chloride could not be made with available equipment. Instead, quantitative determinations of chloride were made to confirm that the stoichiometric composition was correct and that the salt was anhydrous.

Equipment. Freezing points were determined in a borosilicate glass cell approximately 7 inches long \times 1 $\frac{3}{4}$ inches I.D. The stirrer was a borosilicate glass screw-type propeller blade, which operated at a speed, approximately constant, adequate to produce vigorous stirring, both vertically and laterally. The stirrer entered the cell through what has commonly been called a "mercury seal," except that for present use the mercury was replaced by a eutectic mixture of sodium and potassium nitrates. This maintained the system isolated from the atmosphere, but allowed gases expanded during heating to escape the cell. The cell was both heated and cooled sufficiently slowly that passage of air through the seal caused minimal agitation of the seal. The cell was mounted in an electric furnace containing a stainless steel liner to decrease thermal gradients. The cell was placed reproducibly at a depth which provided within it the greatest uniformity of temperature.

The temperature-sensing element was a platinum-platinum, 10% rhodium single-junction thermocouple, which was calibrated shortly before use against an NBS certified standard thermocouple. Reference temperature in thermocouple use was the ice-point. The thermocouple was encased in a thin-wall glass tube inserted into the cell with a standard-taper 10/18 ground glass joint. The encasing tube of the thermocouple was slightly bent to place the tip of the thermocouple approximately $\frac{1}{2}$ inch above the stirrer blade and $\frac{1}{4}$ inch from the stirrer shaft. The output of the thermocouple was nearly balanced with a Leeds and Northrup guarded six-dial potentiometer. The small unbalance was fed through a Leeds and Northrup D.C. microvolt amplifier, and the output of the amplifier was placed on the 5-mv. range of a Sargent Model MR recorder. The potentiometer off-balance was thus amplified by a factor of 200, so that 25 μ v. (2.5°C.) into the amplifier corresponded to 5 mv. (25 cm.) on the recorder. Temperature differences could be measured to the nearest 0.005°C. By the experimental arrangement, cooling curves were traced directly onto the recorder chart paper. The voltage reading from the chart was added to the potentiometer scale reading and the freezing points obtained thereby, as described by Van Artsdalen (15). The temperature-measuring circuitry was guarded and insulated from ground.

Procedure. About 150 grams of previously dried sodium nitrate, weighed to 0.01 gram, was melted and two cooling curves were taken. Following this check of the sodium nitrate, weighed amounts of cadmium chloride, maintained anhydrous, were added in successive increments, and the freezing points determined for each mixture in duplicate. Repeated runs were made with different charges of sodium nitrate; the number of additions of cadmium chloride to achieve a particular concentration had no effect on the measured freezing point. The freezing points were determined from the cooling curves to the nearest 0.01°C. In general, the reproducibility of replicate determinations was within about 0.02°C. for the solutions from which NaNO₃ solid was formed. When CdCl₂ solid was formed, reproducibility was more difficult, and disagreement in replication increased rather monotonically to about 0.5°C. at the highest temperature studied. In no instance was it necessary to carry out successive freezing point measurements because of the slow solution of the added CdCl₂. The efficiency of stirring was clearly adequate.

A uniform cooling rate, reproducible from run to run, was essential to obtain satisfactory freezing points. Therefore, a small fixed heater current was passed through

the furnace for a sufficiently long time prior to freezing to give the desired cooling rate (ca. 0.4° to 0.6°C. per minute). Before cooling was begun, each mixture was maintained several degrees above the freezing point for a time sufficient to achieve temperature uniformity in the cell.

RESULTS

Freezing point depression, θ , vs. the mole fraction of CdCl₂ for the experimentally accessible concentration range is given in Table I. The range is limited because of the thermal decomposition of Cd(NO₃)₂ at mid-concentrations, the volatility of CdCl₂, and mechanical limitations of the glass cell at the higher concentrations of CdCl₂.

For concentrations of CdCl₂ less than that of the eutectic, θ is relative to the experimentally observed thermocouple voltage at the freezing point of pure NaNO₃. Beyond the eutectic, θ is relative to the literature value for the freezing point of pure CdCl₂, 842.1°K. (8). The eutectic reported here is 565.7°K. and 0.0748 mole fraction of CdCl₂. The temperature is from a number of eutectic halts in the cooling curves on both sides of the eutectic, and the composition is by extrapolation of the freezing point depression curves.

For ideal mixtures, freezing point depression is related to the activity, a , of the crystallizing component at the normal freezing point, T_f , of that pure component by the equation (11)

$$\ln(a \cdot a^*) = - \left(\frac{\Delta H_f}{RT_f^2} \right) \theta - \left(\frac{\Delta H_f}{RT_f^2} - \frac{\Delta C_f}{2RT_f^2} \right) \theta^2 - \left(\frac{\Delta H_f}{RT_f^2} - \frac{2\Delta C_f}{3RT_f^2} \right) \theta^3 \quad (1)$$

where

a^* is the activity of the pure component at its normal freezing point

ΔH_f is its molar enthalpy of fusion at T_f

ΔC_f is its molar heat capacity difference between solid and liquid at T_f

The left side of Equation 1 is generally expressed as $\ln a$, due to the assignment of $\ln a^* = 1$. It has been left in the more general form here for reasons described below.

Table I. Freezing Point Depression in the Sodium Nitrate-Cadmium Chloride System

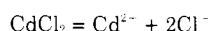
NaNO ₃ as Solid Phase		CdCl ₂ as Solid Phase (?)	
Mole fraction CdCl ₂	θ , °K. ^a	Mole fraction CdCl ₂	θ , °K. ^b
0.00165	0.66	0.07518	274.9
0.00361	1.31	0.08240	269.5
0.00529	1.79	0.09059	265.2
0.00773	2.38	0.1038	258.5
0.00990	2.86	0.1297	247.6
0.01222	3.37	0.1388	244.4
0.01782	4.58	0.1618	234.5
0.02482	5.89		
0.03212	7.22		
0.03685	8.07		
0.04480	9.34		
0.04995	10.02		
0.05714	11.14		
0.06007	11.57		
0.06890	12.66		
0.07104	13.04		
0.07418	13.46		

^a θ relative to experimental melting point of NaNO₃. ^b θ relative to literature value of melting point of CdCl₂, 842.1°K. (8).

Experimental activities of NaNO₃ via Equation 1 are given in Column 2 of Table II for several representative mixtures in the NaNO₃-rich region. Activities of CdCl₂ cannot be reported for this region by the experimental method, of course, and they are also unknown beyond the eutectic because the identity of the solid phase there is unknown. All freezing points have been included in Table I, however, as the system has not previously been described over this total concentration range. For $(a/a^*)_{\text{NaNO}_3}$, the several parameters in Equation 1 are: $\Delta H_f = 3.490$ kcal. per mole, $T_f = 579.2^\circ \text{K.}$, and $\Delta C_f = 1.30$ cal. per deg. mole (7, 12).

Van Artsdalen (15) treated his experimental results with the Raoult-Van't Hoff dilute solution equation to relate θ to the moles of solute particles per kilogram of solvent. This equation assumes a random distribution of solvent particles on particle sites, and a zero enthalpy of mixing. If the solute particles are also assumed to be randomly distributed, this becomes the model of ideal molten salt mixtures proposed by Herasymenko (5). Thus, if the concentrations of the various species present at equilibrium according to Van Artsdalen (15) are calculated, the Herasymenko model may be used to predict the ideal activity for the mixtures.

In the present work it has been assumed that the equilibria involving CdCl₂ vary negligibly with temperature over the range concerned, and that the dissociation constants do not vary with concentration. The latter assumption is, of course, a requirement of an ideal system. For the equilibria, respectively,



and



Van Artsdalen reported (15)

$$K_{20} = 0.0031 \pm 0.0004 \quad \text{and} \quad K_{42} = 0.23 \pm 0.05$$

with the concentrations expressed in moles of particles per kilogram of solvent. It follows that at equilibrium

$$\alpha_4 = \frac{[\text{CdCl}_2^+]}{\text{Total Cd}} = \frac{[\text{CdCl}_2^+]}{[\text{CdCl}_2^+] + [\text{CdCl}_2] + [\text{Cd}^{2+}]} = \frac{[\text{Cl}^-]^4}{[\text{Cl}^-]^4 + K_{42}[\text{Cl}^-]^2 + K_{42}K_{20}}$$

and, similarly, that

$$\alpha_2 = \frac{[\text{CdCl}_2]}{\text{Total Cd}} = \frac{K_{42}[\text{Cl}^-]^2}{[\text{Cl}^-]^4 + K_{42}[\text{Cl}^-]^2 + K_{42}K_{20}}$$

$$\alpha_0 = \frac{[\text{Cd}^{2+}]}{\text{Total Cd}} = \frac{K_{42}K_{20}}{[\text{Cl}^-]^4 + K_{42}[\text{Cl}^-]^2 + K_{42}K_{20}}$$

where α_n is the fraction of the total Cd-containing species present as CdCl_n. These equations for α thus lead to the concentrations of the several species. The values of $(a/a^*)_{\text{NaNO}_3}$ from the random model were then obtained from the Herasymenko form (5)

$$(a/a^*)_{\text{NaNO}_3} = 4 X_{\text{Na}}'' X_{\text{NO}_3}'' \quad (2)$$

where X_j'' is the number fraction of particles of species j ; that is, $N_j/\sum N_j$, summed over all species. The results by this approach are listed in Column 3 of Table II.

If an assumption of total dissociation of CdCl₂ into Cd²⁺ and Cl⁻ is combined with the Herasymenko distribution model, Equation 2 will again express $(a/a^*)_{\text{NaNO}_3}$. The activities calculated with these assumptions are given in Column 4 of Table II.

In the Temkin model, a zero enthalpy of mixing is combined with the concept of anion and cation sites, with each site type available only to ions of that charge type (14). By this model (complete dissociation into simple ions)

$$(a/a^*)_{\text{NaNO}_3} = X_{\text{Na}} X_{\text{NO}_3} \quad (3)$$

where X is the ion fraction

$$X_{\text{Na}} = N_{\text{Na}}/(N_{\text{Na}} + N_{\text{Cd}}) \quad \text{and} \quad X_{\text{Cl}} = N_{\text{Cl}}/(N_{\text{Cl}} + N_{\text{NO}_3})$$

Activities by this model are given in Column 5 of Table II.

Førland (4) has described an extension of the Temkin model for systems containing ions of unlike charge, including effects of charge vacancies. It is possible to treat the charge vacancies by two extreme approaches (4), randomly distributed relative to the ions of double charge or as paired with them. The former leads to

$$(a/a^*)_{\text{NaNO}_3} = X_{\text{Na}}' X_{\text{NO}_3}' \quad (4)$$

and the latter to

$$(a/a^*)_{\text{NaNO}_3} = (X_{\text{Na}}')^2 \exp(X_{\text{Cd}}'/2) \quad (5)$$

where X' is the equivalent ion fraction,

$$X_{\text{Cd}}' = 2N_{\text{Cd}}/(2N_{\text{Cd}} + N_{\text{Na}}) \quad \text{and} \quad X_{\text{NO}_3}' = N_{\text{NO}_3}/(N_{\text{NO}_3} + N_{\text{Cl}})$$

Predicted activities by these last two models are given in, respectively, Columns 6 and 7 of Table II.

Table II. Activity of NaNO₃ as a/a^* in the Cadmium Chloride-Sodium Nitrate System

Mole Fraction CdCl ₂	Exptl. Activity of NaNO ₃	Calculated Activity						
		Partial dissc. of CdCl ₂ , Eq. 2	Ideal behavior				Nonideal behavior, total dissociation	
			Total dissociation					
			Eq. 2	Eq. 3	Eq. 4	Eq. 5	Eq. 9 ^a	Eq. 9 ^b
0.01222	0.982	0.981	0.964	0.964	0.952	0.964	0.962	0.962
0.03212	0.963	0.959	0.907	0.907	0.879	0.907	0.894	0.895
0.04480	0.952	0.945	0.873	0.873	0.836	0.872	0.848	0.850
0.06007	0.940	0.929	0.833	0.833	0.786	0.832	0.792	0.794
0.07418	0.931	0.914	0.797	0.797	0.743	0.796	0.739	0.743

^a Neglecting b terms in Eq. 9. ^b Including b terms in Eq. 9.

All of the above models are related to the calculated activities through

$$a_i/a_i^* = \exp(-\Delta\bar{S}_i/R)$$

in which the relative partial molal entropy is obtained from the assumed distribution of particles. In general, however, the assumption that the enthalpy of mixing—assumed here to be equal to the energy of mixing—is zero is not valid. The nonzero value of the relative partial molal energy, $\Delta\bar{E}_i$, must be included to give

$$a_i/a_i^* = \exp(\Delta\bar{E}_i/RT)\exp(-\Delta\bar{S}_i/R) \quad (6)$$

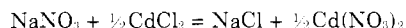
While the energy involved in the mixing will affect the distribution, the magnitude of the energy of mixing is usually such that the effect on the entropy is disregarded and the athermal entropy values are retained.

Assuming an ordered liquid lattice, it is convenient to separate the energy of mixing (ΔE_m) of molten salts into two interactions, nearest-neighbor (ΔE_n) and next-nearest-neighbor (ΔE_{nn})

$$\Delta E_m = \Delta E_n + \Delta E_{nn}$$

The first type of interaction is cation-anion, and the second cation-cation or anion-anion.

Førland has shown (4) that ΔE_n may be considered the energy involved in the exchange of ions between salts. Here this is the change in the reaction



The difference may be approximated using the molar lattice energies at 0° K. (U) of each of the "reactants" and the "products,"

$$\Delta E_n = U_{\text{NaCl}} + \frac{1}{2}U_{\text{Cd}(\text{NO}_3)_2} - U_{\text{NaNO}_3} - \frac{1}{2}U_{\text{CdCl}_2} \quad (7)$$

with $U_{\text{NaCl}} = -183.1$, $U_{\text{Cd}(\text{NO}_3)_2} = -573$, $U_{\text{NaNO}_3} = -173$, and $U_{\text{CdCl}_2} = -584$ kcal. per mole (9, 13, 16).

ΔE_{nn} in a binary system of reciprocal salts may be obtained from mixtures of the four possible binary subsystems, each containing a different one of the four ions in common (4). For the system NaNO_3 - CdCl_2 , the subsystems are NaNO_3 - $\text{Cd}(\text{NO}_3)_2$, NaCl - CdCl_2 , NaCl - NaNO_3 , and CdCl_2 - $\text{Cd}(\text{NO}_3)_2$. Each of the four subsystems characterizes the next-nearest-neighbor interaction with a parameter, b . Thus, b_{NO_3} indicates the interaction between one equivalent of each of sodium and cadmium ions in the presence of nitrate ions—i.e., in the system NaNO_3 - $\text{Cd}(\text{NO}_3)_2$.

Since in ideal behavior the energy of mixing is zero, the energy of mixing is itself an "excess" quantity. If ideal entropy is assumed

$$\Delta\bar{E}_i^* = \Delta\bar{G}_i^* = RT \ln \gamma_i = X_j^2 b_a \quad (8)$$

if ion a is in a mixture of ions j and k , both of charge type opposite to that of ion a . Therefore, a plot of $RT \ln \gamma_i$ as a function of X_j^2 gives b_a as the slope. The phase diagrams of the subsystems necessary for the next-nearest-neighbor calculations have been obtained from the literature (10). The values of the b 's are as follows: b_{NO_3} (-2.77), b_{Cl} (+1.92), b_{Na} (+1.06), and b_{Cd} (-1.54 kcal. per equivalent). The value of b_{Cd} has been approximated by b_{Ca} because the phase diagram of the $\text{Cd}(\text{NO}_3)_2$ - CdCl_2 system is unknown. The system $\text{Ca}(\text{NO}_3)_2$ - CaCl_2 has been substituted because of the similarity of both size and charge for the two cations.

Following Bloom and Welch (3), when ΔE_m , with the appropriate terms in ΔE_n and ΔE_{nn} , is incorporated into Equation 6, the result is

$$(a/a^*)_{\text{NaNO}_3} = \exp[X_{\text{Cd}}X_{\text{Cl}}\Delta E_n + X_{\text{Cd}}^2(X_{\text{NO}_3}b_{\text{NO}_3} + X_{\text{Cl}}b_{\text{Cl}}) + X_{\text{Cl}}^2(X_{\text{Na}}b_{\text{Na}} + X_{\text{Cd}}b_{\text{Cd}}) - T\Delta\bar{S}_{\text{NaNO}_3}/RT] \quad (9)$$

if the Temkin entropy model is assumed. Only this form of Equation 6 will be considered here. In Equation 9, the term in ΔE_n is $\Delta(\bar{E}_n)_{\text{NaNO}_3}$ and the terms in b constitute $\Delta(\bar{E}_{nn})_{\text{NaNO}_3}$. If the terms in $\Delta(\bar{E}_{nn})_{\text{NaNO}_3}$ are neglected, the predicted activity is given in Column 7 of Table II. If they are included, the values in Column 8 are obtained.

DISCUSSION

Present freezing point depressions are in good agreement with those of Van Artsdalen (15) over the limited range of concentrations he reported. His eutectic temperature of 565–6° K. brackets the present 565.7° K., but the present eutectic composition of 7.48 mole % is 1.0 mole % lower. In this work, the eutectic has been bracketed quite closely with experimental points, and 7.51 mole % is clearly beyond the eutectic.

The temperature of the eutectic halt is the same on both sides of the eutectic, indicating the absence of solid solutions over the region of the system studied. NaNO_3 is clearly the solid phase formed on the one side of the eutectic, but on the other side the solid phase cannot be fixed because of the limited range of the study. It was confirmed experimentally, however, that over the concentration range reported, both thermal decomposition and sample loss due to CdCl_2 volatility were negligible.

Activities have been reported here consistently as a/a^* to provide a common basis for comparison. This need arises because in the Herasymenko model, the activity of a pure totally ionized salt is not unity. Thus, it is 1/4 for NaNO_3 and 4/27 for CdCl_2 because the pure salts, themselves, by this model represent a number of complexions greater than unity. For the other models, where activity of the pure salt is unity, a/a^* and a are, of course, identical.

For NaNO_3 , all models assuming total dissociation with zero heat of mixing predict rather similar activities because of the brief concentration range to the eutectic. When, with the Temkin model, enthalpy effects are included, the result is a decrease in the predicted activity. The enthalpy corrections for nearest- and next-nearest-neighbors are of opposite sign, and the former is the more significant. The experimental activities are significantly greater than any of the predicted values which assume total dissociation. The dominant effect thus appears to be the chemical equilibria involving CdCl_2 . Agreement between experimental activities of NaNO_3 and values predicted with a random ideal model for the species proposed by Van Artsdalen (15) is quite good, and the extent of the disagreement may arise from the neglect of temperature effects on the equilibrium constants. This refinement would lessen the disagreement. Van Artsdalen (15) has noted that in passing from NaNO_3 to KNO_3 as solvent, corresponding to an increase of 20° to 30° in temperatures, there is a slight drop in the degree of association and complexing. Bloom and Welch (2) interpreted their results in the system CdCl_2 - Na_2SO_4 at 1003° K. with the assumption of total dissociation of CdCl_2 into Cd^{2+} and Cl^- .

There is valid criticism of the random model, in that it allows a relatively large number of nearest neighbors of like charge and, therefore, an energetically objectionable configuration. Nevertheless this aspect appears not to be the dominant one in this system. That is, the entropy effect associated with particle numbers is of greater significance than that of the distribution of the particles in the liquid lattice.

The assumption that $\Delta E_n = \Delta U$ in Equation 7 is of unknown accuracy, and there is some uncertainty in ΔU itself because U of CdCl_2 is not well known. The two reported values for CdCl_2 are -534 (1) and -584 kcal. per mole (16). The latter value was used in this work because that worker also reported the value used here for

$\text{Cd}(\text{NO}_3)_2$, and greater consistency of results was thereby expected. The sign of the difference of the lattice energies would not be changed by substituting the other value for CdCl_2 into Equation 7. That is, in both instances, a negative correction for nearest-neighbor interaction is obtained.

The data for the b values of Equation 8 were obtained from phase diagrams in the literature containing quite large uncertainties. Because of the small effect of ΔE_{nn} , however, this uncertainty is not important.

NOMENCLATURE

ΔC_f	= molar heat capacity difference between solid and liquid at normal freezing point, cal. per deg. mole
ΔE	= molar energy of mixing, cal. per mole
$\Delta \bar{E}$	= molar partial energy of mixing, cal. per mole
$\Delta \bar{G}$	= molar partial Gibbs free energy of mixing, cal. per mole
ΔH_f	= molar enthalpy of fusion at the normal freezing point, cal. per mole
K	= equilibrium constant
N	= number of particles
$\Delta \bar{S}$	= molar partial entropy of mixing, cal. per deg. mole
T	= temperature, °K.
T_f	= normal freezing point, °K.
R	= molar gas constant, cal. per deg. mole
U	= molar lattice energy at 0° K., cal. per mole
X	= ion fraction
X'	= equivalent ion fraction
X''	= number fraction of particles
a	= activity
a^*	= activity of pure component at its normal freezing point
b	= interaction parameter for next-nearest-neighbors, cal. per mole
α	= fraction of total Cd-containing species
γ	= activity coefficient
θ	= freezing point depression, °K.

Superscripts

xs = excess; that is, exptl. – ideal

Subscripts

f	= fusion
m	= mixing
n	= nearest-neighbor
nn	= next-nearest-neighbor
a, i, j, k	= generalized species

LITERATURE CITED

- (1) Balsonov, S.S., Gorogotskaya, L.I., *Izv. Vysshikh. Uchebn. Zavedenii, Khim. Khim. Tekhnol.* **2**, 858 (1959); *CA* **54**, 10444h (1958).
- (2) Bloom, H., Welch, B.J., *Trans. Faraday Soc.* **57**, 61 (1961).
- (3) Bloom, H., Welch, B.J., *Discussions Faraday Soc.* **32**, 115 (1962).
- (4) Förland, T., *Norg. Tek. Vitenskapskad. Ser. 2*, No. 4 (1957).
- (5) Herasymenko, P., *Trans. Faraday Soc.* **34**, 1245 (1938).
- (6) Isbell, R.E., Wilson, E.W., Jr., Smith, D.F., *J. Phys. Chem.* **70**, 2493 (1966).
- (7) Kelley, K.K., *U. S. Bur. Mines Bull.* **393**, 113 (1936); **476**, 31 (1949).
- (8) Kelley, K.K., *Ibid.*, **584**, 35 (1960).
- (9) Ladd, M.F.C., Lee, W.H., *J. Inorg. Nucl. Chem.* **13**, 218 (1960).
- (10) Levin, E.M., Robbins, C.R., McMurdie, H.F., "Phase Diagrams for Ceramists," Figs. 1212, 1371; Part II, 1964, Fig. 1763, American Ceramic Society, Columbus, Ohio, 1959.
- (11) Lewis, G.N., Randall, M., "Thermodynamics," 2nd ed., Ch. 26, revised by K.S. Pitzer, L. Brewer, McGraw-Hill, New York, 1961.
- (12) *Natl. Bur. Std. (U. S.), Circ. C-500*, 191, 462 (1950).
- (13) Partington, J.R., "An Advanced Treatise on Physical Chemistry," Vol. III, p. 385, Longmans, Green, New York, 1952.
- (14) Temkin, M., *Acta Physicochem. U.R.S.S.* **20**, 411 (1945).
- (15) Van Artsdalen, E.R., *J. Phys. Chem.* **60**, 172 (1956).
- (16) Yatsimirskii, K.B., *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.* **1948**, p. 590; *CA* **43**, 2829f (1949).

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Correlation of Thermodynamic Properties of Chloromethanes

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A correlation for entropy and enthalpy based on the two-parameter law of corresponding states and the reference substance concept has been obtained. For 199 points tested, the over-all average absolute deviation and the maximum deviations in the calculated values of entropy with the available data are 0.74 and 7.20%. The corresponding deviations of enthalpy are 1.86 and 15.0%, respectively. A compressibility chart for chloromethanes has been made and shown to be superior to existing charts. For 102 points tested, the average absolute and maximum deviations in the compressibilities were 1.80 and 19.5%, respectively.

THE pressure-volume-temperature (PVT) properties of a substance are very useful for purposes of design and are frequently used. The substances used in engineering practice include those for which the PVT data are entirely nonexistent. A generalized compressibility chart is useful in filling such a need.

An equation of state, theoretical or empirical, is advantageous mainly because it condenses the PVT data to a large extent, interpolation and possibly extrapolation are more accurate, and partial derivatives which are used in the calculation of thermodynamic properties can be calculated easily and accurately.

An equation of state such as those of Beattie-Bridgeman and Benedict-Webb-Rubin, especially the latter, represents PVT data fairly accurately up to about 1.5 times the critical density.

However, the PVT data needed for the evaluation of the constants are lacking for many substances. In such cases a generalized chart is useful, as it can predict data for all substances fairly accurately.

All the generalized charts are based on the principle of corresponding states formulated by van der Waals (27), that at the same reduced conditions of temperature and pressure, all substances manifest the same reduced volume.