[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

# Heats of Solution of the Cobaltous Nitrate Hydrates in Water and in Certain Organic Solvents and Binding Energies of Molecular Ligands[1a]

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Heats of solution have been measured for the hexahydrate, tetrahydrate, trihydrate and dihydrate of cobaltous nitrate in water and in a series of organic solvents, including isobutyl alcohol, diethyl and monoethyl ether of ethylene glycol, acetone, methyl ethyl ketone, tetrahydrofuran, tributyl phosphate and dimethylformamide. For some solvents, where the solubility of the salt or its reaction product was insufficient, measurements were made in admixture with acetone. Such solvents include diethyl ether, tetrahydrofurfuryl alcohol and pyridine. Measurements were also made with mixtures of the other solvents cited and acetone. In the cases of pyridine, water, tetrahydrofurfuryl alcohol and isobutyl alcohol, evidence is found for a transition from a probably tetrasolvated neutral molecule in solution to a hexasolvated entity, frequently of lowered solubility. The solvents can be arrayed in order of base strengths on the basis of the heat measurements, and it is possible to estimate energies of binding of solvent groups by the metal atom. As a check on these, some measurements of the heats of solution of some cobaltous nitrate pyridinates are also presented.

With the accumulation of evidence that a number of inorganic salts may be as soluble in organic solvents of the types alcohols, ethers, ketones and esters[1–3] as they are in water, the way is open to studying these systems to establish the nature of the interactions between solute and solvent in essentially non-ionizing media. In special cases it has been possible to obtain information on molecular and ionic interactions from spectrophotometric investigation.[4–7] A start toward obtaining data on the energetics of the interactions has been made by measurements of the heats of solution for the uranyl nitrate hydrates in a series of solvents[8]; this is being continued by similar measurements with the hydrates of cobaltous nitrate, to be reported in this paper.

## Experimental

The procedures used in the heat of solution determinations were those used in the prior work on uranyl nitrate[8]: a weighed portion of salt was dissolved in 200 ml. of solvent contained in a dewar flask. Temperatures were followed with a calibrated Beckmann thermometer. Heat capacities were determined through electrical heating with a calibrated nichrome heater. Salt-to-solvent mole ratio in water was 1:180, and in the organic solvents about 1:80.

The cobaltous nitrate hydrates were prepared from commercial chemically pure salt by recrystallization of the hexahydrate, and dehydration of the hexahydrate to the lower hydrates. The crystals of hexahydrate were analyzed, ground in a ball mill and reanalyzed, and then maintained in a closed vessel. In some cases, lower hydrates were prepared by desiccation of the hexahydrate over sulfuric acid; in others, tetrahydrate and trihydrate were prepared by melting the higher hydrates and removing water under vacuum at temperatures below the melting point of the desired hydrate. Composition of final products was always checked by analysis at time of heat measurements.

Water contents of the salts and of the solvents were checked by Karl Fischer titration. The commercial pure solvents were desiccated before use. Cobalt analyses were performed by a standard electrodeposition procedure. With agreement between duplicate cobalt analyses of 0.6–0.9 part in 100, and in water analyses of 0.5–1 part per 100, it is estimated that 5 mole % of another hydrate might be overlooked in one of the lower hydrates, and 2 mole % in the hexahydrate. These might produce an error of 0.03 kcal./mole in a single heat determination with the hexahydrate, and 0.2 kcal./mole for one of the lower hydrates. Duplicate heat determinations generally checked at least this well. Calculation of the heat for the transition

$$Co(NO_3)_2 \cdot 6H_2O(c) = Co(NO_3)_2 \cdot 2H_2O(c) + 4H_2O(l)$$

from the heats of solution of hexahydrate and dihydrate (Table I) and the values in the third column of Table III gave heats (with the exception of tetrahydrofuran) ranging from 0.72 kcal. greater than the 10.24 kcal. value of the heats of solution in water to 0.77 kcal. less than this value, with a mean of 0.55 kcal. This is perhaps a little greater variation than might be expected, even though three experimental heats (one multiplied by 4) are involved, and may indicate the intrusion of some relatively slow reaction (hydrolysis, or reaction between nitrate and the organic solvent) between salt and solvent. In the case of uranyl nitrate,[8] where the chances of reaction are more apparent (more ready hydrolysis, possible reduction of U(VI) to U(IV)), the corresponding variation is larger, and in the case of cobaltous chloride (unpublished data), with smaller reaction possibility, somewhat smaller. The aberrant tetrahydrofuran value has no ready explanation.

**Heats of Solution.**—The results of measurements with the solvents water, dimethyl formamide, mono- and diethyl ether of ethylene glycol, tetrahydrofuran, tributyl phosphate, acetone, methyl ethyl ketone and isobutyl alcohol are given in Table I. Tests were also made with methyl isobutyl ketone, tetrahydrofurfuryl alcohol, diethyl ether and ethyl propionate, but the solubilities in the pure solvents were too limited for satisfactory measurement. In a few cases, heats of solution could be calculated, when solution of the salt sample was sufficiently complete, by analyzing the liquid phase. This procedure gave −9.54 kcal./mole for the dihydrate in tetrahydrofurfuryl alcohol, and

TABLE I

HEATS OF SOLUTION OF THE COBALTOUS NITRATE HYDRATES IN WATER AND IN VARIOUS ORGANIC SOLVENTS (KCAL./MOLE)

| Solute solvent | Co-$(NO_3)_2 \cdot$$2H_2O$ | Co-$(NO_3)_2 \cdot$$3H_2O$ | Co-$(NO_3)_2 \cdot$$4H_2O$ | Co-$(NO_3)_2 \cdot$$6H_2O$ |
|---|---|---|---|---|
| Water | −5.28 | −0.98 | 3.50 | 4.96[a] |
| Monoethyl ether of ethylene glycol | −6.56 | −2.52 | −1.24 | 0.25 |
| Isobutyl alcohol | −1.28 | 4.85 | 6.84 | 8.77 |
| Diethyl ether of ethylene glycol | −4.89 | 0.94 | 3.73 | 4.90[b] |
| Tetrahydrofuran | −4.30 | −0.62 | 3.24 | 4.26 |
| Acetone | −1.65 | 4.28 | 6.82 | 7.79 |
| Methyl ethyl ketone | 0.30 | 6.03 | 8.44 | 10.12 |
| Tributyl phosphate | −4.74 | 0.99 | 2.15 | 5.18 |
| Dimethyl formamide | −17.76 | −15.44 | −12.76 | −11.99 |

[a] Thomsen, "Thermochemischen Untersuchungen," also gives 4.96, according to reference 16. [b] Calculated from solution analysis; solid incompletely dissolved.

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(1a) Presented in part at Cleveland Meeting, American Chemical Society, April 9–12, 1951.

(1) L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

(2) L. I. Katzin and J. R. Ferraro, THIS JOURNAL, **72**, 5451 (1950).

(3) L. I. Katzin and J. R. Ferraro, *ibid.*, **74**, 2752 (1952).

(4) L. I. Katzin and E. Gebert, *ibid.*, **72**, 5455 (1950).

(5) L. I. Katzin and E. Gebert, *ibid.*, **72**, 5464 (1950).

(6) L. I. Katzin and E. Gebert, *ibid.*, **72**, 5659 (1950).

(7) L. Kaplan, R. A. Hildebrandt and M. Ader, Reports ANL-4520, 4521 (unclassified), (1950); AECD Nos. 2920, 3015.

(8) L. I. Katzin, D. M. Simon and J. R. Ferraro, THIS JOURNAL, **74**, 1191 (1952).

5.52 kcal. and −2.28 kcal., respectively, for the trihydrate and dihydrate in methyl isobutyl ketone. Though they seem reasonable as to order of magnitude, these values must be regarded with caution since there is reason to believe that the solid phase in contact with the solution was not of the same composition as that originally added.

Previous experience with salt–water–organic solvent systems[1–3] suggested that insolubility in the solvents indicated was probably related to hexasolvate formation, either with the solvent, water or both. Dilution of the solvent to be tested with a weak base solvent in which water is highly soluble (*e.g.*, acetone) might be expected to give better solubilities. The expectations were realized, and measurements were made with cobaltous nitrate dihydrate and a series of mixtures of other solvents with acetone. The results, in terms of volume %, are shown in Table II, and in mole % are plotted in Fig. 1.

TABLE II

HEATS OF SOLUTION OF COBALTOUS NITRATE DIHYDRATE IN MIXTURES OF ACETONE WITH OTHER SOLVENTS (KCAL./MOLE)

| Second solvent | Vol. % | $\Delta H$ | Second solvent | Vol. % | $\Delta H$ |
|---|---|---|---|---|---|
| Water | 0.3 | −1.65 | Pyridine[a] | 2[b] | − 9.51 |
| | 1.3 | −4.42 | | 2 | −14.39 |
| | 2.9 | −8.54 | | 12.5 | −16.31 |
| | 5.6 | −11.42 | | 25 | −17.61 |
| | 13.1 | −13.46 | | 30 | −17.73 |
| | 20.5 | −11.57 | | 37.5 | [c] |
| Isobutyl alcohol | 25 | −4.20 | Dimethyl formamide | 25 | −9.35 |
| | 50 | −3.90 | | 50 | −12.92 |
| | 75 | −3.70 | | 75 | −15.54 |
| | 87.5 | −3.04 | Ethylene glycol monoethyl ether | 25 | −4.14 |
| Tributyl phosphate | 25 | −1.79 | | 50 | −5.60 |
| | 50 | −2.00 | | 75 | −6.00 |
| | 75 | −3.31 | Tetrahydrofurfuryl alcohol | 25 | −6.18 |
| | 95 | −4.26 | | 50 | −8.19 |
| Tetrahydrofuran | 5 | −2.19 | | 75 | −8.91 |
| | 50 | −3.75 | Diethyl ether | 25 | −2.10 |
| | 87.5 | −4.23 | | 50 | [d] |
| Ethylene glycol diethyl ether | 25 | −2.40 | | | |
| | 50 | −3.07 | | | |
| | 75 | −3.49 | | | |

[a] Salt:solvent = 1:200 instead of 1:80. [b] Salt:solvent = 1:100. [c] $Co(NO_3)_2 \cdot 6Py$ precipitates. [d] Incomplete solubility or precipitate formed.

It had been shown, in earlier experiments with uranyl nitrate,[3] that the heat of reaction of water with a lower hydrate (*e.g.*, the dihydrate) in an organic solvent afforded a measure of the order of base strengths of the solvents so tested. The results of a similar series of measurements for solutions of cobalt nitrate dihydrate in organic solvents are shown in Table III.

TABLE III

HEAT OF REACTION OF WATER WITH COBALTOUS NITRATE DIHYDRATE IN VARIOUS SOLVENTS

| Solvent | $\Delta H$, water to pure solvent (kcal./mole water) | $\Delta H$, water to dihydrate soln. (kcal./mole water) | Mole ratio, water/salt | Heat effect, (kcal./mole salt) |
|---|---|---|---|---|
| Dimethyl formamide | −0.74 | −0.96 | 4.0 | 0.87 |
| Tributyl phosphate | .14 | − .26 | 4.3 | 1.7 |
| Tetrahydrofuran | .51 | − .10 | 4.0 | 2.44 |
| Isobutyl alcohol | .70 | .00 | 4.0 | 2.75 |
| Diethyl ether of ethylene glycol | .80 | .08 | 4.0 | 2.89 |
| Monoethyl ether of ethylene glycol | − .23 | − .94 | 4.3 | 3.04 |
| Acetone | .79 | − .06 | 4.1 | 3.57 |
| Methyl ethyl ketone | 1.09 | .07 | 4.0 | 4.04 |

**Apparent Heat Capacities of Solutes.**—As in the case of the uranyl nitrate experiments, approximate heat capacity measurements for the various solutes appear as a by-product of the heat of solution measurements. The values are appreciably more regular than in the case of the uranyl nitrate salts, and are shown in Table IV. These are rounded values (usually to the nearest multiple of 5) of averages of two determinations, only 5 pairs out of 22 showing a difference greater than 30 cal./mole/deg., and over half differing by less than 20 cal./mole/deg. In most cases there is little difference between the values for the trihydrate and the tetrahydrate as the solute, and in some cases this may be extended to include the dihydrate. The apparent heat capacity of $Co(NO_3)_2 \cdot 6H_2O$ in water is about 190 cal./mole deg.

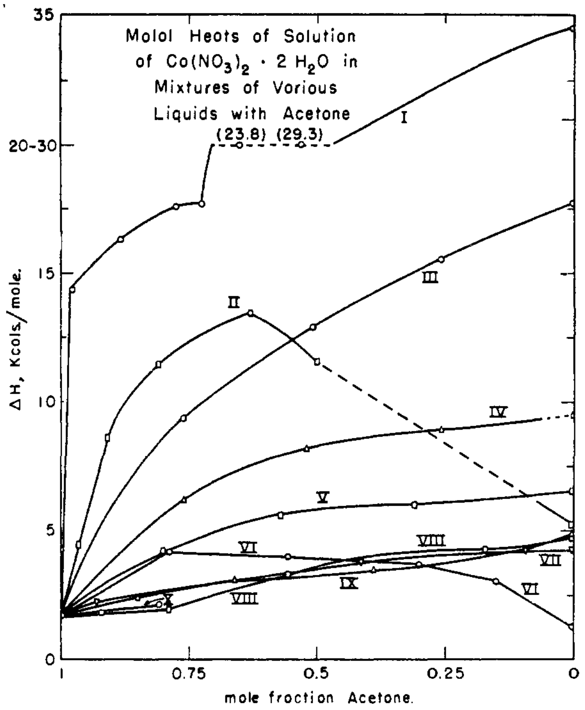

Fig. 1.—Heats of solution of cobaltous nitrate dihydrate in mixtures of various solvents with water: I, pyridine; II, water; III, dimethyl formamide; IV, tetrahydrofurfuryl alcohol; V, ethylene glycol monoethyl ether; VI, isobutyl alcohol; VII, tetrahydrofuran; VIII, tributyl phosphate; IX, ethylene glycol diethyl ether; X, diethyl ether.

TABLE IV

APPARENT HEAT CAPACITIES OF COBALTOUS NITRATE HYDRATES IN VARIOUS SOLVENTS (CALORIES/MOLE DEG.)[a]

| | Dihydrate | Trihydrate | Tetrahydrate | Hexahydrate |
|---|---|---|---|---|
| Tetrahydrofuran | 65 | 260 | 280 | 290 |
| Diethyl ether of ethylene glycol | 155 | 350 | 570 | (760) |
| Monoethyl ether of ethylene glycol | 397 | 440 | 475 | 710 |
| Isobutyl alcohol | (200) | 205 | 235 | 315 |
| Methyl ethyl ketone | 75 | 120 | 170 | 330 |
| Acetone | 165 | 185 | 189 | 220 |

[a] Rounded to nearest 5 calories. Values in parentheses are estimated from single experiments.

## Discussion

As in the case of uranyl nitrate dihydrate in the organic solvents,[3] the order of heats of solution approximates the ordering of the solvents by base strengths, with isobutyl alcohol out of line in appearing to be a weaker base than it should.

Again, in complete parallel to the prior case, dilution of the alcohol with the weaker base, acetone, shows that the formation of hexasolvate is probably a factor in the discrepancy (Table II, Fig. 1).

Another confirmation of the ordering of base strengths of the solvents is given in the curves of Fig. 1. Here the heat effect of the lowest concentration of added base in admixture with acetone determines the early slope of the curve, and it is seen that in decreasing order of slope the curves are those of pyridine, water, dimethyl formamide, tetrahydrofurfuryl alcohol, monoethyl ether of ethylene glycol and isobutyl alcohol, tetrahydrofuran, diethyl ether of ethylene glycol, diethyl ether and tributyl phosphate.

Evidences of the transition from tetrasolvated solute of the type ($Co(NO_3)_2Solv_4$) to the ionized (but not necessarily dissociated) form $(CoSolv_6)^{++}$-$(NO_3)_2^-$ are of two types. In the cases of water and isobutyl alcohol, it is shown by the initial rise from the heat of solution in pure acetone, with increasing water or alcohol concentration, until a maximum is reached, beyond which the heat of solution falls off with increasing water (or alcohol) concentration. This, as discussed in a previous case,[3] is ascribed to the endothermic dissociation process having a larger numerical value than the exothermic solvent association process. The region of the maximum heat value (10–20% water by volume) coincides satisfactorily with the region of spectrophotometrically determined transition[4] between hexahydrated and tetrahydrated solute. A similar incipient heat maximum is obscured, in the case of pyridine, by the heat of precipitation of solid cobaltous nitrate hexapyridine. The latter process itself serves as indicator of the transition.

The formation of a solid on dissolving cobalt nitrate dihydrate in pure tetrahydrofurfuryl alcohol, and its failure to appear in the mixture of 75% alcohol and 25% acetone may indicate that here too hexasolvate is forming.[2] In the case of diethyl ether, clean solution occurs with 25% by volume of ether, and a solid phase is left at 50% by volume. It is not known whether this solid phase is the originally added hydrate or contains another phase.

**Relative Binding Energies of Molecular Addenda.**—Since the solution of a salt such as cobaltous nitrate or uranyl nitrate in an organic solvent contains largely neutral entities which can be designated $MX_2 \cdot 4Solv$, solution of cobaltous nitrate dihydrate in a weak base solvent should yield species which are largely $Co(NO_3)_2 \cdot 2H_2O \cdot 2Solv$. The difference in the heat of solution of the dihydrate in two solvents is then a measure of the difference in the energies with which two groups of each solvent are bound. For illustration, consider a process of vaporizing the starting solid dihydrate to the ion gas, vaporizing two equivalents of the solvent, and allowing the latter to react with the gaseous cation; then allow the cations and anions to associate to a molecular gas, and dissolve the gas in the solvent. The net thermal equation for the solution process appears as

$$MX_2 \cdot 2H_2O(c) + 2S(l) = MX_2 \cdot 2H_2O \cdot 2Solv(soln.) + U + 2H_v - 2E - H_d + H_s \quad (1)$$

with the sum of the energy terms at the right equal to the heat of solution, $\Delta H$. The symbols represent the lattice energy of the solid ($U$), the heat of vaporization of S ($H_v$), the heat of association of the ionic to the molecular gas ($H_d$) and its heat of solution ($H_s$). The binding energy, $E$, is defined as the energy necessary to dissociate the gaseous cation and the bound S. To the extent it is true that $H_d$ is a function only of M and X, for the case under consideration, and that $H_s$ does not vary significantly with S under the situation postulated, the difference in binding energy per mole for two solvents can be represented by

$$E_{S_1} - E_{S_2} = H_{v(S_1)} - H_{v(S_2)} - {}^1/_2(\Delta H_1 - \Delta H_2) \quad (2)$$

which, when one removes the heat of vaporization terms by referring to the liquid rather than the gaseous state of the solvent bound becomes the relation stated above. The assumption about $H_d$ while plausible is not immediately open to test. The assumption about $H_s$ represents an extrapolation of the generalization that heats of solution of molecular substances are generally small, and in particular that the heat of solution of water in the series of solvents under discussion[8] varies only in the interval from −0.4 to 1.6 kcal./mole, or, if one omits the doubly functional alcohol–ethers, 0.2 to 1.6 kcal./mole (*i.e.*, ±0.7 kcal.).

In comparing two dihydrates, such as cobaltous nitrate dihydrate and uranyl nitrate dihydrate, and the same solvent, we see from equation 1 that the difference in the two heats of solution is

$$\Delta H_a - \Delta H_b = U_a - U_b - 2(E_a - E_b) + (H_d - H_s)_b - (H_d - H_s)_a \quad (3)$$

Since all but the binding energy terms are characteristic of the pair of salts considered, if the two salts bind a series of given solvents with the same or very similar energies, the difference in heat of solution of the two salts in a given solvent will be constant. In the case of solvents like isobutyl alcohol and water, where hexasolvation occurs to a variable extent, accompanied in the latter case by ionization, a correction would have to be made. Table V shows this relationship for cobaltous nitrate and uranyl nitrate dihydrates. The clustering of the difference values around 6 kcal. is striking. The two solvents showing most deviation, isobutyl alcohol and ethylene glycol monoethyl ether, are alcohols, and it has already been shown that in the case of the former hexasolvate formation occurs. If one compares the maximum heats of solution in mixtures with acetone, as is done for isobutyl alcohol in the last row of the table, the difference is about 6 kcal. again. As will be shown below, it seems probable that the uranyl ion binds water in the third (and presumably the fourth) coördination position with the same energy as does cobalt; from the evidence of Table V, this is largely true for other solvent groups as well. On the basis of this relationship one might predict that if solution of the cobalt salts in the solvents could be obtained, the heats of solution in ether would be about 4.6 kcal., in methyl isobutyl ketone 0 to 0.5 kcal., and in ethyl propionate approximately zero. In tetrahydrofurfuryl alcohol one would expect something between 6 and 8.5 kcal., in analogy with the other

TABLE V

COMPARISON OF HEATS OF SOLUTION OF COBALTOUS NITRATE DIHYDRATE AND URANYL NITRATE DIHYDRATE[a]

| Solvent | $-\Delta H$ for $Co(NO_3)_2 \cdot 2H_2O$ | $-\Delta H$ for $UO_2(NO_3)_2 \cdot 2H_2O$ | (2) − (1) |
|---|---|---|---|
| Ethylene glycol diethyl ether | 4.90 | 10.87 | 6.0 |
| Tetrahydrofuran | 4.30 | 10.71 | 6.4 |
| Diethyl ether | .. | 10.60 | ... |
| Tributyl phosphate | 4.74 | 10.46 | 5.7 |
| Acetone | 1.65 | 6.67 | 5.0 |
| Methyl ethyl ketone | −0.30 | 5.98 | 6.3 |
| Methyl isobutyl ketone | .. | 6.46 | ... |
| Ethyl propionate | .. | 6.03 | ... |
| Ethylene glycol monoethyl ether | 6.56 | 8.97 | 2.4 |
| Tetrahydrofurfuryl alcohol | .. | 8.51 | ... |
| Isobutyl alcohol | 1.28 | 2.58 | 1.3 |
| Isobutyl alcohol–acetone mixtures[b] | 4.20 | 10.30 | 6.1 |

[a] Data on uranyl nitrate dihydrate from reference 8.
[b] Mixtures giving peak $\Delta H$ values (25% alcohol for cobalt, 50% alcohol for uranyl nitrate).

alcohols, and in fact the data on mixtures with acetone (Table II) bear this out.

The existence of cases such as this, where direct comparisons between salts may be made, is a matter of pure chance. In other cases, such as the corresponding hydrates of cobaltous nitrate and chloride, although one knows that the binding energies for additional molecular groups in the same coördination positions should be the same, actual values of the heats of solution (*e.g.*, in water) are different, and little can be done with respect to general relationships. This points up the need for absolute values of binding energies for molecular groups. The heat for a reaction such as

$$MX_2 \cdot aH_2O\ (c) = MX_2(c) + aH_2O)\ (g)$$

can be seen to differ from a true binding energy by the difference in crystal energy of the initial and product salts. An essential part of the problem therefore is the estimation of lattice energies of salts. In what follows we shall detail a method of estimating these energies with a minimum of data, and shall show that in the particular case considered the method can be applied successfully to calculations of binding energies.

**Calculation of Lattice Energies.**—Equations for crystal lattice energy are found in a form in which molecular volumes, rather than ionic distances, are the parameter. In this form it is necessary to know only the specific gravity and formula weight of the substance, in addition to the crystal type, to calculate the lattice energy,[9] *viz.*

$$U = 279.0\ (\rho/M)^{1/3} A_d\ (1 - 1/n) \qquad (4)$$

where the Madelung constant appropriate to the case is $A_d$, and $n$ is a number of the order of magnitude of 10, related to the ionic repulsions in the derivation of the lattice energy equation. For our purposes, it is convenient to take the form developed by Verwey and de Boer,[10] which replaces $1/n$ by $0.345/R$, where $R$ is an ion-distance parameter (in ångströms). We choose to replace this by the approximation that $R$ equals the cube root of the mean ionic volume, *i.e.*,

$$R = 10^8/(3 \times 6.023 \times 10^{23} \times \rho/M)^{1/3} \qquad (5)$$

In the case of fluorite, $CaF_2$, for example, the agreement between $R$ and the Ca–F radius sum is within 1%, affecting the calculated lattice energy to perhaps 0.1%.

From equation (4) one sees that given a specific gravity for a known salt, its lattice energy is proportional to the Madelung constant, and that when determining the solvent binding energy values for two solvates of the same structure type, by equation (6), the lattice energy difference term is also therefore proportional to the value of the Madelung constant. This point is emphasized, since small errors or uncertainties in the Madelung constants give only small effects on the calculated binding energies. To such a limit one can therefore make use of rather sketchy information on the crystal-structures of the solids involved.

It seems significant that of the 2–1 nitrates investigated crystallographically (calcium, strontium, barium and lead(II)) all show the fluorite structure,[11] even though the radius ratio is below the limit usually taken for that structure ($Ca^{++}$ radius, 0.99 Å., nitrate, 2.1 Å.), while with the chlorides one finds a layer structure even for the hexahydrated chlorides of the alkaline earths[11] similar to the $CdCl_2$ and $CdI_2$ structures (anhydrous $SrCl_2$ is an exception, showing a fluorite structure). Nickelous hexammino nitrate and all the hexammino compounds of the halides show fluorite structure. As a working basis for our calculations, it seems justifiable to assume the fluorite Madelung constant for the hydrated nitrates, even though incomplete studies on the uranyl nitrate hexahydrate structure[12] seem to indicate that this nitrate does not have the fluorite pattern.

Table VI contains density and calculated lattice energy values for the hydrates of cobaltous nitrate, uranyl nitrate and cupric nitrate. The specific gravities of the hydrates have been obtained by pycnometric measurement under xylene. The fluorite Madelung constant ($A_d = 7.3306$) was used in the lattice energy calculations. Values for the cobaltous chloride hydrates are also shown, the $CdI_2$ layer lattice Madelung constant ($A_d = 6.21$) being used for these. It should be emphasized at this point that inherent in this calculation is the assumption that the binding is largely ionic; this point will be returned to later.

**Absolute Binding Energies.**—Consider two solvates of a given salt, and their solution in the same solvent to the same terminal concentration of anhydrous salt. The difference between the two heats of solution, on considering a hypothetical process similar to that leading to equation (1), is given by the relation

$$\Delta H_a - \Delta H_b = U_a - U_b - (a - b)H_v + (a - b)E \qquad (6)$$

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(9) J. Sherman, *Chem. Revs.*, **11**, 93 (1932).

(10) E. J. W. Verwey and J. H. de Boer, *Rec. trav. chim.*, **55**, 431 (1936).

(11) R. W. G. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1948; Vol. II, 1951, Chaps. VII and X.

(12) L. Pauling and R. G. Dickinson, THIS JOURNAL, **46**, 1615 (1924).

TABLE VI

WATER BINDING ENERGIES OF HYDRATES OF COBALTOUS NITRATE, URANYL NITRATE, CUPRIC NITRATE AND COBALTOUS CHLORIDE[a]

| Solid | Density | $U$, kcal./mole | $\Delta Hs$, kcal./mole[g] | Transition | Water binding energy, kcal.[h] |
|---|---|---|---|---|---|
| $Co(NO_3)_2 \cdot 6H_2O$ | 1.87[b] | 350.8 | 4.96 | Hexahyd → tetra | 47.0 |
| $Co(NO_3)_2 \cdot 4H_2O$ | 2.05 | 375.3 | 3.50 | Tetrahyd → trihyd | 33.6 |
| $Co(NO_3)_2 \cdot 3H_2O$ | 2.24 | 393.9 | −0.98 | Trihyd → dihyd | 32.7 |
| $Co(NO_3)_2 \cdot 2H_2O$ | 2.40[b] | 411.8 | −5.28 | ............... | .. |
| $UO_2(NO_3)_2 \cdot 6H_2O$ | 2.742[c] | 333.5 | 5.48 | Hexahyd → trihyd | 54.0 |
| $UO_2(NO_3)_2 \cdot 3H_2O$ | 2.93 | 352.2 | −1.66 | Trihyd → dihyd | 33.7 |
| $UO_2(NO_3)_2 \cdot 2H_2O$ | 3.35 | 371.7 | −5.37 | ............... | .. |
| $Cu(NO_3)_2 \cdot 6H_2O$ | 1.92 | 351.9 | −10.71 | Hexahyd → trihyd | 68.8 |
| $Cu(NO_3)_2 \cdot 3H_2O$ | 2.047[d] | 381.0 | −2.5 | ............... | .. |
| $CoCl_2 \cdot 6H_2O$ | 1.924[e] | 322.1 | 2.85 | Hexahyd → tetra | 50.0 |
| $CoCl_2 \cdot 4H_2O$ | 2.216[f] | 349.3 | (−1.0) | Tetrahyd → dihyd | 64.9 |
| $CoCl_2 \cdot 2H_2O$ | 2.477[e] | 382.3 | −9.85 | Dihyd → anhyd | 95.8 |
| $CoCl_2$ | 3.356[e] | 448.5 | −18.4 | ............... | .. |

[a] Fluorite Madelung constant ($A_d$ = 7.33) used for nitrates, layer structure ($A_d$ = 6.21) for cobaltous chloride and its hydrates. [b] G. L. Clark and H. K. Buckner, THIS JOURNAL, **44**, 230 (1922), give 1.883 for the hexahydrate and 2.397 for the dihydrate. [c] Reference 12. [d] L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **2**, 401 (1845); **3**, 57 (1848). [e] G. L. Clark, A. J. Quick and W. D. Harkins, THIS JOURNAL, **42**, 2483 (1920). [f] A. Neuhaus, *Chem. Erde*, **5**, 554 (1930). [g] Heats of solution of uranyl nitrate hydrates from reference 8, cupric nitrate and cobaltous chloride from reference 16, except for $CoCl_2 \cdot 4H_2O$ which was estimated from values for the nitrate hydrates. [h] Heat of vaporization of water = 10.48 kcal./mole.

TABLE VII

ENERGY OF BINDING PYRIDINE TO COBALTOUS ION

| Salt | Density,[a] g./cc. | $U$,[d] kcal./mole | $\Delta Hs$,[e] acetone | $\Delta Hs$,[f] HCl | Transition | Pyridine binding energy, kcal. Acetone | Pyridine binding energy, kcal. HCl |
|---|---|---|---|---|---|---|---|
| $Co(NO_3)_2 \cdot 6Py$ | 1.25 | 240.2 | 16.00 | −19.43 | Hexa → tetra | 54.4 | 54.6 |
| $Co(NO_3)_2 \cdot 4Py$ | 1.36 | 268.7 | 10.35 | − 8.93 | Tetra → tri | 38.3 | ... |
| $Co(NO_3)_2 \cdot 3Py$ | 1.47 | 290.6 | .... | − 7.00 | Tri → di | 39.8 | ... |
| $Co(NO_3)_2 \cdot 2Py$ | 1.52 | 313.2 | −5.43 | − 5.91 | Tetra → di | 78.1 | 80.5 |
| $CoCl_2 \cdot 6Py$ | 1.30 | 211.5 | .... | −20.1 | Hexa → tetra | .. | 53.3 |
| $CoCl_2 \cdot 4Py$ | 1.36 | 235.9 | .... | −12.40[b] | Tetra → di | .. | 80.1 |
| $CoCl_2 \cdot 2Py$ | 1.61 | 284.5 | .... | − 7.33[b] | Di → anhyd | .. | 211.3 |
| $CoCl_2$ | 3.356 | 448.5 | .... | −18.4[c] | .......... | .. | ... |

[a] Pycnometrically determined in mineral oil; $CoCl_2$ value from Clark, Quick and Harkins (1920). [b] From reference 14. [c] From reference 16. [d] Fluorite Madelung constant for nitrates, layer ($CdI_2$) for chlorides. [e] Terminal pyridine formal concentration, 5% by volume. [f] Terminal acidity, *p*H 2, except last 3 values; heat of solution of pyridine in HCl to *p*H 2, −8.2 kcal./mole (see also reference 14).

in which the subscripts refer to the solids with solvation $a$ and $b$, respectively. The binding energy $E$ is a mean energy for the $(a - b)$ solvent groups involved, since it may vary from coördination position to coördination position, and in general may be dependent on the other molecular groups bound. In this formulation $E$ represents the energy necessary to dissociate the solvent molecules from the gaseous solvated cation, with the end-products also being in the gaseous state. Coupling the available data on heats of solution and vaporization with electrostatic lattice energy calculations of the type above, values for $(a - b)E$ are derived for a series of hydrates in Table VI.

The first point of interest in the binding energies of Table VI is that where they overlap (dihydrate through hexahydrate) the binding energies for water in corresponding hydration states of the cation in the cases of cobalt chloride and cobalt nitrate check closely. For this comparison at least, the method of calculation of lattice energies introduces an error not appreciably greater than the uncertainty introduced with the experimental specific gravity and heat of solution values, even though the two series of salts are of different structure type. One can make a similar calculation for the pyridinates[13] of cobaltous nitrate and cobaltous chloride, using the heats of solution in HCl to a fixed terminal acidity and concentration, for which the relationship is

$$(m - n)E_{py} = (U_n - U_m) + (m - n)H_v - (m - n)H_{neut} + (\Delta H_m - \Delta H_n) \quad (7)$$

where $H_v$ is the heat of vaporization of pyridine and $H_{neut}$ is its heat of solution[14] in HCl. Another experimental procedure is to dissolve the pyridinates in acetone to a fixed composition in terms of pyridine and cobalt, in which case equation (6) can be used. We have made measurements with both procedures, and the heats of solution have been used to calculate binding energies for pyridine to cobaltous ion. The data in Table VII show that the agreement between values obtained for coördination positions 3 through 6 for cobaltous nitrate and chloride check very well, considering the possible errors in the method. The success with the hydrates and pyridinates lends confidence to deductions from other binding energy relations found in this manner.

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(13) L. I. Katzin, J. R. Ferraro and E. Gebert, THIS JOURNAL, **72**, 5471 (1950).

(14) W. Hieber and A. Woerner, *Z. Elektrochem.*, **40**, 256 (1934).

One such relation of interest (Tables VI and VII) is the essential equality for the energy to bind a given group in coördination positions 3 and 4. The energy to bind water in the two positions is 33 kcal. each, and for pyridine, 40 kcal. Another interesting value is the energy calculated (Table VI) for the binding of water in the third coördination position of uranyl ion, which is essentially the same as the corresponding value for cobalt. Combined with the assumption that the binding is the same for the fourth coördination position, and the material of Table V and equation (3), there seems to be basis for the assertion that the corresponding energies for binding groups other than water in these two positions are essentially equal for the two cations.

On the basis of unpublished data on the specific gravities and heats of solution of the monohydrate and monopyridinate of cobaltous chloride it seems that although the binding energies for the third and fourth coördination positions are equal, the binding in the first coördination position is most energetic, and that in the second position, while on the order of 60% as large, is still greater than that in the third and fourth positions.

**Conversion of Relative Binding Energies to Absolute Values.**—As a preliminary step, the values of $(H_v - 0.5\ \Delta H)$ for the heats of solution of cobalt nitrate dihydrate may be tabulated (Table VIII) according to equation (2). With the absolute binding energy known for one of these solvents, the quantity $E - (H_v - 0.5\ \Delta H)$ can be determined which, added to the tabulated values, will give the absolute values of the energy for binding these molecular groups in the third and fourth coordination positions of cobalt. The practical difficulty is twofold: it is hard to define the heat of solution for either of the two possible reference solvents, water or pyridine, with the precision with which their binding energies can be calculated; and for the apparently reasonable heat values of either, the binding energy calculated for the second is apparently in error.

TABLE VIII

ENERGIES OF BINDING VARIOUS MOLECULAR BASES TO COÖRDINATION POSITIONS 3 AND 4 OF COBALTOUS NITRATE (KCAL./BOND)

| Molecular base | $H_v$ | $-^1/_2\Delta H_{\text{dihyd.}}$[a] | $E - x$ | $E(x = 18.3)$ |
|---|---|---|---|---|
| Water | 10.5 | 4.2 | 14.7 | 33.0 |
| Tetrahydrofurfuryl alcohol | 12.2[c,d] | <4.4 | <16.6 | <34.9 |
| Ethylene glycol monoethyl ether | 11.0[c] | 3.3 | 14.3 | 32.6 |
| Isobutyl alcohol | 12.0[b] | 2.1[b] | 14.1 | 32.4 |
| Ethylene glycol diethyl ether | 10.0[c] | 2.45 | 12.45 | 30.75 |
| Tetrahydrofuran | 7.3[c] | 2.15 | 9.45 | 27.75 |
| Diethyl ether | 6.7[b] | (2.3) | 9.0 | 27.3 |
| Acetone | 7.7[b,e] | 0.83 | 8.5 | 26.8 |
| Methyl ethyl ketone | 9.0[b] | − .15 | 8.85 | 27.15 |
| Methyl isobutyl ketone | 8.3[c] | ( .25) | 8.55 | 26.85 |
| Ethyl propionate | 8.8[b] | ( .0) | 18.8 | 27.1 |
| Tributyl phosphate | 6.4[b] | 2.4 | 8.8 | 27.1 |
| Pyridine | 10.1[b] | 7.2 | 17.3 | 35.6 |

[a] Parenthetical values are taken from uranyl nitrate data, with 6 kcal. subtracted from $\Delta H$. [b] From Landolt–Bornstein "Tabellen," Julius Springer, Berlin, 5th ed. [c] Calculated from miscellaneous vapor pressure data. [d] Based on unreliable high temperature data. [e] From maximum value for alcohol–acetone mixtures.

Thus, the heat of solution curve for the dihydrate in pyridine–acetone mixtures shows −9.51 kcal. for a solution with 2.0 molecules of pyridine per molecule of salt, −14.4 kcal. for the solution with 4 to 5 pyridines per salt molecule, and a slow change from this to a plateau of about −17.7 kcal. before precipitation of $Co(NO_3)_2{\cdot}6Py$ at higher pyridine concentrations. From the spectrophotometric data on the chloride,[8] it might be judged that the pyridine addition is almost complete at the stoichiometric ratio of pyridine to salt, and has proceeded somewhat toward the stage of $Co(NO_3)_2{\cdot}4Py$ at the ratio of 4–5 pyridines per molecule of salt. The heat value desired therefore probably lies somewhere between −9.5 and −14.4 kcal.; −17 kcal. is certainly too high. The situation for water is much less clear, although it may be considered that the maximum point in the water–acetone mixtures (−13.4 kcal. at 13 vol. % water) corresponds to the plateau of the pyridine curve, and is therefore a maximum possible value for the addition of water in the third and fourth coördination positions. The −8.5 kcal. value at 2.9 vol. % water may be analogous to the −14.4 value in the pyridine series. Because of the variation in point of intrusion of hexasolvation and ionization due to larger ionic radius, the constant-difference relation of the uranyl nitrate data is no assistance here. The data on isobutyl alcohol–acetone mixtures, free of the dielectric constant influence of water, indicate only that the water value is probably below 11 kcal. The significant point is that no combination of the reasonable values for pyridine and water, with almost identical heats of vaporization, will show a difference approximating the 12–14 kcal. in the heats of solution that would match a difference in the binding energies of 6–7 kcal. per molecule bound.

A further limitation is introduced on considering that the binding energy for water probably should not be less than the value for the alcohols, or a value of $(H_v - 0.5\Delta H)$ on the order of 14.5. This is satisfied by the −8.5 kcal. $\Delta H$ value at 2.9 vol.-% water, which is therefore the value used in Table VIII. Because the −17.7 kcal. value of the pyridine series certainly includes a water replacement component, the value −14.4 kcal. (for the 4:1 mole ratio of pyridine) is used. This leaves only a 2.6 kcal. difference in the binding energies for water and pyridine. By an arbitrary choice, the calculated "absolute" binding energies in Table VIII are normalized to the binding energy of water, 33 kcal. A possible basis for the discrepancy in the absolute and relative pyridine–water binding differences will be discussed later in this report.

Although there are considerable uncertainties in some of the heats of vaporization, and there has been no correction in the tetrahydrofurfuryl alcohol and ethylene glycol monoethyl ether cases for certain higher solvation contribution, the binding energy values fall into several distinct groups. There is no second nitrogen base with which to compare the pyridine, but water and the alcohols form a sharply separated group at about 33 kcal., with the ethers at 27.3–30.8 kcal. less sharply distinguished from the ketones and esters at 26.8–27.1 kcal. The general falling into groups is not surprising, since a tendency for ordering is already remarked not only in the heat of solution values, but also in the heats of vaporization, as can be seen. It is remarkable that greater variation does not exist in the combination of these values.

Although the information on the lattice energy of anhydrous cobaltous nitrate is lacking, it is possible to estimate the binding energies for water and for pyridine in coördination positions 1 and 2 from the data for the chloride. As indicated in Tables VI and VIII, the energy of binding of the first two water groups is 96 kcal., and of the first two pyridines, 211 kcal., assuming a layer structure. This surprisingly high number seems to find support from other directions. Thus, from the heat of solution of cobaltous nitrate dihydrate in acetone containing 5% of pyridine (Fig. 1), the heat of solution of cobaltous nitrate dipyridinate in acetone, to the same final pyridine concentration, the heats of vaporization of pyridine and of water, and the heats of solution of pyridine and of water in the mixed solvent (these last terms being almost negligible), one calculates the difference in binding energy for two pyridines and two waters in positions 1 and 2 to be 108.6 kcal., in reasonable agreement with the difference (116 kcal.) in the numbers mentioned above. Similarly, from the lattice energy and heat of solution in water of cobaltous nitrate dihydrate, the binding energy of the first two waters (from the chloride data), and the heat of solution of anhydrous $Co(NO_3)_2$ of 11.88 kcal.,[15] the lattice energy of anhydrous cobaltous nitrate can be calculated to be 480.3 kcal. (equation 6). Combination of this with the lattice energy and heat of solution of cobaltous nitrate dipyridinate in HCl (Table VIII), and the approximation that the heat of solution of the anhydrous salt is the same in dilute HCl as in water, gives 209.7 kcal. for the energy to bind two pyridine groups, in agreement with the 211 kcal. from the chloride. As qualitative evidence for a large water–pyridine binding difference may be cited the behavior of $Co(NO_3)_2 \cdot 2H_2O \cdot 2Py$. This compound,[13] heated at 120° in vacuum, yields a distillate of essentially pure water, and a residue of what, to the limits of analytical reliability, is pure $Co(NO_3)_2 \cdot 2Py$. A binding energy for the two water groups, calculated from the lattice energies and the difference in heats of solution of the two compounds cited, is 36.5 kcal., only slightly more than half the value for positions 3 and 4 when coördination positions 1 and 2 are filled by water.

From literature data it is possible to get a comparison with the energy for binding ammonia, inasmuch as the hexammines of a large number of 2–1 halides have been studied and have been found to show the fluorite structure.[11] With approximate values of the heats of formation from the anhydrous salt and gaseous ammonia available,[16] the binding energies for six ammonia groups are calculable (see Table IX). The anhydrous halides, with the exception of strontium chloride, and possibly calcium chloride and bromide, have layer structures. It is also possible to obtain comparisons with the water binding energies of cations other than cobalt from data on hexahydrates, all of which have layer structures. These are summarized in Table IX.

Aside from some details which will be discussed further, one may conclude that with respect to the energy with which water and ammonia are bound, cobaltous ion is not markedly different from divalent cations such as the alkaline earths. Essentially similar conclusions are reached on comparing the total solvation energies for the cations in aqueous solution (Table X) obtained by use of literature estimates of the hydration heats of the anions.[17] Magnesium, with much the same ionic radius as cobaltous ion, shows very similar solvation energy for the hexahydrated cation and about 10 kcal. larger for the bare ion, in keeping with its slightly small radius. It is of interest, perhaps, in connection with the question of sizes of hydration spheres, that over half of the total solvation energy of the cations is consumed in binding the first six water groups.

TABLE IX

ENERGIES OF BINDING AMMONIA OR WATER TO VARIOUS BIVALENT CATIONS

| Salt | α,[a] Å. | ρ,[b] g./cc. | $U$ | $\Delta H^c_f$, kcal. | ΔL,[d] kcal. | Energy of binding ligands, kcal.[e] |
|---|---|---|---|---|---|---|
| $CoCl_2$ | | 3.356 | 448.5 | | | |
| $CoCl_2 \cdot 6NH_3$ | 10.10 | .... | 350.7 | 96.1 | ..... | 193.9 |
| $CoCl_2 \cdot 6H_2O$ | .... | | 322.1 | ... | 21.25 | 210.7 |
| $CoBr_2$ | .... | 4.909 | 429.4 | | | |
| $CoBr_2 \cdot 6NH_3$ | 10.389 | .... | 342.0 | 109.0 | ..... | 196.4 |
| $CoI_2$ | .... | 5.68 | 405.6 | | | |
| $CoI_2 \cdot 6NH_3$ | 10.914 | .... | 326.4 | 98.4 | ..... | 177.6 |
| $MgCl_2$ | .... | 2.316 | 440.8 | | | |
| $MgCl_2 \cdot 6NH_3$ | 10.158 | .... | 348.9 | 93.4 | ..... | 185.3 |
| $MgCl_2 \cdot 6H_2O$ | .... | 1.56 | 313.4 | ... | 33.0 | 223.4 |
| $MgBr_2$ | .... | 3.72 | 418.0 | | | |
| $MgBr_2 \cdot 6NH_3$ | 10.468 | .... | 340.0 | 102.5 | ..... | 180.5 |
| $MgBr_2 \cdot 6H_2O$ | .... | 2.00? | 306.0 | ... | 43.3(?)[f] | 218.3(?) |
| $MgI_2$ | .... | 4.244 | 385.0 | | | |
| $MgI_2 \cdot 6NH_3$ | 10.978 | .... | 324.5 | 114.2 | ..... | 174.7 |
| $CaBr_2$ | .... | 3.353 | 395.9[g] | | | |
| $CaBr_2 \cdot 6NH_3$ | 10.706 | .... | 332.9 | 82.3 | ..... | 145.3 |
| $CaI_2$ | .... | 3.956 | 371.1 | | | |
| $CaI_2 \cdot 6NH_3$ | 11.24 | .... | 317.6 | 94.5 | ..... | 148.0 |
| $SrCl_2$ | .... | 3.052 | 486.4 | | | |
| $SrCl_2 \cdot 2H_2O$ | .... | 2.6715 | 373.3 | ... | 8.64 | 142.7 |
| $SrCl_2 \cdot 6H_2O$ | .... | 1.93 | 308.0 | ... | 18.66 | 260.1 |

[a] $(\rho/M) = \left(\frac{4}{6.023 \times 10^{23}} \times \frac{10^{24}}{\alpha_0{}^3}\right)$. [b] From "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, 19, Ohio, for alkaline earth salts. [c] Differences in heats of formation of $(MX_2 + 6NH_3)$ and $MX_2 \cdot 6NH_3$ listed in reference 16. [d] Heat of solution of hydrate minus heat of solution of anhydrous salt. [e] Heat of vaporization of water = 10.5 kcal./mole. [f] Assumes heat of solution of hydrate to be zero, probably correct to 5 kcal. [g] Using layer structure Madelung constant; rutile constant introduces 90 kcal. disagreement with iodide on ammonia binding energy.

TABLE X

SOLUTION HYDRATION ENERGIES OF DIVALENT CATIONS[a] (KCAL./MOLE)

| Salt | Cation | Lattice energy (kcal./mole) | Heat of solution (kcal./mole)[b] | Cation hydration energy |
|---|---|---|---|---|
| $MgCl_2$ | $Mg^{++}$ | 440.8 | −35.9 | 299.3 |
| $MgBr_2$ | | 418.0 | −43.3 | 298.5 |
| $MgI_2$ | | 385.0 | −49.8 | 290.6 |
| $MgCl_2 \cdot 6H_2O$ | $Mg(H_2O)_6{}^{++}$ | 313.4 | − 2.94 | 138.9 |
| $MgBr_2 \cdot 6H_2O$ | | 306.0 | X[c] | 143.2-X[c] |
| $CaCl_2$ | $Ca^{++}$ | 431.8[d] | −18.0 | 272.4 |
| $CaBr_2$ | | 395.9[d] | −24.5 | 257.6 |
| $CaI_2$ | | 371.1 | −27.7 | 254.6 |
| $CaCl_2 \cdot 6H_2O$ | $Ca(H_2O)_6{}^{++}$ | 313.3 | + 4.56 | 131.3 |
| $SrCl_2$ | $Sr^{++}$ | 486.4 | −11.15 | 321.1 |
| $SrCl_2 \cdot 2H_2O$ | $Sr(H_2O)_2{}^{++}$ | 373.3 | − 2.51 | 198.4 |
| $SrCl_2 \cdot 6H_2O$ | $(SrH_2O)_6{}^{++}$ | 308.0 | 7.51 | 123.1 |
| $SrBr_2 \cdot 6H_2O$ | | 299.8 | 6.45 | 130.6 |
| $CoCl_2$ | $Co^{++}$ | 448.5 | −18.4 | 289.5 |
| $CoBr_2$ | | 429.4 | −18.4 | 285.0 |
| $CoI_2$ | | 405.6 | −18.8 | 280.2 |
| $CoCl_2 \cdot 6H_2O$ | $Co(H_2O)_6{}^{++}$ | 322.1 | + 2.85 | 141.9 |

[a] $Q_+ = U - Q_- - L$; values for $Q_-$ are from reference 17. [b] Heats of solution ($L$) are from reference 16. [c] A value for the heat of solution is not available. [d] Layer structure ($CdI_2$) Madelung constant used to bring values in line with iodide value. Use of rutile constant would alter energy by approx. 100 kcal.

An obvious peculiarity of the data in Table IX is that the calculated binding energy for the first two ammonia groups to cobalt is almost 30 kcal. greater than that for binding the first two water groups, while the binding energy for six ammonia molecules is less than that for 6 water molecules by perhaps 15 kcal. The energy to bind six ammonia groups to magnesium ion is perhaps 10 kcal. less than that for cobalt,

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(15) A. Guntz and F. Martin, *Bull. soc. chim. France*, **5**, 1004 (1909).

(16) F. R. Bichowsky and F. R. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(17) W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

while the energy to bind six water groups is an equal amount greater than the cobaltous value. The ammoniation energy of calcium ion, based largely on the iodide, is a few tens of kilocalories lower than that of magnesium, while the hydration energy of strontium ion seems 50 kcal. larger than that of cobaltous ion, primarily because of the binding energy for the first two water groups, the last four being bound with much the same energy as in the cobaltous case.

All of these cases share the circumstance in common of a shift in crystal type between the unsolvated and solvated salts. Thus, with the halides, the anhydrous salts are generally of the layer lattice types, and the hexammine is of the fluorite type. Since the Madelung constant of the latter structure is much higher than the former, one obtains a smaller difference in lattice energies than would be the case if there were no change in structure type. Professor W. H. Zachariasen has pointed out to us that in the layer-structure lattices there exists a dipole energy component not allowed for in the electrostatic calculation, and of the order of magnitude of the repulsion correction (about 10% of the lattice energies involved here). This cancels out between two layer-lattice crystals but remains as a correction when the two crystal types differ. Such a correction, of the order of 30–40 kcal., would put the ammonia and water binding energies (for six groups) in the order expected from evidence of general chemical behavior.

The anomaly of the energy for binding the first two pyridines seems even more marked with these comparisons, the value being as great as for six water groups, and little different from six ammonia groups, while the latter is a stronger Lewis base. Here one might suggest that some strain factor operates, related to the geometry of the flat ring molecule, and leading to a crystal spacing considerably greater than is appropriate to the true lattice energy. Such a factor would need to be independent to a large extent of the crystal structure type, to give the concordance found between the calculations for the binding energy with both nitrate and chloride. Extended further, such a factor might also account for the discrepancy between the water and pyridine binding energy difference from the heats of solution of the dihydrates, and from the lattice energy calculations.

The comparative data in Table VI offer a possible explanation of another phenomenon, long known, which has led to considerable speculation. This is the very ready extraction of uranyl nitrate from aqueous solution into various immiscible organic solvents. It has been shown[1] that the form so extracted is a tetrahydrated molecule, in line with other evidence on the role of $MX_2 \cdot 4S$ entities in the phenomenon of 2–1 salt solubility in organic solvents. If the assumptions of Table VI were true, that the several uranyl nitrate hydrates were of the fluorite structure, an explanation of the phenomenon would be ready to hand, namely, that the extractability is a function of the weakness with which the water is held in the 5th and 6th coördination positions, and the ease of replacement of these waters by anions. This explanation would be further substantiated by the cupric nitrate numbers, since although cobaltous nitrate hydrates are completely insoluble in diethyl ether, and uranyl nitrate is very soluble, cupric nitrate displays a significant solubility before hydrolysis sets in to precipitate the copper. Since the existing crystallographic data on uranyl nitrate hexahydrate[12] are not compatible with a fluorite structure, it is possible that (providing the lower hydrates are fluorite-like) the binding of the last two groups may be closer to that for the other salts than appears in Table V. There also exists the possibility, although less probable, that the Madelung constant of the structure is at least as high as that of the fluorite structure, or that the lower nitrates themselves may have a structure with a smaller Madelung constant than the fluorite constant, in which case the binding energy for the last water groups could be even smaller than that calculated. Although the numerical value is therefore quite uncertain, this possible answer to the problem of the relative extractabilities seems more in accord with the evidence as a whole[18] than postulation of specific complex formation dependent on 5f electron orbitals.[19]

CHICAGO 80, ILLINOIS

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(18) L. I. Katzin. *Nature*, **166**, 605 (1950).

(19) E. Glueckauf and H. A. C. McKay, *ibid.*, **165**, 594 (1950); **166**, 606 (1950).

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[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, THE UNIVERSITY OF CHICAGO]

# A Thermodynamic Study of Liquid Metallic Solutions. IV. Approximate Thermodynamic Data from the Phase Diagram for the Systems Copper–Bismuth, Copper–Lead and Copper–Thallium

BY O. J. KLEPPA

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For the systems copper–bismuth and copper–thallium some new data have been presented on the solubility of copper in the low-melting metal. Some comments have been presented on earlier attempts at obtaining thermodynamic data for liquid metal mixtures from the phase diagram. The methods do not take into account the entropy deviations frequently found in such mixtures. A new method has been described which, for certain types of phase diagrams, makes it possible to separate the calculated partial molal free energies (along the liquidus) into approximate heat and entropy terms. The method has been applied to the systems copper–lead, copper–bismuth and copper–thallium. The calculated heat data have been compared with calorimetric data where such data are available.

## Introduction

It is well known that the electromotive force and the vapor pressure methods, which are most commonly used for the study of the thermodynamic properties of metallic mixtures, are subject to serious limitations in their application. In recent years attention has therefore been given to the use of the binary equilibrium phase diagram for obtaining thermodynamic data for liquid metallic mixtures. The systems that are especially well suited for investigation are those of a simple eutectic type.

In general, these calculations are limited to systems where the corresponding data are known for the terminal solid solutions. Unfortunately, this condition is very seldom fulfilled. However, for a considerable number of systems the solid solubility is negligible, which makes the calculations particularly simple.

The methods adopted are based on the following