as the oxygen atom. The calculated molecular areas agree within 1–2% with the experimental values and this is about as good agreement as can be expected.

The film potential was measured[9] at intervals as the irradiation proceeded and the maximum $\Delta V$ values eventually came to around 550 mv. Rideal and Mitchell record a $\Delta V$ value for stearic acid of 545 mv. This indicates that the decomposition product remaining in the mono-layer is stearic acid in all cases.

The amines resulting from the photolysis remain in the hydrochloric acid solution substrate, as may be expected. Aniline was identified colorimetrically in the hydrochloric acid solution after irradiation for as short a period as ten minutes by the red color produced by diazotizing and coupling with β-naphthol. Benzylamine and β-phenylethylamine were identified as picrates, m. p. 195° (cor.)[10] and 168° (cor.),[11] respectively, after prolonged irradiation and frequent renewal of the mono-layer. Mixed melting points of each of these were done with the respective pure picrates prepared from the pure amines and confirmed the identity of the photolysis products. Between 4 and 5 mg. of the respective picrates was actually crystallized after about twenty-four hours of irradiation. That the reaction with stearic anilide is a photolysis and not hydrolysis in the presence of hydrochloric acid was definitely proved by inserting a glass filter in the optical system which excluded wave lengths below 3000 Å. Under these conditions no aniline was detected after thirty minutes exposure.

Acknowledgment is made to Mr. B. E. Babcock and the American Philosophical Society for grants-in-aid and to the Bausch and Lomb Optical Company for the use of the ultraviolet sector-photometer for the absorption spectrum studies.

## Summary

The absorption spectra of stearic anilide, benzylstearylamine and β-phenylethylstearylamine have been determined and the molecular areas when spread on hydrochloric acid solution have been measured. These substances as mono-layers have been irradiated at 2483 and 2537 Å. and found to undergo photolysis at the CONH linkage. The products of the reaction have been identified by film potential measurements (stearic acid) and colorimetric tests (aniline) and as crystalline picrates (benzylamine and β-phenylethylamine).

It seems reasonable to expect that peptides and proteins containing amino acids with light-absorbing side chains may undergo breakage of the adjacent CONH linkages in an analogous manner.

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[9] Schulman and Rideal, *Proc. Roy. Soc.* (London), **130A**, 259 (1931).

[10] Moureu and Lazennec, *Bull. soc. chim.*, [3] **35**, 1183 (1906): Jerusalem, *J. Chem. Soc.*, 1283 (1909).

[11] Michaelis and Linow, *Ber.*, **26**, 2167 (1893): Weinhagen, *Biochem. J.*, **11**, 275 (1917).

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[COMMUNICATION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANITOBA]

# The Heats of Solution, Heats of Formation, Specific Heats and Equilibrium Diagrams of Certain Molecular Compounds

BY A. N. CAMPBELL AND A. J. R. CAMPBELL

A very great number of studies of the freezing point (or melting point) diagrams of binary organic systems has been made.[1] As a result of these studies it appears that a molecular compound frequently is formed. In this connection the question of the relative stability of these numerous compounds has arisen. This question can only be answered with complete precision when the free energy of formation is known and this cannot be obtained readily for the systems under consideration, since the calculation requires a knowledge of the behavior of the specific heats from absolute zero upward. It is known, however, that in condensed systems the heat of formation very often approximates to the free energy of formation. It was thought that determinations of the heats of formation via the heats of solution of some of these organic molecular compounds would give at least the order of magnitude of the free energy change involved. Furthermore, if the specific heats, at room temperature, of reactants and products are known, an approximate calcula-

[1] *Cf.*, for instance, Kremann, *Monatsh.*, **25**, 1215 (1904), and following volumes to 1930.

tion can be made by means of the Kirchhoff equation of the heat of formation at absolute zero, assuming that the difference of molar heats of reactants and products remains constant down to absolute zero. At absolute zero the heats of formation are strictly a measure of the free energy change involved, since at that temperature

$$\Delta H = \Delta F$$

The experimental data required for the evaluation of the above relationships are the heat of formation and the specific heats of reactant and product. In most cases these data were unknown, and we have had to determine them, developing for the purpose methods which are to some extent new, or at least modifications of existing methods, to deal with organic substances, which are for the most part bad thermal conductors.

As this investigation was essentially one of relative stability, using that term in not too precise a sense, we investigated the equilibrium diagrams with a suitable solvent, in certain cases. The effect of this is to extend the information obtained from the freezing curve to a lower temperature. It answers the question of whether or not the compound continues to exist at the lower temperature. In addition it is usually considered that the extent of that portion of the curve, in both cases, along which compound is the stable solid, is a qualitative indication of the stability of the compound, that is, of its distance from a transition temperature. The systems studied were:[2] (1) phenol–urea: compound of 2 phenol:1 urea, congruent melting point, sharp maximum; (2) urea–*p*-toluidine: compound of 1 urea:1 *p*-toluidine, congruent melting point, sharp maximum; (3) β-naphthylamine–*p*-nitrosodimethylaniline: compound of 2 β-naphthylamine:3 *p*-nitrosodimethylaniline, congruent melting point, very flat maximum; (4) salicylic acid–acetamide: compound of 1 salicylic acid:1 acetamide, incongruent melting point, transition temp. 63–65°.

## Experimental

**Heats of Formation.**—Attempts were first made to determine the heats of formation from the heats of combustion, but these were soon abandoned when it was realized that, owing to the large molecular heats of combustion, the difference figure was hopelessly inaccurate. A property of much smaller numerical value per mole was sought and found in the heat of solution, and the heats of formation were determined throughout from this quantity. As all the heats of solution were negative (heat absorbed), the method used was essentially that in which solute and solvent are mixed and the temperature then restored to its original value by electrical heating. The beauty of this method is that a knowledge of the water equivalent is not required. The electrical energy consumed was measured potentiometrically as the fall in potential across a standard ohm in series and across the heating coil of the calorimeter. The energy consumed is then $H = E_1E_2t$, where $t$ is time in seconds and $E_1$ and $E_2$ the respective voltage drops. Minor precautions consisted in having large capacity lead accumulators as source of energy, using heavy copper leads, and packing the standard ohm in ice, in case of heating. Currents used were about 0.7 and 1.4 amp., with 2- and 4-volt circuits, respectively. The accuracy of the electrical measurement is said to be 1 in 10,000, certainly 1 in 1000, and therefore much in excess of the accuracy of the thermal measurement, which is 1 in 100 at best. As usual the calorimeter consisted of a dewar flask with beckmann thermometer, but it was found indispensable to immerse the calorimeter in a thermostat at 20°; otherwise radiation losses were appreciable, even through the wall of a silvered vacuum flask. In general, if the temperature of the contents of the dewar fell more than one degree below that of the environment, radiation losses were appreciable. As this was liable to occur when the heavier charges of solute were first introduced, the device was adopted of immediately switching in the 4-volt circuit whereby the temperature was brought to a few tenths below the equilibrium temperature in a few minutes (say, five minutes). The temperature was then restored exactly to its original value by means of the 2-volt circuit (energy input one quarter of the preceding). The energy input in each phase, each of about five minutes duration, was separately determined. A difficulty was encountered in stirring. Blank experiments showed that all kinds of mechanical stirrers raised the temperature several hundredths of a degree during the course of a run. The difficulty was overcome by using as stirring agent a fine stream of air injected through a coarse capillary. The air current passed first through a metal coil and then through a bubbler containing the solvent used in the calorimeter, both coil and bubbler being immersed in the thermostat. The variation of temperature produced by this means was not more than 0.01° during a run. The powdered solute was immersed in the thermostat for some time before its introduction to the calorimeter. In order to allow for any possible existence of a molecular compound in solution, the heats of solution were determined, not only in pure solvent, but also in solvent containing an equivalent amount of the other component.

**Preparation of Molecular Compounds.**—The lower melting component was melted completely, the calculated quantity of the second component added, the whole stirred until clear, if necessary with further heating, and then allowed to crystallize very slowly. The freezing point, in comparison with the literature, showed the purity of each compound. The molecular compound of *p*-

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(2) Literature relating to equilibrium diagrams: (1) Kremann and Rodinis, *Monatsh.*, **27**, 138 (1906); J. C. Philip, *J. Chem. Soc.*, **83**, 823 (1903); H. Rheinboldt, *J. prakt. Chem.*, (2), **111**, 242 (1925). (2) Philip, *J. Chem. Soc.*, **83**, 821 (1903). (3) Kremann, *Monatsh.*, **25**, 1322 (1904); H. Rheinboldt, *loc. cit.* (4) Kremann and Auer, *Monatsh.*, **39**, 466 (1918); Rheinboldt, *loc. cit.*

toluidine and urea is stated to exist in two forms. The form used by us was the high melting and therefore stable form (m. p. 31.1°). This stable form is readily obtained by powdering the samples before use; even mere scratching with a glass rod appears to produce a change in crystalline structure.

**Preparation of Materials.**—**Phenol** was distilled repeatedly. One distillation is insufficient and, even then, for specific heat determinations, distillation must be carried out directly into the container, since the slightest trace of water lowers the melting point very abruptly.

**Urea** was recrystallized from alcohol.

**_p_-Toluidine,** taken as pure, m. p. 44.2°.

**β-Naphthylamine** was recrystallized from benzene.

**_p_-Nitrosodimethylaniline** was prepared from dimethylamine, crude product extracted with ether and first crystals separated.

**Salicylic acid** was recrystallized from water.

**Acetamide** was distilled several times and protected from access of moist air. The specific heat sample was distilled straight into its container.

**Specific Heats.**—Perhaps the best method of determining specific heats is to heat the substance electrically in an evacuated container determining the rise of temperature from the increase in resistance of the heating coil. We attempted something similar to this, using, however, a beckmann thermometer and solidifying a large block of substance around the bulb and heating coil, but we found our attempts defeated by the poor thermal conductivity of the materials. If the bulb of the thermometer was near the coil, the thermometer rose rapidly to a high value, and then, when current was cut off, fell to an uncertain final value. If the bulb were far removed from the coil, it commenced to rise only after a considerable interval of time, during which radiation was perhaps considerable and certainly unknown. Determination of temperature from the resistance of the coil would only have made matters worse. This uncertainty in the final temperature led us to adopt the following method, which is a modification of the method of mixtures. From 50 to 100 g. of substance sealed in a bulb of hard glass was placed in a metal container, packed in melting ice and left overnight. The same electrical circuit as was used in the determination of heats of solution was employed, and the same calorimeter, which contained 150 cc. of water, together with the same stirring device. The cooled sample was rapidly introduced into the calorimeter and the 4-volt circuit immediately switched on. The temperature was thus brought to about 0.1° below that of the thermostat, and then brought exactly to the equilibrium value by means of the 2-volt circuit. As the heat of the calorimeter penetrated the badly conducting organic material the temperature again fell but it was not allowed to fall more than 0.1° before the 2-volt circuit was again switched in. In this way radiation loss was reduced practically to zero, despite the comparatively long duration of the experiment (about half an hour). Completion of the experiment was clearly marked by the temperature not dropping, or even rising a little, after the heating current was cut off. In common with all applications of the method of mixtures, this method can only give the specific heat over a range, in this case from 20 to 0°, but, at temperatures so far removed from the absolute zero, the variation of specific heat with temperature will not be great.

**Numerical Results.**—All measurements were made in a thermostat at 20°.

### 1. Phenol-Urea

### Heats of Solution in Water:

TABLE I

| | Solvent | Diln. in l. per mole | Heat of soln. in kj. per mole | |
|---|---|---|---|---|
| | | | Our value | Lit. value[a] |
| Phenol | Water | 1.79 | −11.9 | |
| | | 2.15 | −11.82 | |
| | | 2.29 | −11.26 | |
| | | 2.02 | −11.30 (mean of 12 detns.) | |
| | | ∞ | . . . | −10.9 |
| Urea | Water | 7.16 | −13.81 | |
| | contg. | 3.07 | −14.0 | |
| | equiv. | 1.85 | −13.7 | |
| | phenol | 4.03 | −13.8 (mean of 12) | |
| Urea | Pure water | 1.63 | −14.65 | |
| | | ∞ | . . . | −15.1 |
| 2 Phenol:1 Urea | | 5.30 | −49.5 | |
| | Water | 4.07 | −46.75 | |
| | | 3.90 | −46.8 | |
| | | 4.10 | −46.2 | |
| | | 4.03 | −46.58 (mean of 12) | |

[a] From "International Critical Tables."

### Results

While the heats of solution of phenol and of urea appear to be only slightly dependent on dilution, that of the compound is appreciably greater at the higher dilutions. This is due to the increased dissociation of the compound which is not complete, as can be seen from a comparison of the heat of solution of urea in water containing equivalent phenol and in pure water. Taking the heat of formation of the compound as 10.18 kj. per mole (*cf.* below), the percentage of double compound remaining undissociated at a dilution of about 4 liters per mole is calculated from the difference in the heats of solution of urea in equivalent phenol and in pure water (= 0.85 kj. per mole) as 8.35%. This point was checked by determining the molecular conductivities in water of phenol, of urea, and of the compound. These were:

| | $\mu$, mho | Diln. in l./mole |
|---|---|---|
| Phenol | 0.00921 | 1.84 |
| Urea | .0464 | 3.69 |
| Compound | .0578 | 3.69 |

Hence, 2 phenol + 1 urea = 0.0648, and the percentage of compound, undissociated, results as 10.8, assuming what is obviously incorrect, that the compound molecules are non-conducting.

**Heat of Formation.**—Taking mean values for corresponding dilutions, we have

$$2 \text{ phenol} + 1 \text{ urea} = 1 \text{ compound} + x \text{ kj.}$$
$$2(-11.3) + (-13.8) = -46.58 + x \text{ kj.}$$
$$x = 10.18 \text{ kj.} = 2.43 \text{ kcal./mole}$$

**Specific Heats.**—

| | Sp. ht. in cal./g. Obsd. | Sp. ht. in cal./g. Lit. value | Molar heat obsd. in cal./mole |
|---|---|---|---|
| Phenol | 0.239 | 0.561 (liquid)[3] | 22.45 |
| Urea | .274 | .321[3] | 16.4 |
| 2 Phenol:1 Urea | .240 | ... | 59.8 |

**Heat of Formation of 2 Phenol:1 Urea, at Absolute Zero (Approximate).**—Equation used: $(\Delta H_T - \Delta H_0)/T = C_{\text{products}} - C_{\text{reactants}}$.

$$\begin{aligned} 2 \text{ Molar heat phenol} + \text{molar ht. urea} &= 61.3 \\ \text{Molar heat compound} &= 59.8 \\ C_{\text{products}} - C_{\text{reactants}} &= -1.5 \\ T = 293\,°\text{A} & \\ \text{Hence, } \Delta H_0 = 1990 \text{ cal.} = 1.99 \text{ kcal.} & \end{aligned}$$

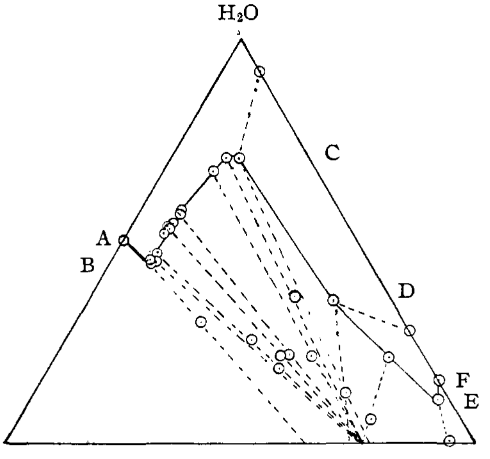

Fig. 1.—AB, urea, solution; B, urea, compound, solution; BC, compound, solution; CD, two liquids, compound; DE, compound, solution; E, compound, phenol, solution; EF, phenol solution.

**Equilibrium Diagram.**—The complete equilibrium diagram of the system phenol–urea–water was outlined at 20°. Urea was determined by the Kjeldahl method; phenol by the method of Redman, Weith and Brock.[4] The end-point of the latter method was greatly improved by filtering off the precipitated tribromophenol through glass wool, prior to titration. The results are contained in Table II and are expressed graphically in Fig. 1. The diagram has been rendered more complete by the incorporation of the results of Hill and Malisoff[5] for the mutual solubility of phenol/water at 20°.

Table II

| | Solution % Compn. | | Wet Solid % Compn. | | Nature of equil. solid phase |
|---|---|---|---|---|---|
| | Phenol | Urea | Phenol | Urea | |
| 1 | ... | 49.8 | ... | ... | Urea |
| 2 | 7.85 | 46.8 | Not analyzed | | Urea (?) |
| 3 | 8.5 | 46.9 | 26.6 | 43.7 | Urea + compd., invariant pt. |
| 4 | 9.3 | 45.3 | 48.8 | 32.7 | Compound |
| 5 | 8.7 | 44.0 | 39.3 | 35.1 | Compound |
| 6 | 7.7 | 40.2 | Not analyzed | | Compound |
| 7 | 8.0 | 38.3 | 47.4 | 30.5 | Compound |
| 8 | 7.5 | 38.2 | Not analyzed | | Compound |
| 9 | 8.2 | 37.0 | Not analyzed | | Compound |
| 10 | 7.9 | 34.6 | 49.6 | 28.7 | Compound |
| 11 | 8.2 | 33.7 | Not analyzed | | Compound |
| 12 | 10.15 | 22.2 | 54.1 | 24.1 | Compound |
| 13 | 11.6 | 17.8 | 43.2 | 20.9 | Compound |
| 14a | 14.35 | 15.15 | 66.3 | 21.2 | Two liquid layers + compd. |
| 14b | 51.9 | 12.8 | 66.3 | 21.2 | |
| 15 | 70.7 | 7.95 | 74.8 | 19.6 | Compound |
| 16 | 86.8 | 2.5 | 94.7 | 5.1 | Compd. + phenol, invariant pt. |
| 17 | 84.5 | 0.0 | ... | ... | Phenol |

If, in Fig. 1, a line is drawn joining the apex ($H_2O$) to the composition of the compound, it is apparent that on treatment with water the compound gives rise to two liquid layers; this is, indeed, visibly the case whenever the compound is treated with water.

## 2. Phenol-*p*-Toluidine

**Heats of Solution in Alcohol.**—For the determination of heats of solution commercial alcohol was used as solvent. This had $d^{20}_4$ 0.8147, corresponding to 95.5% alcohol by weight.

From the approximate coincidence of the heats of solution of *p*-toluidine in alcohol only and in alcohol containing equivalent phenol, it appears that the compound is completely dissociated in solution.

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(3) Magie, *Phys. Rev.*, **16**, 381 (1903). specific heats determined by introducing a weighed portion into one of the cups of the Pfaundler calorimeter.

(4) Thorpe and Whiteley, "Manual of Organic Chemical Analysis," 1925, p. 161.

(5) Hill and Malisoff, This Journal, **48**, 918 (1926).

TABLE III

| Compound | Solvent | Diln. in l. per mole | Heat of soln. in kj. per mole |
|---|---|---|---|
| Phenol | 95.5% EtOH | 7.47 | − 4.00 |
| | | 2.18 | − 4.25 |
| | | 1.14 | − 4.20 |
| | | 0.96 | − 4.00 |
| *p*-Toluidine | EtOH containing equiv. phenol | 21.0 | −14.0 |
| | | 2.91 | −13.4 |
| | | 1.40 | −12.85 |
| | | 1.00 | −12.6 |
| | Alcohol only | 1.10 | −12.45 |
| Compound: 1 Phenol: 1 *p*-Toluidine | Alcohol | 29.7 | −26.1 |
| | | 12.85 | −23.2 |
| | | 5.2 | −22.8 |
| | | 2.38 | −21.9 |
| | | 1.155 | −21.6 |

**Heat of Formation.**—Taking the values for the highest concentrations, where the experimental error is least, we have

1 phenol + 1 *p*-toluidine = 1 compound + $x$ kj.
$-4.00 + (-12.6) = -21.6 + x$
$x = 5.0$ kj. = 1.195 kcal.

**Specific Heats.**—

| | Sp. ht. in cal./g. Obsd. | Lit. value | Molar heat obsd. in cal./mole |
|---|---|---|---|
| *p*-Toluidine | 0.277 | 0.387[a] | 29.7 |
| | | .232[a] | |
| Compound: 1 Phenol: 1 *p*-toluidine | .258 | .... | 51.8 |

[a] "Int. Crit. Tables."

**Heat of Formation of Phenol:*p*-Toluidine, at Absolute Zero.**—

Molar heat phenol + molar heat *p*-toluidine = 52.1
Molar heat compound = 51.8
$C_{\text{products}} - C_{\text{reactants}} = -0.3$
$\Delta H_0 = 1.195 - 0.3(293)/1000 = 1.11$ kcal.

**Equilibrium Diagram.**—Analytical difficulties rendered the exact working out of the equilibrium diagram (in water) difficult. The results, however, were sufficient to show that the greater part of the diagram is occupied by the equilibrium of two liquid layers: invariance is produced with *p*-toluidine, not compound, as the solid phase.

### 3. β-Naphthylamine:*p*-Nitrosodimethylaniline

**Heats of Solution (in Acetone).**—

TABLE IV

| Compd. | Solvent | Diln. in l. per mole | Heat of soln. in kj. per mole |
|---|---|---|---|
| β-Naphthylamine | Acetone | 13.65 | −12.0 |
| | | 4.33 | −12.35 |
| | | 2.86 | −11.35 |
| | Acetone contg. equiv. *p*-nitrosodimethylaniline | 4.10 | −11.9 |
| *p*-Nitrosodimethylaniline | Acetone | 6.70 | −10.9 |
| | | 3.67 | −10.25 |
| | | 2.77 | −11.6 |
| Compound: 2 β-naphthylamine 3 *p*-nitrosodimethylaniline | Acetone | 56.0 | −66.3 |
| | | 24.5 | −62.6 |

The compound is completely dissociated in acetone solution, as an inspection of the heats of solution shows.

**Heat of Formation.**—The accuracy of the determinations of heat of solution is not good, owing to the slow rate of solution, even in acetone, which was the best solvent found. Mean values are therefore taken for the calculation, despite the fact that in strictness only values for the same dilution should be used; in other words, we assume that the heats of solution do not vary with dilution, and that the observed variations are errors of experiment. The calculation gives

2 β-Naphthylamine + 3 *p*-nitrosodimethylaniline = compound + $x$ kj.
$2(-11.9) + 3(-10.9) = -64.6 + x$
$x = 8.1$ kj./mole = 1.94 kcal./mole

**Specific Heats.**—

| | Sp. ht. in cal./g. obsd. | Molar heat in cal./mole |
|---|---|---|
| β-Naphthylamine | 0.210 | 30.1 |
| *p*-Nitrosodimethylaniline | .329 | 49.4 |
| Compound | .279 | 205.0 |

**Heat of Formation of 2 β-Naphthylamine: 3 *p*-Nitrosodimethylaniline at Absolute Zero.**—

2 Molar heat naphthylamine + 3 molar heat nitrosodimethylaniline = 208.4
Molar heat compound = 205.0
$C_{\text{products}} - C_{\text{reactants}} = -3.4$
$\Delta H_0 = 1.94 - 3.4(293)/1000 = 0.94$ kcal.

**Equilibrium Diagram.**—Analytical difficulties made the study of the equilibrium diagram impossible. There were, however, indications that the molecular compound lies within the transition interval at 20°.

### 4. Salicylic Acid–Acetamide

**Heats of Solution (in 95.5% alcohol).**—

TABLE V

| | Solvent | Diln. in l. per mole | Heat of soln. in kj. per mole |
|---|---|---|---|
| Salicylic acid | Alcohol | 3.68 | −13.0 |
| | | 1.78 | −13.2 |
| | | 1.17 | −13.65 |
| Acetamide | Alc. contg. equivalent sal. acid | 3.92 | −11.4 |
| | | 1.74 | −10.15 |
| | | 1.04 | −10.3 |
| | Alcohol | 1.9 | −10.6 |

Table V (*Concluded*)

| | Solvent | Diln. in l. per mole | Heat of soln. in kj. per mole |
|---|---|---|---|
| Compound: | Alcohol | 17.9 | −24.3 |
| 1 Salicylic | | 6.45 | −23.2 |
| acid | | 2.79 | −23.3 |
| | | 1.87 | −24.0 |
| 1 acetamide | | 1.41 | −24.9 |
| | | 1.13 | −24.1 |

The compound is almost completely dissociated in alcohol solution.

**Heat of Formation.**—If the assumption is made that the variation in the heats of solution are errors of measurement and the means taken for the calculation, the heat of formation results as +0.1 kj./mole. In view of the smallness of this heat of formation, it was thought better to graph the results for salicylic acid (decreasing with dilution) and for acetamide (increasing with dilution) and to apply the interpolated values to each experimental value for the heat of solution of the compound. In this way the following results were obtained.

| Diln. | Heat of formation, kj. per mole |
|---|---|
| 17.9 | +1.5 |
| 6.45 | +0.2 |
| 2.79 | −0.1 |
| 1.87 | +0.4 |
| 1.41 | +1.1 |
| 1.13 | +0.7 |

Mean = +0.63 kj. = 0.15 kcal.

**Specific Heats.**—

| | Sp. heat in cal./g. | Molar heat in cal./mole |
|---|---|---|
| Salicylic acid | 0.1809 | 24.9 |
| Acetamide | .270 | 15.9 |
| Compound | .2055 | 40.5 |

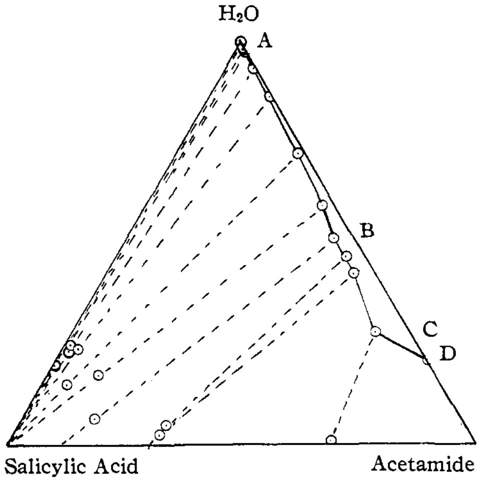

Fig. 2.—AB, Salicylic acid, solution; B, salicylic acid, compound, solution; BC, compound, solution; C, compound, acetamide, solution; CD, acetamide, solution.

**Heat of Formation of Salicylic Acid : Acetamide at Absolute Zero.**—

Molar heat salicylic acid + molar heat acetamide = 40.8
Molar heat compound = 40.5
$C_{\text{products}} - C_{\text{reactants}} = -0.3$
$\Delta H_0 = 0.15 - 0.3(293)/1000 = 0.06$ kcal.

**Equilibrium Diagram.**—The complete equilibrium diagram for salicylic acid–acetamide–water at 20° was readily determined, the salicylic acid being estimated by titration and the acetamide by distillation with sodium hydroxide. The results are contained in Table VI and expressed graphically in Fig. 2.

Table VI

| | Solution, % compn. | | Wet solid, % compn. | | Nature of equil. solid phase |
|---|---|---|---|---|---|
| | Salicylic acid | Acetamide | Salicylic acid | Acetamide | |
| 1 | 0.19 | ... | | | Salicylic acid |
| 2 | .225 | 0.4 | 86.5 | 0.1 | Salicylic acid |
| 3 | .28 | 1.6 | 79.7 | 0.6 | Salicylic acid |
| 4 | .26 | 2.0 | 73.4 | 1.3 | Salicylic acid |
| 5 | .375 | 6.2 | 74.8 | 1.9 | Salicylic acid |
| 6 | .53 | 12.85 | 72.4 | 3.5 | Salicylic acid |
| 7 | 1.30 | 25.9 | 79.7 | 5.1 | Salicylic acid |
| 8 | 2.71 | 37.8 | 71.7 | 11.0 | Salicylic acid |
| 9 | 4.13 | 44.3 | 78.0 | 15.3 | Sal. acid + compd. invariant pt. |
| 10 | 4.24 | 48.9 | 63.7 | 31.2 | Compound |
| 11 | 4.91 | 52.4 | 66.7 | 31.2 | Compound |
| 12 | 7.53 | 64.5 | 30.4 | 68.3 | Compound + acetamide, invariant pt. |
| 13 | .. | 79.3 | .. | .. | Acetamide |

The molecular compound lies within the transition interval.

**Numerical Values Obtained.**—In work of this kind the possible sources of error are so many that it is difficult to assess the final error with any degree of certainty, but we would represent the results for heat of formation as follows

| | System number | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $\Delta H$, in kj. | 10.18 ∓ 0.03 | 5.0 ∓ 0.3 | 8.1 ∓ 2.4 | 0.63 ∓ 0.53 |

The high uncertainty in 3 is due, as mentioned above, to a slow rate of solution in this system.

The only error in the specific heats that we can assess is that of reproducibility in different determinations, which we put at ∓0.01 calorie per gram. The specific heats are all mean values applying to the range 0–20°.

## Discussion of Results

It is apparent that the heats of formation of all these double compounds are small, though not always as small as might be expected from the feebleness of chemical union usually attributed to such compounds. If the rather gross assumption is made that the difference of molar heats of reactants and products remains constant down to absolute zero, then the resulting heats of formation at absolute zero are also the free energies of formation at that temperature. These quantities stand in the relation: 33 : 19 : 16 : 1 for the compounds in the order treated. In agreement with this order, it is found that the compound phenol : urea is by no means completely dissociated in aqueous solution, while salicylic acid : acetamide is. On the other hand the compounds of phenol and *p*-toluidine and of $\beta$-naphthylamine and *p*-nitrosodimethylaniline are also completely dissociated in solution. Dissociation in solution, however, is governed by other factors than free energy of formation; neither is it certain that the order of the free energies of formation at absolute zero remains quantitatively or even qualitatively the same at room temperature. The assumption also that the difference $C_{\text{products}} - C_{\text{reactants}}$ remains constant down to the neighborhood of absolute zero is certainly incorrect, so that the values obtained can only be considered crude approximations. Exact calculations can be made by means of the Nernst heat theorem, but this requires an exact knowledge of the behavior of the specific heats between absolute zero and room temperature.

The determination of equilibrium diagrams in the presence of a solvent was only experimentally possible for the systems phenol–urea–water, and salicylic acid–acetamide–water. In the former case the equilibrium solid phase over a large portion of the diagram is the double compound, while in the latter the double compound is still the stable solid phase over a fairly extensive branch of the diagram. Here, again, there is no direct connection between the heat of formation, or free energy of formation, and the portion of the diagram occupied by double compound, other factors, such as solubility, entering in.

## Summary

1. The object of this paper is to obtain some measure of the energy change involved in the formation of organic addition compounds.

2. Using the systems phenol–urea, phenol–*p*-toluidine, $\beta$-naphthylamine–*p*-nitrosodimethylaniline, and salicylic acid–acetamide, experimental determinations have been made, both for reactants and products, of heat of solution, specific heat, and solubility diagram (in the case of two systems only).

3. The heats of formation at room temperature and at absolute zero, have been calculated, the latter approximately only.

4. The equilibrium diagrams for the systems phenol–urea–water and salicylic acid–acetamide–water at 20°, have been outlined. In both cases the molecular compound is stable at room temperature.

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# Thermal Data XI. The Heat Capacities and Entropies of Guanidine Carbonate, Glutamic Acid Hydrochloride, Ornithine Dihydrochloride, *d*-Lactic Acid and *l*-Lactic Acid

BY HUGH M. HUFFMAN, EMORY L. ELLIS AND HENRY BORSOOK

In this paper we present the low temperature heat capacity data for the salts of three nitrogen containing organic compounds and the two optically active forms of lactic acid. These data have been utilized in conjunction with an empirical extrapolation formula to calculate the entropies of these compounds at 298.1°K.

## Experimental

In principle the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heat. The details of the method have been described elsewhere[1] so that only a brief account need be given. In brief it consists of supplying, electrically, a measured amount of energy to the gold calorimeter containing the substance under investigation. To ensure rapid attainment of thermal equilibrium, the substance is pressed into dense pellets, about 2 mm. thick, and spaced along the centrally located thermocouple well by means of thin gold disks which are in good thermal contact with the walls of the calorimeter. The electrical measurements of current and voltage are made on a "White" double potentiometer

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[1] Parks, THIS JOURNAL, **47**, 338 (1925).