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The Heat of Formation of Binary Liquid Solutions from Their Liquid Components

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It is pointed out that an equation giving the relation of the heat of formation per mol of liquid solutions from their liquid components, to temperature and composition can be used as the foundation equation for their thermodynamical theory. The empirical equation

$$\Delta H = N_1(1-N_1)(\alpha+\beta e^{\gamma N_1}),$$

in which ΔH is the heat of formation per mol of the solution, N_1 is the mol fraction of one of the components of the binary solution, and α, β and γ are constants or functions of temperature, is presented. There are two degenerate forms of this equation. (Eqs. (7) and (8).) There are listed values of α, β and γ (or the values of the corresponding quantities in Eqs. (7) and (8)) for 59 solutions for one temperature and sometimes for several temperatures. It is noted that according to the data assembled in the *International Critical Tables*, some solutions composed of "unassociated" liquids present a behavior more irregular than those composed of "associated" liquids. It is suggested that this unexpected behavior may mean that some of these data are not as precise as they are indicated to be.

I. Use of the Heat of Formation Equation as the Foundation Equation for the Complete Thermodynamical Theory of the Solution

It has long been known that many of the problems of solutions can be reduced to that of finding the dependence of their thermodynamical properties upon temperature and composition. This has been done for dilute solutions, for "ideal" solutions,[1] for van der Waals solutions[2] (i.e., those in which the van der Waals equation can be used as the equation of state of the components of the solutions in both the liquid and gaseous state) and for one or two other types of solutions. Only the theory of van der Waals solutions has any general application and this yields only qualitative results.

We cannot get all of these relations from thermodynamics alone. We must have at least one of them to start with. In the case of "ideal" solutions we can take as the fundamental extra-thermodynamical relation

$$f_1 = N_1 f_1^0 \qquad (1)$$

where f_1 is the fugacity of any component in the solution, N_1 is its mol fraction, and f_1^0 is its fugacity in a pure phase of the same kind (solid, liquid or gaseous) as that of the solution.

Now by the methods of K. Watanabe[3] we can derive the equation, valid for any component in any solution

$$\ln f_1 = \ln N_1 f_1^0 - \int_{(P,\ N_1)} \frac{\overline{H}_1 - H_1^0}{RT^2} dT, \qquad (2)$$

in which $\overline{H}_1$ is the partial molal heat content of the component in the solution, H_1^0 is its molal heat content in the pure phase, T is the temperature and R is the gas constant. The integration is indicated to be at constant pressure and composition. This integral is evidently the correction term necessary to make (1) (written in the logarithmic form) applicable to non-ideal solutions. And the $\overline{H}_1 - H_1^0$ appearing in the integrand can be related to the heat of formation of the solution by differentiation of the obvious equation

$$H_s - n_1 H_1^0 - n_2 H_2^0 = \Delta H(n_1+n_2)$$

(in which H_s is the heat content of a solution containing n_1 mols of component one and n_2 mols of component two and ΔH is the heat of formation *per mol* of the solution) with respect to

[1] Lewis and Randall, *Thermodynamics*, Chapters XIX and XX.

[2] van der Waals and Kohnstamm, *Lehrbuch der Thermostatik*, Part II.

[3] Watanabe, *On the Vapour Pressure of Liquid*, Tokyo Science Reports, Sect. A, No. 6 (1931).

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n_1(T, p and n_2 constant). This gives

$$\bar{H}_1 - H_1^0$$
$$= (n_1+n_2)\left[\frac{\partial \Delta H}{\partial n_1}\right]_{n_2,\ T,\ p} + \Delta H$$
$$= (n_1+n_2)\left[\frac{\partial \Delta H}{\partial N_1}\right]_{n_2,\ T,\ p}\left[\frac{\partial N_1}{\partial n_1}\right]_{n_2,\ T,\ p} + \Delta H \quad (3)$$
$$= (1-N_1)\left[\frac{\partial \Delta H}{\partial N_1}\right]_{T,\ p} + \Delta H.$$

(There is a similar equation for solutions of more than two components but we are concerned with binary solutions only in this article.)

It is evident then that Eq. (2) enables us to use any relation giving the dependence of ΔH on N_1 and T as the fundamental extra-thermodynamical equation for non-ideal solutions. But before turning to such equations we will give a derivation of (2).

For the change

dn_1 (pure liquid)

$+(n_1+n_2)$ (solution)$\rightarrow(n_1+n_2+dn_1)$ (solution)

we have a change of free energy and of heat content

$$dn_1(\bar{F}_1 - F_1^0), \qquad dn_1(\bar{H}_1 - H_1^0).$$

These two quantities are related by an equation from the general theory of thermodynamics

$$\left[\partial\frac{(\bar{F}_1 - F_1^0)dn_1}{T}\Big/\partial T\right]_{N_1,\ p} = -\frac{(\bar{H}_1 - H_1^0)dn_1}{T^2}.$$

Here dn_1, the amount dissolved, is, of course, independent of T. Cancelling this out and integrating we get (after dividing by R)

$$\frac{\bar{F}_1 - F_1^0}{RT} = \ln\frac{f_1}{f_1^0}$$
$$= -\int_{(N_1,\ p)} \frac{\bar{H}_1 - H_1^0}{RT^2}dT + g(N_1, p), \quad (4)$$

in which $g(N_1, p)$ is an arbitrary function.

Consider now the solution under any pressure p and any temperature T. If we first increase the pressure until it exceeds the critical pressure of the solution and then increase the temperature until it exceeds the critical temperature, we will have passed by a series of *continuous* states from a liquid solution to a gaseous solution. It seems safe to assume that the form of the function $g(N_1, p)$ is not altered in the first step of this process and that it is not changed at all by the second step; and since the gaseous solution is ideal or can be made so by a further increase in temperature we can use the relations for ideal solutions

$$\bar{H}_1 - H_1^0 = 0, \quad f_1 = N_1 f_1^0,$$

which give us

$$g = \ln N_1.$$

Substitution into (4) then gives the desired Eq. (2).

II. The Baud-Heitler Equation

In 1915 Baud[4] brought forth the equation

$$\Delta H = bN_1(1-N_1), \quad (5)$$

in which b is a constant, and showed that his equation served for a number of solutions. Later Heitler[5] gave a derivation of this equation based upon statistical mechanics and gave some of the thermodynamical relations for solutions for which this equation holds. Hildebrand[6] also used this equation in developing the thermodynamics of a new class of solutions which he has called "regular solutions." It is probably the most serviceable equation for the heat of formation of binary solutions that has been previously developed.

III. A New Heat of Formation Equation

It is evident then that the study of the function $\Delta H(T, N_1)$ offers a promising approach to the problem of extending the thermodynamical theory of solutions. We have sought first to find an equation for the relation between ΔH and N_1 which would serve for solutions in which the

[4] Baud, *Analyse Thermique des Melanges Binaires*, Bull. Soc. Chim. (4) **17**, 329–45 (1915).

[5] Heitler, Ann. d. Physik (4) **80**, 630 (1926).

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Baud-Heitler one fails. A purely empirical analysis of the results assembled in the *International Critical Tables* resulted in the following equation:

$$\Delta H = N_1(1-N_1)(\alpha+\beta e^{\gamma N_1}), \qquad (6)$$

where α, β and γ are either constants or functions of temperature. This formula was found to have a wide application, but before turning to this we will consider some interesting special cases.

If α and β are of opposite sign then it may happen that ΔH changes in sign as we proceed over the composition range. This is a frequent phenomenon. If γ is small enough to enable us to use the approximation $e^x = 1+x$ then Eq. (6) reduces to

$$\Delta H = N_1(1-N_1)(\alpha_1+\beta_1 N_1), \qquad (7)$$

in which α_1 and β_1 are new constants or functions of temperature. If either β or γ is zero then the equation reduces to the Baud-Heitler form

$$\Delta H = N_1(1-N_1)\alpha_2. \qquad (8)$$

Finally if α, β and γ are all zero we have, of course, the case of the "ideal" solution.

In Table I we have listed values for α, β and γ (or α_1 and β_1, or α_2 as the case may be) for a number of solutions. In the first four columns we give these and the temperature (or interval within which the temperature lies). In columns five to eight we give some data which are intended to give some notion of how well the equation serves. In column five is listed the maximum value of a deviation index which is the numerical value of

$$\frac{\Delta H \text{ given by the equation} - \Delta H \text{ given by experiment}}{\text{Average of experimental values (all considered positive)}} \times 100.$$

We did not use the percentage deviation for if we had sought to make this a minimum, it would have meant giving the greater weight to observations of smaller numerical value, where the relative precision is lower. We assumed that, unless otherwise indicated, the absolute precision was the same for all measurements. Hence we sought to keep the absolute deviations as small as possible and our index indicates how well we were able to do this. In some cases all of the data except one could be represented nicely by our equation. In these cases we ignored this one result in the determination of α, β and γ and the index of deviation. Hence we have given in columns six and seven the number of observations ignored and the total number of them. (In this last we included the two zero values of ΔH at $N_1=1$ and $N_1=0$.) In some cases while what data there were could be easily represented by our equation, their distribution over the composition range was so poor as to make uncertain the applicability of the equation or, assuming this, the values for α, β and γ given. Hence in column eight we have commented on the distribution of the data.

In Figs. 1 and 2 we give two illustrations. In Fig. 1 we have plotted the heat of formation of CS_2-$C_{10}H_{16}$ (pinene) solutions against the mol fraction of CS_2. The solid line is the plot of the

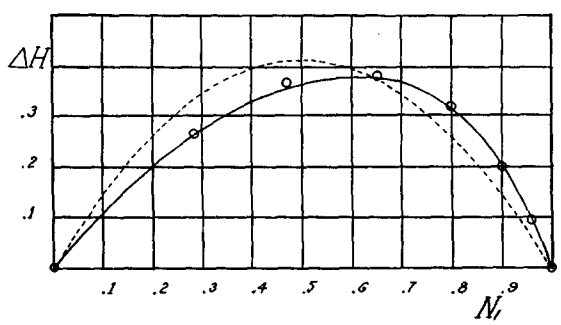

FIG. 1. Variation of heat of formation of $CS_2-C_{10}H_{16}$ solutions with mol fraction of CS_2.

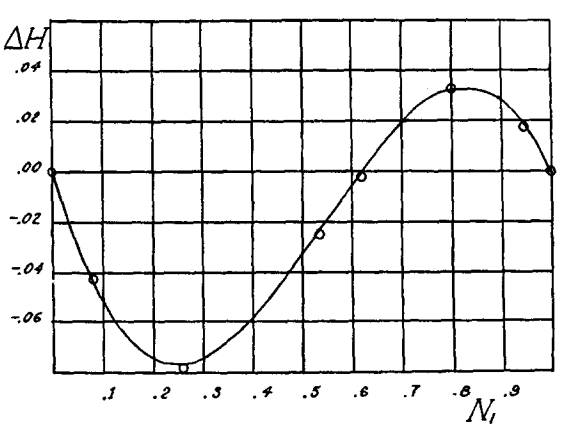

FIG. 2. Variation of heat of formation of $C_2H_4Cl_2-C_7H_8$ solutions with mol fraction of $C_2H_4Cl_2$.

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TABLE I.

(The heat unit used is the kilojoule.)

Component two	t°C	α, α_1 or α_2	β or β_1	γ	Maximum index of deviation	Number of observations ignored	Total number of observations	Distribution	Observer
H_2O (Component one)									
CH_4O Methyl alcohol	0	− 2.95	− .0525	5.00	3	0	21	Good	1
CH_4O Methyl alcohol	19.69	− 2.55	− .103	4.00	9	0	21	Good	1
CH_4O Methyl alcohol	42.37	− 1.33	− .234	3.00	3	0	21	Good	1
C_2H_6O Ethyl alcohol	0	− 1.75	− .038	6.06	5	0	21	Good	1
$C_2H_6O_2$ Glycol	32	− 1.40	− .232	3.00	7	1	11	Good	2
$C_2H_6O_2$ Glycol	55	− 1.27	− .213	3.00	2	1	11	Good	2
$C_2H_6O_2$ Glycol	76	− 1.27	− .191	3.00	9	0	11	Good	2
CCl_4 (Component one)									
$C_2H_4Br_2$ Ethylene Bromide	25	1.92	.31	—	5	0	9	Good	3
C_6H_6 Benzene	25	.44	—	—	7	0	8	Good	4
C_6H_7N Aniline	25	4.67	.01	6.20	3	0	13	Good	4
C_7H_8 Toluene	17	.106	.106	—	7	0	11	Good	6
CS_2 (Component one)									
CCl_4 Carbon tetrachloride	25	1.14	.0239	3.00	2	0	11	Good	3
$CHCl_3$ Chloroform	25	1.93	.48	—	2	0	11	Good	3
$C_2H_4Br_2$ Ethylene bromide	25	2.52	.222	2.00	1	0	8	Good	3
$C_4H_8O_2$ Ethyl acetate	25	3.95	.159	2.70	1	0	9	Good	3
$C_4H_{10}O$ Ethyl ether	25	− 1.52	− .63	—	3	0	9	Good	3
C_6H_6 Benzene	4	1.77	.0531	3.00	3	0	11	Good	7
C_6H_6 Benzene	14.5	1.73	.055	3.00	2	0	10	Good	6
C_6H_6 Benzene	25	1.93	.67	—	4	0	8	Good	3
$C_6H_{12}O_3$ Paraldehyde	25	3.90	.222	3.00	7	0	9	Good	3
$C_{10}H_{16}$ Pinene	25	1.10	.0790	3.00	5	0	9	Good	3
$CHCl_3$ (Component one)									
CCl_4 Carbon tetrachloride	25	.890	.11	—	5	0	8	Good	3
C_2H_6O Ethyl alcohol	25	− 6.30	11.3	—	8	1	11	Good	3
$C_4H_8O_2$ Ethyl acetate	25	− 5.77	−4.55	—	5	0	10	Fair	3
$C_4H_{10}O$ Ethyl ether	25	−10.5	—	—	4	0	10	Good	3
$C_4H_{10}O$ Ethyl ether	14	− 9.96	—	—	7	1	11	Good	6
C_6H_5Cl Chlorobenzene	15–20	− .598	− .210	—	1	0	6	Poor	5
C_6H_6 Benzene	15–20	− 1.00	− .75	—	5	0	8	Good	5
C_6H_6 Benzene	25	− 1.40	− .70	—	8	0	8	Good	3
C_6H_{10} Cyclohexene	15–20	− .443	—	—	3	0	5	Poor	5
C_6H_{12} Cyclohexane	15–20	2.63	—	—	3	0	7	Fair	5
$C_6H_{12}O_3$ Paraldehyde	25	− 6.05	−4.65	—	5	0	9	Good	3
C_8H_{10} p-Xylene	15–20	− 3.23	− .80	—	1	0	8	Good	5
CH_4O Methyl alcohol (Component one)									
C_2H_6O Ethyl alcohol	3	.053	—	—	2	0	5	Fair	8
C_3H_8O n-Propyl alcohol	25	3.00	0.146	3.00	3	0	5	Fair	3
$C_4H_{10}O$ Ethyl ether	25	.57	2.48	—	4	0	9	Good	3
$C_5H_{12}O$ Isoamyl alcohol	25	.22	1.08	—	2	0	5	Fair	3
$C_2H_4Br_2$ Ethylene bromide (Component one)									
$C_2H_4O_2$ Acetic acid	?	2.20	.0722	3.00	2	0	10	Good	12
C_6H_6 Benzene	15–20	1.16	—	—	3	0	9	Good	5
C_6H_{12} Cyclohexane	15–20	5.56	—	—	3	0	14	Good	5
$C_2H_4Cl_2$ Ethylene chloride (Component one)									
C_7H_8 Toluene	15–20	− .690	1.11	—	4	1	9	Good	5
C_2H_4O Acetaldehyde (Component one)									
$C_4H_{10}O$ Ethyl ether	25	−2.29	—	—	2	0	8	Good	3
$C_2H_4O_2$ Acetic acid (Component one)									
C_6H_{12} Cyclohexane	15–20	6.77	—	—	4	1	9	Good	5
C_7H_8 Toluene	15–20	1.49	—	—	3	0	8	Fair	5
H_2O Water	?	2.25	−.376	2.00	9	0	11	Fair	9
C_2H_6O Ethyl alcohol (Component one)									
C_3H_6O Acetone	25	4.63	—	—	9	0	10	Good	3
C_3H_6O Acetone (Component one)									
CH_4O Methyl alcohol	25	2.32	.82	—	2	0	10	Good	3
$C_4H_8O_2$ Ethyl acetate	25	.544	—	—	4	0	9	Good	3
$C_3H_6O_2$ Propionic acid (Component one)									
H_2O Water	8	1.20	7.90	—	4	0	13	Good	9
$C_3H_6O_2$ Methyl acetate (Component one)									
$C_4H_8O_2$ Ethyl acetate	16	.279	—	—	3	1	11	Good	6
$C_4H_8O_2$ Ethyl acetate (Component one)									
C_2H_6O Ethyl alcohol	25	4.70	.114	3.00	4	0	9	Fair	3
C_3H_8O n-Propyl alcohol	25	5.88	.0106	6.00	3	1	10	Good	3
$C_4H_{10}O$ Ethyl ether	25	1.04	—	—	2	0	10	Good	3
$C_4H_{10}O$ Isobutyl alcohol	25	7.43	—	—	4	0	9	Good	3
$C_4H_{10}O$ Ethyl ether (Component one)									
CH_4O Methyl alcohol	25	.57	2.48	—	4	0	9	Fair	3
C_3H_8O n-Propyl alcohol	25	1.94	.189	3.00	4	0	10	Good	3
$C_4H_{10}O$ Isobutyl alcohol	25	2.27	.417	2.00	1	0	10	Good	3
$C_5H_{12}O$ Isoamyl alcohol	25	1.95	.397	2.00	6	0	10	Good	3
$C_6H_{12}O_3$ Paraldehyde	25	1.03	.45	—	5	0	9	Good	3
C_6H_5Cl Chlorobenzene (Component one)									
C_8H_{10} p-Xylene	15–20	− .48	—	—	5	0	7	Good	5
C_6H_6 (Component one)									
CH_4O Methyl alcohol	15	1.10	.240	3.00	10	0	11	Good	6
$C_2H_4O_2$ Acetic acid	?	1.73	.47	—	9	0	15	Good	12
C_6H_{12} Cyclohexane	15–20	3.31	—	—	8	0	7	Good	5
C_6H_{14} n-Hexane	15–20	3.86	—	—	4	0	6	Fair	5
C_7H_8 Toluene	15–20	.298	—	—	7	0	8	Good	5
C_7H_8 Toluene	16	.298	—	—	10	0	11	Good	6
C_6H_{12} Cyclohexane (Component one)									
C_7H_8 Toluene	15–20	2.43	.47	—	10	0	9	Good	5
C_8H_{10} p-Xylene (Component one)									
C_6H_7N Aniline	0	−3.80	−.150	3.00	3	0	8	Poor	11

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equation

$$\Delta H = N_1(1-N_1)(1.10+0.0790e^{3N_1}),$$

the dotted line is the plot of the equation

$$\Delta H = N_1(1-N_1)1.64$$

and the circles represent the experimental data. The dotted line indicates that in this case a Baud-Heitler equation will serve as a rough approximation. The maximum value of the deviation index (for the first equation) ignoring none of the experimental results is five. In Fig. 2 we give a similar graph for $C_2H_4Cl_2-C_7H_8$ (toluene) solutions. The equation is

$$\Delta H = N_1(1-N_1)(-0.690+1.11N_1).$$

The maximum deviation index, ignoring one of the experimental results, is four. The result ignored ($\Delta H = 0.661$, $N_1 = 0.385$) cannot be shown on the graph. The Baud-Heitler equation cannot, of course, be applied to solutions of this type.

There are a large number of cases in which the equation cannot be made to represent the data and it is quite evident that it is not perfectly general. However, solutions composed of such notoriously bad behavers as water and the alcohols gave points on a plot of $\Delta H/N_1(1-N_1)$ against N_1 which could be represented by a simple smooth curve and so it was expected that solutions of simpler (i.e., "unassociated") liquids would do the same. But these in many cases gave very irregular plots. This unexpected behavior suggests that it might be well to check some of these data.

There are not sufficient data available to enable us to attack the remaining part of the problem, the determination of the dependence of α, β and γ on T, in this direct empirical fashion without some preliminary experimental work. We could proceed at once to deduce thermodynamical relations for solutions for which Eq. (6) serves, leaving the α, β and γ in as undetermined functions of temperature. But the resulting equations are so clumsy that their application would be extremely difficult. Hence it seems best to delay this until we have further information concerning α, β and γ. One looks to statistical mechanics for an interpretation of this equation and such investigations when successful will, no doubt, throw some light on these quantities.

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