from which they were calculated. For the ten amino acids the relation $(\bar{S}_1 - \bar{S}_1^0) = km^2$ holds fairly well; the dependence on m^2 is a further reflection of the relative importance of the heat content term in the equation for $(\bar{S}_1 - \bar{S}_1^0)$. The *k* values are listed.

	k
Glycine	0.0023
α-Alanine	−.0023
β-Alanine	−.0020
α-Amino-*n*-butyric	−.0058
α-Amino-*i*-butyric	−.0076
β-Amino-*n*-butyric	−.0056
γ-Aminobutyric	−.0076
α-Amino-*n*-valeric	−.0109
Valine	−.0084
ε-Aminocaproic	−.0185

These negative $(\bar{S}_1 - \bar{S}_1^0)$ values (for all cases except glycine) have been interpreted[7] as structure strengthening effects on the water, the effect increasing with the size of the hydrocarbon residue.

Regardless of the value of these suggestions, it seems clear that purely electrostatic interactions, calculated[18,19,20] for various simplified models, do not suffice to explain the thermochemical behavior of these solutions. The aliphatic radicals seem responsible for the large differences of properties measured.

Summary

Heats of dilution of aqueous solutions of α-amino-*n*-butyric acid, valine, norleucine and ε-aminocaproic acid at 25° have been measured to below 0.001 *m*. From these measurements relative apparent molal heat contents, relative partial molal heat contents, and differential entropies of dilution have been calculated.

Results for eleven amino acids are compared and discussed.

[18] G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

[19] J. G. Kirkwood, *Chem. Revs.*, **19**, 275 (1936).

[20] R. M. Fuoss, THIS JOURNAL, **56**, 1027 (1934); **58**, 982 (1936).

PITTSBURGH, PA. RECEIVED OCTOBER 6, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Liquidus Curve for Aluminum in Mercury

BY HERMAN A. LIEBHAFSKY

The liquidus curve for the aluminum–mercury system is well established above 400° by the concordant results of two investigations.[1,2] Data which complete this curve were obtained in 1934 as part of an investigation into the chemical problems of the mercury boiler and are given below.

Experimental

The "solubility" of commercial (99+%) aluminum in pure mercury was measured by rotating an aluminum-glass stirrer (see Fig. 1) in the solubility vessel, which was inside a cylindrical furnace whose temperature was taken as the temperature of the experiment. Because aluminum amalgam is very easily oxidized, the experiments were carried out in a hydrogen atmosphere. (The hydrogen, passed over copper at 400° and then through a liquid air trap, was pure enough not to cause appreciable oxidation of the amalgam. Since the analytical method measured dissolved metal only, a slight oxidation would not have vitiated the results.) The stirrer fitted into a metal chuck and was driven at approximately 300 r. p. m. with an electric motor. From time to time, samples of amalgam were withdrawn by means of previously evacuated sampling tubes, whose lower tips could easily be broken by forcing them against the bottom of the solubility vessel. The mercury withdrawn was usually replaced.

These samples were immediately analyzed by breaking the bulbs beneath approximately 2 *N* hydrochloric acid in the reaction vessel (Fig. 1) and measuring the evolved hydrogen in a gas buret containing mercury. The vessel was flushed out with hydrogen, stoppered tightly, and connected to the gas buret before each bulb was broken. Gentle warming ensured complete liberation of hydrogen. When the analytical system had returned to room temperature, the volume of hydrogen (assumed to be saturated with water vapor) was read on the buret. The volume of mercury was measured in the graduated side tube attached to the reaction vessel. With room temperature and pressure known, the aluminum content of the sample of amalgam could then be calculated.

As in all investigations of the interaction of mercury with metals, wetting—which does not occur until the natural oxide (or oxygen) film on the metal has been penetrated or removed—had first to be established. In this investigation, wetting was accomplished by simply heating the stationary stirrer in the assembled apparatus in the presence of hydrogen, the rod having been previously sandpapered and rubbed with a clean towel. Usually the wetting was uniform; for example, when such a rod was immersed in mercury and rapidly heated to 360°, wetting began within ten minutes and was complete on the immersed portion of the rod in approximately ten minutes more. Wetting above the liquid line did not occur, which shows that mercury vapor is not so effective in penetrating the natural oxide film. Occasionally, wetting occurred preferentially on the immersed area; aluminum would then disappear most rapidly from the wetted areas, where the rod would be eaten away. The experiments were scheduled so that the amount of aluminum passing into the mercury from the stationary rod did not exceed the solubility at the temperature of the first experiment after a new rod was wetted. Since the hydrogen atmosphere was usually maintained even between experiments, it was possible to use a wetted rod more than once.

The time required to saturate the relatively small volume (*ca.* 35 cc.) of mercury used in the experiments could not be readily determined. With an unwetted rod, this time would depend largely upon the rate at which the mercury penetrated the natural oxide (or oxygen) film, and this unreproducible rate increases markedly with the temperature. For a wetted rod, the usual case, detailed experimental data indicated that the time in question was probably less than an hour. When only one value of the

---

[1] (a) Smits and de Gruijter, *Proc. Kon. Akad. Wetensch Amsterdam*, **23**, 966 (1921); (b) Smits, *Z. Elektrochem.*, **30**, 423 (1924).

[2] Klemm and Weiss, *Z. anorg. allgem. Chem.*, **245**, 285 (1940).

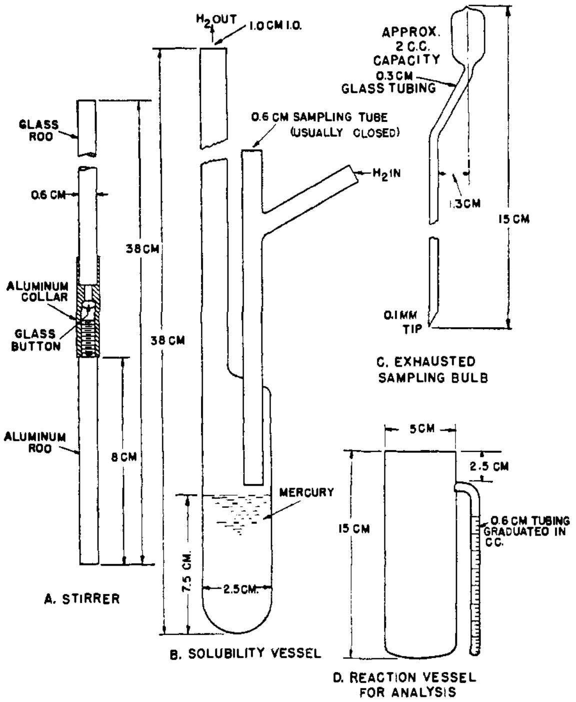

Fig. 1.—Apparatus for solubility measurements and for analysis.

solubility was obtained, about three hours was allowed for saturation. The final results are given in Table I.

TABLE I

SOLUBILITY OF ALUMINUM IN MERCURY

T, °C.	76	101	103	125	160	260	312
No. of values	1	1	2	1	3	2	2
Al (meas.), %	0.0090	0.015	0.017	0.024	0.035	0.11	0.18
Al (calc.),[a] %	.0099	.016	.017	.025	.042	.13	.20

[a] Percentages calculated from the equation $\log_{10} s = 1.240 - 1132/T$.

Discussion

The data of interest in connection with the present results are summarized in Fig. 2, which contains two previously unpublished values by Messrs. F. J. Norton and R. H. Harrington of this Laboratory, whose experimental method closely resembled that of Klemm and Weiss.[2]

In contrast with the results obtained at higher temperatures, the data of the present investigation agree fairly well with the straight line in Fig. 2. (Obviously, this agreement does not mean that the linear relationship is rigorously valid.) In drawing this straight line, the equation for which is given below Table I, the results obtained above 300° have been given some weight. The extrapolated value of the solubility for 20° is 0.0023%, in satisfactory accord with Fogh's[3] statement that all but 0.002 g. of aluminum separates from 100 g. of a saturated solution of aluminum in boiling mercury subsequently cooled to room temperature. Though it is conventional to speak of solubility in cases such as these, it is important to realize that the actual equilibria are established between a liquid solution of aluminum in mercury and a solid phase containing mercury and aluminum, about whose composition the information is incomplete and conflicting.[4]

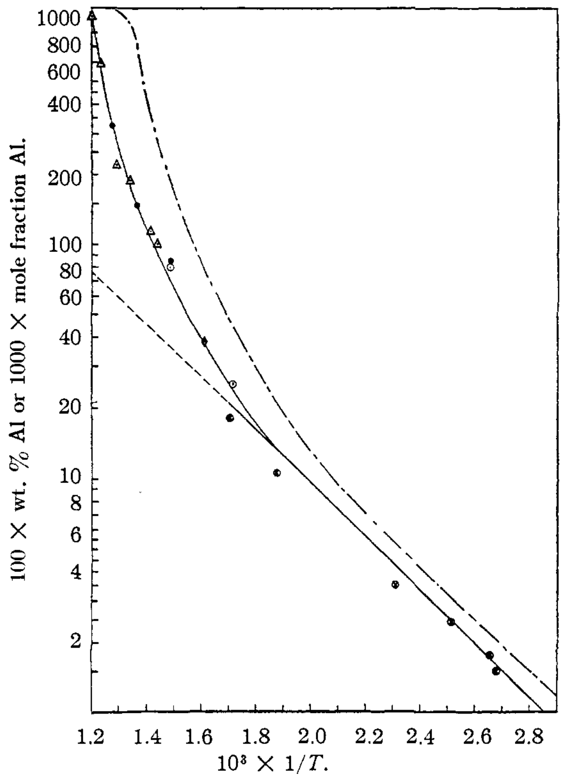

Fig. 2.—Liquidus curve of aluminum in mercury: △, reference 2; ●, ref. 1; ⊙, Norton and Harrington; ⊗, this investigation; ◇, ref. 3; — — —, mole fraction Al (points not shown, abscissa transposed so that 1.2 = 1.0); —, wt. % Al.

As is well known, it is possible in principle to calculate the heat of fusion of aluminum from data like those in Fig. 2.[5] Though a definitive treatment of these data must await the establishment of the solidus curve, it is useful to calculate values of the *apparent* heat of fusion defined by

$$\Delta H^{a}_{A} = -4.575(\Delta \log N_A/\Delta 1/T)_P \qquad (1)$$

where N_A is the mole fraction of aluminum in the liquid phase at temperature T and constant pressure P, and the increments are taken between successive temperatures conveniently spaced. The variation of ΔH^{a}_{A} with composition is clear from Fig. 3, the ordinates for which were obtained as indicated. In the most concentrated region, N_A was calculated by use of the equation % aluminum by weight = 100 − (660 − t°), where t is the centigrade temperature, which adequately

---

[3] Fogh, *Kgl. Danske Videnskab. Selskab. Math.-phys. med.*, **3**, No. 15, 6 pp. (1921), abstracted in *Chem. Zentr.*, **94**, III, 993 (1923).

[4] Hansen, "Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936, pp. 117–118, gives a comprehensive bibliography.

[5] Kelley, "Contributions to the Data on Theoretical Metallurgy, V. Heats of Fusion of Inorganic Substances," Bull. 393, Bureau of Mines, 1936.

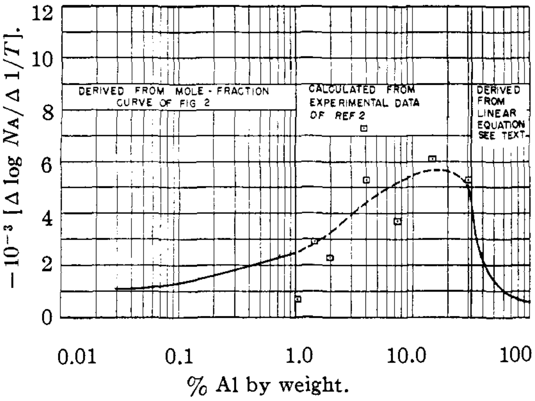

Fig. 3.—Variation of apparent heat of fusion with composition.

expresses the results of Smits and de Gruijter[1a] (*cf.* ref. 4, Fig. 59). In the intermediate region, where the mole-fraction curve has an inflection point, it seemed best to calculate ordinates directly from the experimental results of Klemm and Weiss.[2]

In the aluminum-rich region, the ordinate of Fig. 3 corresponds very closely to +2550 cal., the heat of fusion recommended for aluminum by Kelley.[5] (+2547 cal. was calculated for the interval 90–100% Al.) The pronounced variability over the rest of Fig. 3 may be due to variations in the activity coefficients, to changes in the composition of the solid in equilibrium, or to both.

I wish to thank my colleagues, Messrs. F. J. Norton and R. H. Harrington for permission to publish their two experimental results, and Mr. K. Berman for helping with the calculations.

Summary

1. The aluminum–mercury liquidus curve has been completed by the making of measurements designed to give good results with dilute aluminum amalgams.

2. Within the temperature range 76–312°, the per cent. by weight of aluminum "soluble" in mercury is given by the equation $\log_{10}s = 1.240 - (1132/T)$ to within about 10%.

3. The apparent heat of fusion in this system passes through a maximum as the aluminum content is increased. In nearly pure aluminum, the value of this heat agrees remarkably well with the heat of fusion recommended by Kelley for this element.

Schenectady, New York
Received September 14, 1948

[Contribution from the Research Laboratories of the Institutum Divi Thomae and the Department of Chemistry, Siena Heights College]

The Ultraviolet Absorption Spectra of Some Pyrimidines. Chemical Structure and the Effect of *p*H on the Position of $\lambda_{max.}$[1]

By Miriam Michael Stimson[2]

It has been suggested by Brooker[3] that symmetrical ions should be more stable than unsymmetrical ones. So far this has not been demonstrated experimentally although symmetrical dyes are more stable to *p*H changes than are unsymmetrical ones. In the following discussion an attempt will be made to correlate symmetry and *p*H response in a group of pyrimidines.

One of the most striking of the absorption characteristics of the pyrimidines is the effect of *p*H on the intensity and, frequently, on the position of the absorption maximum (λ_{max}). This change in the position of the absorption maximum with *p*H-($\Delta\lambda_{max}$) seems not to be solely dependent on the nature of the substituent on the pyrimidine ring, since barbituric acid[4] although having a pronounced change in the molar absorbancy index, shows no appreciable change in the position of λ_{max}, while uracil has $\Delta\lambda_{max}$ of 24 mμ. Again it may be noted that in the case of 2-hydroxy-4,6-diaminopyrimidine there is no appreciable change in the position of the absorption maximum with change in *p*H; such a change is observed with both cytosine and isocytosine. From these various types of response to change in *p*H it is suggested that the effect of *p*H might be empirically related to the symmetry of the molecule. Thus both barbituric acid and 2-hydroxy-4,6-diaminopyrimidine may be considered as symmetrical, if the plane of symmetry be imagined to pass through the 2,5-positions. On this basis the pyrimidines under consideration may be classified as symmetrical or unsymmetrical.

In Table I are listed seven pyrimidines, all of which are considered symmetrical with respect to the above mentioned plane. From the data presented the following empirical conclusions may be drawn: (1) The long wave absorption maximum of these compounds seems to be either unaffected or only slightly shifted by the *p*H values employed. (2) In either the 4,6-dihydroxy- or the 4,6-diaminopyrimidines, in which there is also a hydroxy

(1) From the dissertation presented to the faculty of the Institutum Divi Thomae in partial fulfillment of the requirements for the Ph.D., June 1948.

(2) Sister Miriam Michael Stimson, O.P.

(3) Brooker, "Resonance and Organic Chemistry" in "Advances in Nuclear Chemistry and Theoretical Organic Chemistry," ed. Burk and Grummitt, Interscience Publishers, Inc., New York, N. Y., 1945.

(4) Loofbourow and Stimson, *J. Chem. Soc.*, 1275 (1940); Stuckey, *Quart. J. Pharm. Pharmacol.*, **15**, 370 (1942).