that the anion packing is distorted cubic rather than hexagonal close packing. The layers have triangular arrangements of bromine atoms as surfaces, two of the sides of the triangle being equal (3.90 Å.) and corresponding to bromine–bromine contacts between chains and a short side (3.46 Å.) corresponding to contacts within a chain. The arrangement of one layer on another is such that all bromine–bromine contacts are equal within the limits of error of the determination. As might be expected the crystal shows good cleavage in the direction parallel to (100).

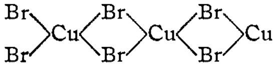
Since the forces orienting one layer over another are relatively weak, the existence of twinning on the (100) face might be expected. This was the most frequent type of twinning found and occurred in almost all crystals of dimensions greater than 0.1 mm.

The fact that the habit of the crystal does not correspond to the X-ray symmetry is disturbing, but the observance of this phenomenon is not limited to this crystal. Attempts to find X-ray evidence for lower symmetry have been unavailing. It is not apparent why the structure as determined should lead to growth in the observed habit

I should like to express my appreciation to the John Simon Guggenheim Foundation for the opportunity to pursue this research, and to the Chemistry Department of the California Institute of Technology for permitting me to use their laboratories.

## Summary

The crystal structure of cuprous bromide has been determined and found to be made up of parallel packing of chains having the arrangement



The arrangement of these chains is such that the copper atoms have two more Br atoms in their coördination sphere but these are at considerably greater, "non-bonded," distances.

The structure is discussed in relation to the similar $PdCl_2$ structure and the arrangement in copper complex ions.

ST. LOUIS, MISSOURI RECEIVED OCTOBER 21, 1946

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[CONTRIBUTION NO. 587 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

# The Heats of Dilution of Aqueous Solutions of Four Amino Butyric Acids at 25°[1]

BY L. S. MASON AND A. L. ROBINSON

The physiological importance of amino acids[2] and the theoretical significance of their dipolar ionic character in aqueous solution[3] have led to a considerable interest in the properties of solutions of such substances. Precise thermochemical data, however, are not extensive. Prior to 1940, the literature contains measurements of the heats of dilution of solutions of glycine[4] at three concentrations from 1.0 to 0.1 $M$, and of eleven amino acids[5] (from one to ten concentration intervals) down to 0.5 $m$ for eight acids, and to 0.1 $m$ for glycine, *dl*-alanine and *dl*-valine. More precise results for glycine[6,7,8] and for $\alpha$- and $\beta$-alanine[9] have been reported.

Using a simplified structural model, Scatchard and Kirkwood[10] examined the activity of zwitterions in salt solutions from the standpoint of the Debye–Hückel theory and concluded that zwitterions behave more like highly polar non-electrolytes than real ions in salt solutions of low ionic strength. The influence of the dielectric constant of the solvent, in addition to the effect of salts, upon the activity of a spherical ion having a complex charge distribution has been studied[11] for the case corresponding to zwitterions in which the net charge is zero and the dipole moment is large. It has been shown[12] for spherical molecules containing point dipoles at the centers that there is a linear limiting relationship between the function, $j$,[13] and the concentration; a linear relationship between the partial molal heat capacity and the concentration was also derived. The latter relationship appears to be corroborated experimentally[14] for glycine, $\alpha$- and $\beta$-alanine. Dependency of $\Phi L_2$, the relative apparent molal heat content, upon the first power of the molality, $m$, seems to be indicated in the case of the amino acids for

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(1) The generous support of the Buhl Foundation in this study is acknowledged.

(2) C. L. A. Schmidt, Editor, "The Chemistry of the Amino Acids and Proteins," Charles C. Thomas, Publisher, Baltimore, Md., 1938.

(3) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides as Ions and Dipolar Ions," Reinhold Publishing Corp., New York, N. Y., 1943.

(4) S. M. Naudé, *Z. physik. Chem.*, **135**, 209 (1928).

(5) C. A. Zittle and C. L. A. Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

(6) J. M. Sturtevant, THIS JOURNAL, **62**, 1879 (1940).

(7) F. T. Gucker, Jr., H. B. Pickard and W. L. Ford, *ibid.*, 2698 (1940).

(8) W. E. Wallace, W. F. Offutt and A. L. Robinson, *ibid.*, **65**, 347 (1943).

(9) H. A. Benesi, F. S. Mason and A. L. Robinson, *ibid.*, **68**, 1755 (1946).

(10) G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(11) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1945).

(12) R. M. Fuoss, THIS JOURNAL, **58**, 982 (1936).

(13) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, Chapter XXVII.

(14) F. T. Gucker, Jr., I. M. Klotz and T. W. Allen, *Chem. Rev.*, **30**, 181 (1942).

TABLE I

INTERMEDIATE HEATS OF DILUTION OF AMINOBUTYRIC ACIDS

| Moles/1000 g. of water | | | No. of expts. | Calories | | | | | | | | Cal./mole of acid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^4 m_1$ | $10^4 m_2$ | $10^4 m_3$ | | Expt. $-10^3$ $q_{1\rightarrow 2}$ | $10^3\delta$ | Eq. $-10^3$ $q_{1\rightarrow 2}$ | $10^3$ $\Delta q_{1\rightarrow 2}$ | Expt. $-10^3$ $q_{3\rightarrow 2}$ | $10^3\delta$ | Eq. $-10^3$ $q_{3\rightarrow 2}$ | $10^3$ $\Delta q_{3\rightarrow 2}$ | $-\Delta H_{1\rightarrow 2}$ | $-\Delta H_{3\rightarrow 2}$ |
| | | | | | | *α*-Amino-*i*-butyric Acid | | | | | | | |
| | | | | | | Eq. 3 | | | | Eq. 2 | | | |
| 8417 | 82.42 | 164.1 | 5 | 1116 | 10 | 1123 | +7.4 | 23 | 11 | 13 | −10 | 136.23 ± 0.51 | 1.43 ± 0.26 |
| 4097 | 41.41 | 82.42 | 5 | 274.5 | 1.3 | 274.6 | +0.1 | 2.9 | 0.7 | 3.3 | +0.4 | 66.71 ± .13 | 0.35 ± .04 |
| 2027 | 20.80 | 41.41 | 4 | 70.4 | 0.3 | 68.3 | −2.1 | 1.2 | .5 | 0.8 | − .4 | 34.05 ± .08 | .28 ± .06 |
| 1010 | 10.45 | 20.80 | 7 | 17.0 | .9 | 17.1 | +0.1 | 0.0 | .5 | .2 | + .2 | 17.22 ± .30 | − .01 ± .07 |
| 505.9 | 5.252 | 10.45 | 7 | 5.3 | .2 | 4.3 | −1.0 | .1 | .2 | .1 | .0 | 10.18 ± .15 | .05 ± .07 |
| 253.7 | 2.639 | 5.252 | 3 | 1.5 | .4 | 1.1 | −0.4 | − .1 | .1 | .0 | + .1 | 5.67 ± .88 | − .16 ± .13 |
| | | | | | | *α*-Amino-*n*-butyric Acid | | | | | | | |
| | | | | | | Eq. 8 | | | | Eq. 7 | | | |
| 8406 | 82.42 | 164.1 | 4 | 874.3 | 8.0 | 877.0 | +2.7 | 13.7 | 3.7 | 11.4 | −2.3 | 106.77 ± .48 | 0.84 ± .11 |
| 4095 | 41.40 | 82.42 | 5 | 215.0 | 3.7 | 214.6 | −0.4 | 7.0 | 2.7 | 2.9 | −4.1 | 52.25 ± .39 | .86 ± .14 |
| 2026 | 20.80 | 41.40 | 3 | 55.0 | 0.2 | 53.4 | −1.6 | 0.5 | 0.2 | 0.7 | +0.2 | 26.61 ± .05 | .11 ± .02 |
| 1011 | 10.45 | 20.80 | 9 | 14.3 | 1.1 | 13.4 | −0.9 | .7 | .3 | .2 | −0.5 | 13.76 ± .29 | .32 ± .05 |
| | | | | | | *β*-Amino-*n*-butyric Acid | | | | | | | |
| | | | | | | Eq. 13 | | | | Eq. 12 | | | |
| 8413 | 82.41 | 164.0 | 4 | 789.9 | 9.2 | 791.4 | +1.5 | 6.8 | 3.7 | 3.1 | −3.7 | 96.46 ± .55 | 0.42 ± .13 |
| 4096 | 41.40 | 82.41 | 3 | 195.4 | 0.4 | 193.6 | −1.8 | 1.5 | 0.5 | 0.7 | −0.8 | 47.48 ± .07 | .19 ± .04 |
| 2027 | 20.80 | 41.40 | 6 | 48.4 | 1.1 | 48.1 | −0.3 | 0.8 | .9 | .2 | − .6 | 23.40 ± .20 | .24 ± .07 |
| 1011 | 10.45 | 20.80 | 8 | 11.4 | 0.7 | 12.1 | + .7 | .0 | .6 | .0 | .0 | 10.93 ± .21 | − .02 ± .10 |
| 505.9 | 5.252 | 10.45 | 4 | 3.2 | .1 | 3.0 | − .2 | − .4 | .1 | .0 | + .4 | 6.04 ± .06 | − .36 ± .03 |
| | | | | | | *γ*-Aminobutyric Acid | | | | | | | |
| | | | | | | Eq. 18 | | | | Eq. 17 | | | |
| 8391 | 82.41 | 164.1 | 4 | 890.4 | 3.0 | 898.7 | +8.3 | 11.9 | 3.1 | 8.3 | −3.6 | 108.73 ± .18 | 0.75 ± .09 |
| 4091 | 41.40 | 82.41 | 5 | 226.6 | 4.8 | 219.7 | −6.9 | 0.5 | 4.9 | −0.1 | −0.6 | 55.08 ± .53 | .06 ± .25 |
| 2025 | 20.80 | 41.40 | 8 | 57.6 | 2.5 | 54.4 | −3.2 | −0.6 | 3.5 | + .4 | +1.0 | 27.96 ± .33 | − .15 ± .27 |
| 1010 | 10.45 | 20.80 | 8 | 13.5 | 0.9 | 13.8 | −0.3 | −1.8 | 1.7 | + .1 | +1.9 | 12.99 ± .29 | − .86 ± .26 |

which sufficiently precise data are available up to the present time.[7,8,9]

Because of the uncertainties in the values of the limiting slopes of $\Phi L_2$ *vs.* $m$ in previous studies, and to obtain systematic information for a group of related substances, a study of the heats of dilution of four isomeric amino butyric acids was undertaken. Values for *α*-amino-*n*-butyric acid and *α*-amino-*i*-butyric acid might be expected to indicate differences in heat effects due to structural variation. Values for *β*-amino-*n*-butyric acid and *γ*-amino-*n*-butyric acid might afford a comparison of the effect of the amino group in the *α*, *β* and *γ* positions in the otherwise identical compounds.

## Experimental

### Apparatus and Method

The only significant change in the heat of dilution calorimeter which has been previously fully described[15,16] was the introduction of a new thermopile. The details of design and construction of this unit have been described.[17]

Solutions were diluted from 10-ml. monel metal pipets into about a liter of water or dilute solution. The pipets were calibrated by weighing the amount of water delivered from them. They were also calibrated in the following manner. The pipets, mounted in the calorimeter, were filled with standard 0.1 *M* sodium chloride solution in the same manner as when a dilution experiment was to be performed. The sodium chloride solution was then withdrawn, the pipets carefully rinsed, and the sodium chloride solution titrated with standard silver nitrate solution. The volumes of the pipets calculated from these determinations agreed within 0.1% with the volumes determined by weighing the water delivered.

The highest sensitivity of the thermopile-galvanometer system, determined by electrical heating, corresponded to a heat effect of $2.5 \times 10^{-4}$ cal. per mm. galvanometer deflection.

### Materials

**Distilled water** from the stock supply was distilled again from a Yoe still. This water was boiled to remove carbon dioxide, saturated with nitrogen, and kept out of contact with the atmosphere. Frequent checks of the conductivity and *p*H of the dilution water demonstrated the absence of significant amounts of impurities. Preceding dilution experiments, the calorimeter was swept out with nitrogen, filled with carbon dioxide-free water, and operated as a closed system. Elimination of carbon dioxide seemed advisable in order to prevent disturbances of the dissociation equilibria of the amino acids. The interior of the calorimeter and all internal accessories were coated with paraffin in an effort to eliminate any possible extraneous heat effects due to adsorption.

**The Amino Acids.**—The origin, purification, and determination of purity of the *α*-amino-*i*-butyric acid, *α*-amino-*n*-butyric acid, *β*-amino-*n*-butyric acid, and *γ*-aminobutyric acid, together with determinations of the densities of aqueous solutions of the four acids, have been reported.[18]

All of the solutions for the dilution experiments were prepared by volume from carefully dried samples just before use. In no case were solutions allowed to stand long enough for the composition to be altered by the growth of molds.

## Experimental Results and Treatment of Data

**Relative Apparent Molal Heat Contents.**—In Table I are shown the measured heat effects (column 5, expt., $-10^3\ q_{1\rightarrow 2}$), the number of experiments (column 4) performed at each concen-

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[15] E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931).

[16] W. E. Wallace and A. L. Robinson, THIS JOURNAL, **63**, 958 (1941).

[17] L. S. Mason, *Rev. Sci. Instruments*, **15**, 205 (1944).

[18] L. S. Mason, unpublished.

TABLE II

DERIVED VALUES FOR $S$, $\Phi L_2$, $\bar{L}_1$ AND $\bar{L}_2$ FOR AMINOBUTYRIC ACID SOLUTIONS

| | α-Amino-*i*-butyric acid | α-Amino-*n*-butyric acid | β-Amino-*n*-butyric acid | γ-Amino-butyric acid |
|---|---|---|---|---|
| $S$ | (1) 97 | (6) 86 | (11) 23 | (16) $-86.1 + 14{,}300\ m$ |
| $\Phi L_2$ ($m < 0.02$) | (2) $97\ m$ | (7) $86\ m$ | (12) $23\ m$ | (17) $-86.1 + 7150\ m^2$ |
| $\Phi L_2$ | (3) $165\ m$ | (8) $128\ m$ | (13) $115\ m$ | (18) $131\ m$ |
| $\bar{L}_1$ | (4) $-2.96\ m^2$ | (9) $-2.31\ m^2$ | (14) $-2.07\ m^2$ | (19) $-\ 2.36\ m^2$ |
| $\bar{L}_2$ | (5) $329\ m$ | (10) $257\ m$ | (15) $230\ m$ | (20) $262\ m$ |

tration interval, the average deviation from the mean value (column 6, $10^3\ \delta$), and the molal heats of dilution (column 13, $-\Delta H_{1\rightarrow 2}$) for the long chord dilutions ($m_1$ to $m_2$); and the corresponding quantities (columns 9, expt., $-10^3\ q_{3\rightarrow 2}$; 10, $10^3\ \delta$; 14, $-\Delta H_{3\rightarrow 2}$) for the short chord dilutions ($m_3$ to $m_2$) for solutions of α-amino-*i*-butyric, α-amino-*n*-butyric, β-amino-*n*-butyric and γ-aminobutyric acids.

Established methods[19,20,21] were used for the treatment of the heats of dilution data.

Figures 1, 2, 3 and 4 are plots of the short chords, $\bar{P} = \Delta H/\Delta m$ *vs.* $m$, used for the determination of the slope, $S = \partial(\Phi L_2)/\partial m$, which after integration gives $\Phi L_2$ for the short chord concentration region. $\Phi L_2$ values calculated from these equations (eq. 2, 7, 12, 17 in Table II) for $m_2$ were combined with the experimental $\Delta H$'s for the long chord dilutions to give values of $\Phi L_2$ for the concentrations, $m_1$. Equations for $\Phi L_2$ for the entire concentration range studied were then derived from the long chord and short chord $\Phi L_2$'s for each of the compounds (eq. 3, 8, 13, 18 in Table II).

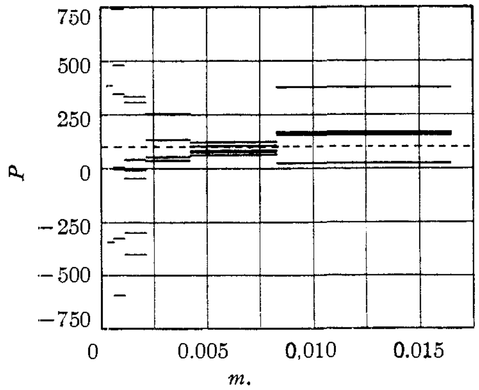

Fig. 1.—Plot of short chords $\bar{P}$ *vs.* $m$ for α-amino-*i*-butyric acid: - - - -, weighted average $\bar{P}$.

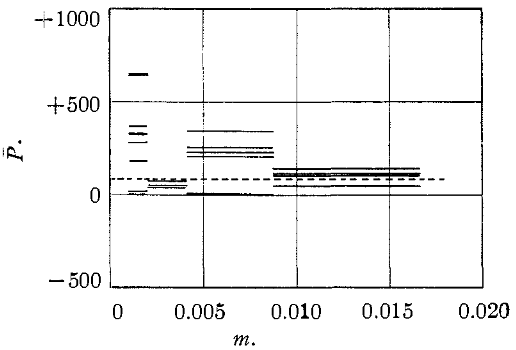

Fig. 2.—Plot of short chords $\bar{P}$ *vs.* $m$ for α-amino-*n*-butyric acid: - - - -, weighted average $\bar{P}$.

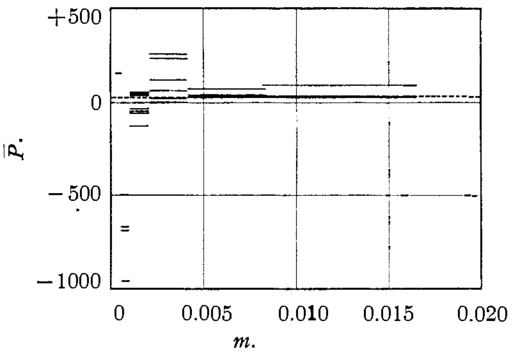

Fig. 3.—Short chords, $\bar{P}$ *vs.* $m$, for β-amino-*n*-butyric acid: - - - -, weighted average $\bar{P}$.

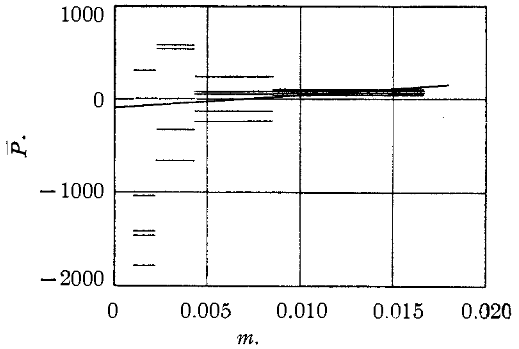

Fig. 4.—Plot of short chords, $\bar{P}$ *vs.* $m$, for γ-aminobutyric acid: curve is $S = \partial(\Phi L_2)/\partial m$.

Plots of $\Phi L_2$ *vs.* $m$ for the four acids are shown in Fig. 5.

$q$-Values for the long chords calculated from the derived equations for $\Phi L_2$ are listed in the tables in column 7 (eq., $-10^3\ q_{1\rightarrow 2}$). The differences between measured and calculated values are in column 8 ($10^3\ \Delta q_{1\rightarrow 2}$). The corresponding quantities for the short chords calculated from the $\Phi L_2$ equations derived for the short chord concentrations are shown in columns 11 (eq., $-10^3\ q_{3\rightarrow 2}$) and 12 ($10^3\ \Delta q_{3\rightarrow 2}$).

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[19] T. F. Young, *et al.*, THIS JOURNAL, **54**, 3030 (1932); **58**, 187 (1936); **60**, 2379 (1938).

[20] A. L. Robinson and W. E. Wallace, *ibid.*, **63**, 1582 (1941).

[21] A. L. Robinson and W. E. Wallace, *Chem. Rev.*, **30**, 195 (1942).

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS

| | α-Amino-*i*-butyric acid | | | α-Amino-*n*-butyric acid | | | β-Amino-*n*-butyric acid | | | γ-Aminobutyric acid | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $m$ | $\Phi L_2$ Cal./ mole acid | $-\bar{L}_1$ Cal./mole $H_2O$ | $\bar{L}_2$ Cal./ mole acid | $\Phi L_2$ Cal./ mole acid | $-\bar{L}_2$ Cal./mole $H_2O$ | $\bar{L}_1$ Cal./ mole acid | $\Phi L_2$ Cal./ mole acid | $-\bar{L}_1$ Cal./mole $H_2O$ | $\bar{L}_2$ Cal./ mole acid | $\Phi L_2$ Cal./ mole acid | $-\bar{L}_1$ Cal./mole $H_2O$ | $\bar{L}_2$ Cal./ mole acid |
| 1.2 | 198 | 4.27 | 395 | 154 | 3.33 | 308 | 138 | 2.99 | 276 | 157 | 3.40 | 314 |
| 1.0 | 165 | 2.96 | 329 | 128 | 2.31 | 257 | 115 | 2.07 | 230 | 131 | 2.36 | 262 |
| 0.8 | 132 | 1.90 | 263 | 102 | 1.48 | 205 | 92.0 | 1.33 | 184 | 105 | 1.51 | 210 |
| .6 | 99.0 | 1.07 | 198 | 76.8 | 0.832 | 154 | 69.0 | 0.747 | 138 | 78.6 | 0.850 | 157 |
| .4 | 66.0 | 0.474 | 132 | 51.2 | .370 | 103 | 46.0 | .332 | 92 | 52.4 | .378 | 105 |
| .2 | 33.0 | .119 | 65.8 | 25.6 | .092 | 51.3 | 23.0 | .083 | 46 | 26.2 | .094 | 52.4 |
| .1 | 16.5 | .029 | 32.9 | 12.8 | .023 | 25.7 | 11.5 | .0207 | 23 | 13.1 | .024 | 26.2 |
| .01 | 1.65 | $3.0 \times 10^{-4}$ | 3.29 | 1.28 | $2.3 \times 10^{-4}$ | 2.57 | 1.15 | $2.1 \times 10^{-4}$ | 2.30 | 1.31 | $2.4 \times 10^{-4}$ | 2.62 |
| .001 | 0.165 | $3.0 \times 10^{-6}$ | 0.329 | 0.128 | $2.3 \times 10^{-6}$ | 0.257 | 0.115 | $2.1 \times 10^{-6}$ | 0.230 | 0.131 | $2.4 \times 10^{-6}$ | 0.262 |
| .0001 | .017 | $3.0 \times 10^{-8}$ | .033 | .013 | $2.3 \times 10^{-8}$ | .026 | .012 | $2.1 \times 10^{-8}$ | .023 | .013 | $2.4 \times 10^{-8}$ | .026 |

**Relative Partial Molal Heat Contents.**—Values of $\bar{L}_1$ and $\bar{L}_2$ for each compound were calculated from equations derived from the equations for $\Phi L_2$ ($m_1$) by means of the Rossini expressions.[22]

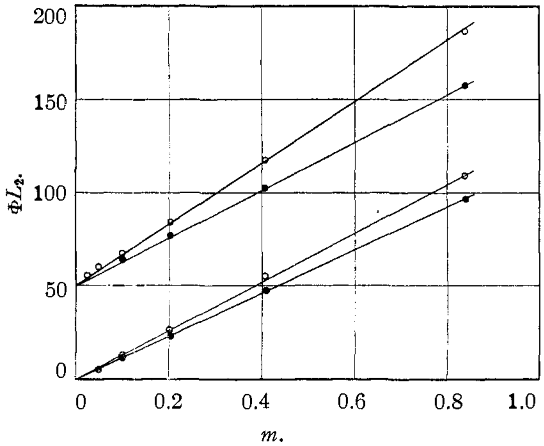

Fig. 5.—Plot of $\Phi L_2$ *vs.* $m$ for α-*i*, α-*n*, β-*n*, and γ-aminobutyric acids. Upper curves: ○ = α-amino-*i*-butyric acid; ● = α-amino-*n*-butyric acid. Lower curves: ○ = γ-aminobutyric acid; ● = β-amino-*n*-butyric acid.

Numerical values of $\Phi L_2$, $\bar{L}_1$ and $\bar{L}_2$ at several rounded concentrations for each acid are shown in Table III.

The equations derived for each of the substances investigated are shown in tabular form in Table II.

## Discussion of Results

The small magnitude of the heat effects in the short chord regions makes difficult the obtaining of highly consistent data. In the cases of the α-*i*, α-*n*, and β-*n*-acids, examination of the plots of $\bar{P}$ *vs.* $m$ for the short chord dilutions indicated that a precise mathematical derivation for $S = \partial(\Phi L_2)/\partial m$ was unwarranted. The dotted lines in Figs. 1, 2 and 3 represent an average $\bar{P}$ value for the range $m < 0.02$. This value was derived by averaging the mean values of the determinations at each concentration interval, weighting each mean value in terms of its probable error. In the case of the γ-acid there appeared to be a sufficiently pronounced trend in the $\bar{P}$ values to warrant a least squares treatment of the data to derive the slope equation. This curve is shown in Fig. 4 as a solid line. These slopes for $\Phi L_2$ *vs.* $m$ at the very low concentrations are somewhat smaller in each case than the slopes of the $\Phi L_2$ curves for the complete concentration ranges. This discrepancy is probably due to experimental errors rather than to actual behavior.

In the case of the present compounds, the $\Phi L_2$ values for $m < 0.02$ are useful chiefly for providing values at $m_2$ to be added to the $\Delta H$ values for dilutions from $m_1$ to $m_2$ to evaluate $\Phi L_2$ for $m_1$. The limiting slopes for $\Phi L_2$ for the complete concentration ranges are considered more significant than the limiting slopes of the equations for the very low concentration ranges. Experimental points for $m_2$'s are not shown in Fig. 5 because their inclusion would require a graph enormously expanded in $m$. The agreement between the curves for the derived $\Phi L_2$ equations and the experimental values seems to establish a linear relationship between $\Phi L_2$ and $m$ for these compounds at least up to $m = 1.0$.

It has been suggested[23] that the presence of carbon dioxide in the dilution water could influence the magnitude of the heat effects at low concentrations by disturbing the dissociation equilibria of the amino acids in solution. In the present study, sufficient care was exercised to exclude carbon dioxide so that any effect due to it might be negligible. However, some experiments were performed with equilibrium water for comparison. As has been reported previously,[8] a consistent effect due to carbon dioxide could not be observed. It seems doubtful that the concentration of carbon dioxide in equilibrium water ($10^{-5}$ $M$) could exert significant buffering effect in the presence of dissolved amino acids at concentrations of $10^{-3}$ and greater. The heat effects at low concentrations of the amino acids are considerably smaller in general than for electrolytes at comparable concentrations.

Examination of the heats of dilution data for glycine, α- and β-alanine and the four amino butyric acids seems to indicate that the size and

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[22] F. D. Rossini, *J. Research Bur. Standards*, **4**, 313 (1930).

[23] J. M. Sturtevant, THIS JOURNAL, **62**, 3519 (1940).

structure of the organic radical have a greater effect on the thermochemical properties of these solutions than the location of the amino group. Over most of the concentration range studied the $\Phi L_2$ values for glycine solutions[3] are negative. The addition of a methyl group in α-alanine and an ethyl group in α-amino-*n*-butyric acid are accompanied by large increments in $\Phi L_2$ values. Only one case of radical isomerism is available for examination; the two methyl groups in α-amino-*i*-butyric acid seem to have a greater influence on the property measured than the normal radical. In the alanines and the four amino butyric acids, the location of the amino group seems to be the factor of least importance. The magnitude of the $\Phi L_2$ values for *dl*-valine solutions[5] is in general agreement with these considerations.

## Summary

The heats of dilution of aqueous solutions of α-amino-*i*-butyric, α-amino-*n*-butyric, β-amino-*n*-butyric, and γ-aminobutyric acids at 25° have been measured from 0.8 to 0.001 *m*. Linear equations for $\Phi L_2$ as a function of *m* have been derived for each of the four acids. The slopes of these curves are as follows: $\alpha\text{-}i = 165$; $\alpha\text{-}n = 128$; $\beta\text{-}n = 115$; $\gamma = 131$. Relative partial molal heat contents of the solutes and the solvent have been evaluated.

PITTSBURGH, PA. RECEIVED MARCH 7, 1946

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[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, U. S. BUREAU OF MINES]

# Preparation and X-Ray Diffraction Studies of a New Cobalt Carbide[1]

BY L. J. E. HOFER[2] AND W. C. PEEBLES[3]

At atmospheric pressure and 226–230° carbon monoxide and finely divided cobalt will react to form a product whose composition (9.3% carbon) corresponds to the formula $Co_2C$.[4] The reaction is slow under the above conditions, requiring some five hundred hours to come to completion. The product reacts readily and completely with hydrogen at 240–250° to form cobalt metal and methane. When the temperature of carburization is higher than 230°, the rate of reaction is greater; furthermore, the amount of carbon deposited is not limited to 9.3% but increases without apparent restriction as long as the metal is exposed to carbon monoxide. The product so formed does not react completely with hydrogen at 240–250° to form methane and cobalt; instead a residuum of carbon remains, which reacts with hydrogen only at temperatures above 350°, and complete reaction of the carbon is not achieved even at 620°. The amount of carbon in the product which reacts readily with hydrogen at 240–250° or lower may equal but never exceeds the amount which corresponds to the formula $Co_2C$. Carbon may thus be deposited upon or in cobalt metal in two forms, which are quite sharply differentiated by the temperature ranges at which they react with hydrogen. No sample carburized above 315° contained appreciable amounts of carbon capable of hydrogenation at or below 250°. Bahr and Jessen called the easily hydrogenated carbon (capable of hydrogenation below 250°) "carbidic carbon"; the residuum they called "free carbon." Bahr and Jessen infer that carbon combined with cobalt to form a homogeneous phase is more highly reactive than free carbon. However, this homogeneous phase may be either a terminal solid solution of carbon in α-cobalt (hexagonal close-packed) or a carbide of a distinct crystal structure. Meyer[5] made an X-ray diffraction study of cobalt carburized at various temperatures with illuminating gas. He concluded that the easily hydrogenated carbon produced by carburization in the 225–300°, range was held in solid solution in the interstices of the lattice of α-cobalt. However, he did find a distinct crystalline carbide isomorphous with cementite, $Fe_3C$, in samples carburized between 450–600°. The present paper will demonstrate that the easily hydrogenated carbon is combined with cobalt to form a distinct new crystalline species.

## Experimental

**Materials.**—The carbon monoxide gas was prepared by the action of concentrated sulfuric acid on A. C. S. specification formic acid, density 1.2, at 120-150°. The gas was passed over solid sodium hydroxide pellets and stored in a gas-holder over water. It was then passed over calcium chloride, copper at red heat, soda lime, calcium chloride, and magnesium perchlorate.

Electrolytic hydrogen from tanks was further purified by passing over palladized asbestos at 300° and then successively over soda lime, calcium chloride, and magnesium perchlorate.

Nitrogen from tanks (99.7% pure), was passed over copper at red heat, soda lime, calcium chloride and magnesium perchlorate.

The cobalt oxide was prepared by precipitation. A 0.1 *M* solution of cobalt nitrate, A. C. S. specification, was heated to 85°. Ammonium hydroxide, 24% solution, was then added with stirring until further addition caused no more precipitation. The rose-colored precipitate was washed by decantation with a very dilute ammonium hydroxide solution (0.028%) until a sample of the precipitate dissolved in hydrochloric acid gave a negative nitrate test. The X-ray diffraction pattern of this pre-

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(4) H. A. Bahr and V. Jessen, *Ber.*, **63**, 2226 (1930).

(5) W. Fr. Meyer, *Z. Krist.*, **97**, 145 (1937); *Metallwirtschaft*, **17**, 413 (1938).