

## The Compressibility of Solutions of Three Amino Acids

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This equation, important in the determination of entropy from heat capacity, yields an  $f_1^1$ -family of eight members.

### 8. The equations of the type:

$$(\partial H/\partial T)_{P, n_i} - (\partial E/\partial T)_{V, n_i} = T(\partial P/\partial T)_{V, n_i} \cdot (\partial V/\partial T)_{P, n_i}. \quad (23)$$

Eq. (23) is the familiar relation between the two heat capacities written as an  $f_1^1$ -equation. It is found to belong to an  $f_1^1$ -family of four members.

### 9. Remark on the number of members in an $f_1^1$ -family

The number of members in an  $f_1^1$ -family evidently cannot exceed eight. All the families mentioned above have either eight or four members. These are however not the only possibilities because the two  $f_1^1$ -equations:

$$E - F = TS - PV, \quad (24)$$

$$E - H + F - A = 0, \quad (25)$$

are seen to belong to  $f_1^1$ -families of two members and one member, respectively. Some theorems

concerning the number of members in a family will be given in a later paper (communication II).

### 10. Concluding remarks

It is evident that the method here described greatly increases the number of fundamental equations which are readily available. The method can however scarcely be regarded as an alternative to P. W. Bridgman's<sup>4</sup> condensed summary of differential coefficients because it differs too much from the latter both in requirements and in results. It may perhaps find some use as a supplement to the method of Bridgman.

More valuable than the proliferation of formulae seems the way in which the above considerations reveal the symmetry of the equations of thermodynamics, a keen sense of which is helpful to any student of the subject.

The author is indebted to Dr. C. F. Luther of the Department of Mathematics, Stanford University, for much valuable advice.

<sup>4</sup> P. W. Bridgman, *Phys. Rev.* [2] **3**, 273 (1914); see also G. N. Lewis and M. Randall, *Thermodynamics*, etc. pp. 163-165 (1923).

## The Compressibility of Solutions of Three Amino Acids

P. W. BRIDGMAN AND R. B. DOW, *Research Laboratory of Physics, Harvard University*

(Received October 22, 1934)

The compressibility of aqueous solutions of glycine,  $\alpha$ -amino butyric acid, and  $\epsilon$ -amino caproic acid have been measured over the concentration range up to 2.5 N at 25° and 75°C and up to a maximum pressure of 8000 kg/cm<sup>2</sup>. The results are exhibited in tables giving the volume in cm<sup>3</sup> as a function of pressure, temperature, and concentration of that amount of solution which contains one gram of water, and in figures showing the apparent

molal volume at 25° as a function of pressure and concentration. The general character of the results is complicated; the most striking result is that at low pressures the apparent compressibility of the acid in solution is positive, which is opposite in sign from all other known solutes. A connection is probable with the high dielectric constant. Other qualitative aspects of the phenomena are discussed.

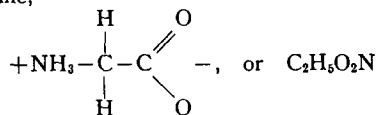
**A** NUMBER of the physical properties of that very interesting group of highly polar substances known as Zwitterions have been studied during the last few years. Dr. E. J. Cohn,<sup>1</sup> of the Harvard Medical School, who has contributed so much to our knowledge of these substances suggested that a study of the com-

pressibility at high pressures might be expected to be of interest, and he very kindly undertook to provide the materials from his highly purified stock. It was desired to study the compressibility over as wide a range of concentration as possible, which demanded that the substance have high solubility, and also over as wide a range of composition as possible. The following representatives of the class of Zwitterions were therefore

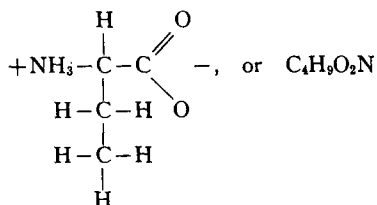
<sup>1</sup> Edwin J. Cohn, *Die Physikalische Chemie der Eiweisskörper*, *Ergebnisse der Physiologie* **33**, 782-882 (1931).

selected with Dr. Cohn's advice, as best meeting these requirements:

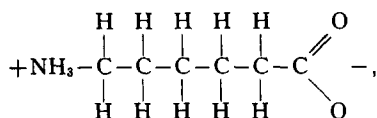
Glycine,



$\alpha$ -amino, butyric acid,



$\epsilon$ -amino caproic acid,



or



The method of measurement was the sylphon method, which has already been used in determining the compressibility of some 50 different liquids, and which has been described in detail elsewhere.<sup>2</sup> The pressure range was limited by the solubility of the acid. The solubility of these three acids decreases under pressure, so that if pressure is pushed high enough, separation into two phases, solution and solid acid, takes place. Precipitation of the solid is in practice an irreversible process, because, although on reducing pressure re-solution will take place and the solution will eventually become homogeneous again by diffusion, the process of homogenization after precipitation is so very slow because of high viscosity that it is impossible to wait for completion of the process. The upper pressure limit in the following was 8000 kg/cm<sup>2</sup>, and in a number of cases the limit was lower. No attempt was made to get exact values for the effect of

pressure on solubility, and the pressure limits of the tables should not be taken as having any significance in this regard. Sometimes 8000 kg may have exceeded the solubility limit, but precipitation failed to take place because of supersaturation phenomena, while at other times the saturation limit doubtless was not reached, but the pressure limit may have been set instead by incidental considerations peculiar to that particular experiment. No runs were accepted in computing the final results in which precipitation was known to have occurred; the criterion was that the points obtained with decreasing pressure failed to coincide with those obtained with increasing pressure.

The compositions studied of glycine were: 0.5, 1.0, 1.5, 2.0 and 2.5 molal; of  $\alpha$ -amino butyric acid 0.5 and 1.5 molal, and of  $\epsilon$ -amino caproic acid 0.5, 1.0, 1.5, 1.75, 2.0, and 2.5 molal. The concentration 1.75 molal was at first omitted from the  $\epsilon$ -amino caproic series. On calculating and plotting the results such surprising departures from linearity appeared that a check was imperative, although the method had shown itself capable of high precision when used before. Accordingly the runs at 1.5 and 2.0 molal on  $\epsilon$ -amino caproic acid were repeated with freshly prepared material, and the new composition 1.75 molal was interpolated. The results for this new composition lay within the error of the repetition on the curve which had been previously drawn to represent the results previously obtained, thus checking the reality of the nonlinear effects. The order of reproducibility of the results can be estimated from the fact that the average departure from the mean of all the readings of the relative volume was 0.0010, and the maximum departure, which occurred at the maximum pressure 8000, was 0.0030. This agreement is not as good as has usually been obtained with other liquids. The irregularities were not explained with complete satisfaction, but were doubtless connected with the material itself. The solutions were usually found to be slightly discolored when the sylphon was emptied at the end of a pressure run, and the conventional chemical tests showed the presence of some iron after the runs, although the sylphon was made entirely of brass, copper, and solder, and the same test

<sup>2</sup> P. W. Bridgman, Proc. Am. Acad. Sci. **66**, 185 (1931); **67**, 1 (1932); **68**, 1 (1933).

TABLE I. Volume of glycine solutions.

Pressure kg/cm <sup>2</sup>	Pure Water Vol. of 1 g		0.5 Molal Vol. of 1 g water 0.03847 g acid		1.0 Molal Vol. of 1 g water 0.07874 g acid		1.5 Molal Vol. of 1 g water 0.12097 g acid		2.0 Molal Vol. of 1 g water 0.16523 g acid		2.5 Molal Vol. of 1 g water 0.21222 g acid	
	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C
1	1.0029		1.0255		1.0490		1.0747		1.1015		1.1307	
250	.9929		1.0148		1.0370		1.0635		1.0909		1.1191	
500	.9834	1.0055	1.0050	1.0300	1.0254	1.0530	1.0533	1.0822	1.0807	1.1051	1.1081	1.1356
750	.9741	.9969	.9962	1.0214	1.0149	1.0426	1.0437	1.0723	1.0713	1.0954	1.0978	1.1254
1000	.9637	.9885	.9880	1.0130	1.0050	1.0324	1.0344	1.0628	1.0620	1.0860	1.0880	1.1152
1500	.9494	.9729	.9726	.9967	.9878	1.0143	1.0171	1.0444	1.0442	1.0683	1.0705	1.0969
2000	.9355	.9578	.9593	.9824	.9722	.9981	1.0016	1.0277	1.0279	1.0528	1.0551	1.0808
2500	.9232	.9444	.9467	.9689	.9583	.9836	.9873	1.0129	1.0141	1.0394	1.0409	1.0664
3000	.9119	.9325	.9352	.9566	.9451	.9701	.9739	.9993	1.0006	1.0258	1.0278	1.0535
4000	.8918	.9117	.9153	.9359	.9227	.9460			.9785	1.0036	1.0045	1.0296
5000	.8739	.8938	.8984	.9187	.9028	.9258			.9596	.9845	.9838	1.0089
6000	.8578	.8777	.8842	.9039	.8848	.9079			.9424	.9666		.9901
7000	.8428	.8698		.8905		.8921				.9501		.9736
8000	.8289	.8509		.8784		.8780				.9350		.9587

had shown no iron before the run. However, the original material from which the acid was purified was known to contain some iron, so that it is perhaps possible that iron may have been initially present in the solution in a form undetectable by the conventional test and then transformed by pressure into a detectable form. Any irregularities of this nature are, however, entirely too small to change appreciably the results when shown on the scale of magnitude of the figures, and any conclusions to be drawn here will not be affected. But a complete thermodynamic discussion of the properties of solutions under pressure, such for example as that recently given by Adams and Gibson<sup>3</sup> at the Geophysical Laboratory in deducing the solubility limits, demands that differentiations be performed with respect to the various variables, pressure, temperature and composition. Care should be used in subjecting the data of this paper to operations of this sort, and conclusions drawn from such operations should be carefully examined.

The results were computed according to methods already described, which give immediately the relative volumes, the volume of each solution at 25° at atmospheric pressure being taken as unity. For purposes of discussion the results may be presented in many ways, depending on the use to which they are to be put. It has seemed that perhaps the best general idea of the nature of the results is given by tabulating the volumes, as function of pressure, temperature and concentration, of that amount

of solution which contains one gram of water. In comparing solutions of different strengths the water factor thus remains constant, and the difference is due to the different amounts of acid. The results are presented in this form in Table I for glycine, Table II for  $\alpha$ -amino butyric

TABLE II. Volume of  $\alpha$ -amino butyric acid solutions.

Pressure kg/cm <sup>2</sup>	Pure Water Vol. of 1 g		0.5 Molal Vol. of 1 g water 0.0537 g acid		1.5 Molal Vol. of 1 g water 0.1751 g acid	
	25°C	75°C	25°C	75°C	25°C	75°C
1	1.0029		1.0425		1.1324	
250	.9929		1.0301		1.1213	
500	.9834	1.0055	1.0189	1.0449	1.1109	1.1394
750	.9741	.9969	1.0094	1.0351	1.1016	1.1298
1000	.9637	.9885	1.0009	1.0258	1.0933	1.1206
1500	.9494	.9729	.9863	1.0108	1.0784	1.1038
2000	.9355	.9578	.9732	.9970	1.0649	1.0894
2500	.9232	.9444	.9613	.9841	1.0518	1.0764
3000	.9119	.9325	.9504	.9725	1.0385	1.0635
4000	.8918	.9117	.9301	.9527	1.0141	1.0387
5000	.8739	.8938	.9115	.9339		
6000	.8578	.8777	.8968	.9172		
7000	.8428	.8698	.8834			
8000	.8289	.8509	.8714			

acid, and Table III for  $\epsilon$ -amino caproic acid. In recalculating the results for presentation in this form in the tables the densities of the solutions at 25° and atmospheric pressure and the molecular weights were involved. It is possible to reconstruct the densities from the values given in the tables, but for convenience they are given here explicitly; they were originally determined in Dr. Cohn's laboratory, and are still partially unpublished.

	Glycine	Densities at 25°C. $\alpha$ -amino butyric	$\epsilon$ -amino caproic
0.5 M	1.01268	0.5 M 1.01075	0.5 M 1.01041
1.0	1.02822	1.5 1.03767	1.0 1.02338
1.5	1.04303		1.5 1.03620
2.0	1.05775		1.75 1.04221
2.5	1.07181		2.0 1.04822
			2.5 1.06016

<sup>3</sup> L. H. Adams and R. E. Gibson, J. Am. Chem. Soc. 52, 4252 (1930). R. E. Gibson and L. H. Adams, *ibid.* 55, 2679 (1933). L. H. Adams, *ibid.* 53, 3769 (1931); 54, 2229 (1932).

TABLE III. Volume of  $\epsilon$ -amino caproic acid solutions.

Pressure kg/cm <sup>2</sup>	Pure Water Vol. of 1 g		0.5 Molal 1 g water Vol. of { 0.0694 g acid 75°C		1.0 Molal 1 g water Vol. of { 0.1469 g acid 75°C		1.5 Molal 1 g water Vol. of { 0.2342 g acid 75°C		1.75 Molal 1 g water Vol. of { 0.2823 g acid 75°C		2.0 Molal 1 g water Vol. of { 0.3336 g acid 75°C		2.5 Molal 1 g water Vol. of { 0.4476 g acid 75°C	
	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C	25°C	75°C
1	1.0029		1.0583		1.1207		1.1913		1.2307		1.2723		1.3655	
250	.9929		1.0473		1.1073		1.1818		1.2204		1.2610		1.3542	
500	.9834	1.0055	1.0369	1.0632	1.0946	1.1281	1.1726	1.1967	1.2106	1.2370	1.2502	1.2822	1.3435	1.3712
750	.9741	.9969	1.0274	1.0537	1.0827	1.1157	1.1637	1.1873	1.2018	1.2281	1.2407	1.2706	1.3336	1.3607
1000	.9657	.9885	1.0181	1.0448	1.0721	1.1043	1.1557	1.1784	1.1937	1.2196	1.2305	1.2607	1.3240	1.3506
1500	.9494	.9729	1.0012	1.0278	1.0537	1.0836	1.1403	1.1629	1.1790	1.2047	1.2130	1.2419	1.3086	1.3324
2000	.9355	.9578	.9857	1.0118	1.0381	1.0663	1.1267	1.1486	1.1658	1.1900	1.1973	1.2248	1.2914	1.3156
2500	.9232	.9444	.9721	.9972	1.0237	1.0507	1.1143	1.1356	1.1535	1.1764	1.1838	1.2098	1.2763	1.3006
3000	.9119	.9325	.9595	.9840	1.0099	1.0363	1.1026	1.1237	1.1425	1.1644	1.1698	1.1954	1.2646	1.2870
4000	.8918	.9117	.9368	.9616	.9849	1.0108	1.0822	1.1022	1.1225	1.1432	1.1463	1.1713	1.2406	1.2627
5000	.8739	.8938		.9432	.9633	.9889	1.0642	1.0829	1.1044	1.1249	1.1253	1.1498	1.2206	1.2417
6000	.8578	.8777		.9275	.9446	.9688	1.0490	1.0663	1.0884	1.1084	1.1057	1.1301	1.2021	1.2226
7000	.8428	.8698			.9269	.9509	1.0348	1.0518	1.0732	1.0934	1.0872	1.1121	1.2065	
8000	.8289	.8509			.9112	.9346	1.0218	1.0391	1.0572	1.0797	1.0697	1.0940	1.1919	

The molecular weights used in the calculations were, respectively, 75.047, 103.077 and 131.108.

The "apparent molal volume" of the acid in solution may be readily obtained from the data in the tables. The apparent molal volume is defined as the difference between the volume of that amount of solution in which is dissolved one gram molecule of the acid and the volume in the pure state of the amount of water contained in the same solution. To illustrate the method of calculation, the apparent molal volume of glycine in 0.5 molal solution at 25° is obtained by subtracting the volume of pure water listed in column 2 of Table I from the volume of the 0.5 M solution listed in column 4, and multiplying the difference by 75.047/0.03847. The apparent molal volumes at 25°, calculated in this way, of the three solutions are shown in Figs. 1 to 3 as a function of pressure.

If there were no interaction between the water and the acid in the solution, that is, if our calculation of the apparent molal volume had been applied not to the solution but to a compound system containing pure water and the solid acid, the curves of apparent molal volume against pressure would have been the same for all concentrations, and would fall smoothly with pressure, the slope being a measure of the compressibility of the solid. The failure of the curves to possess this simple property is due to the interaction between water and acid in the solution.

The state of affairs in the solution as revealed by these curves is most complicated, so complicated that it would be hopeless, in the present condition of the theory of solutions, to attempt

a detailed explanation of all the features; all that will be attempted will be a qualitative comment on a couple of the most striking features.

In one important particular the behavior of these three acid solutions under pressure is sharply different from that of all other solutions hitherto investigated. The curve of apparent molal volume against pressure of solutions of electrolytes and those few non-electrolytes which have been measured rises over the entire range of pressure, except possibly in a very few cases at the highest pressures. This result for ordinary electrolytes at first appears paradoxical, for it means that the apparent molal compressibility of the dissolved substance, defined as the negative pressure derivative of the apparent molal volume is negative. This paradoxical result receives qualitative explanation in Tammann's theory of solutions, which is that any aqueous solution behaves approximately like pure water under some higher pressure. The essential role of the dissolved substance according to this picture is merely to increase the internal pressure of the solvent water by a fixed amount; except for this the dissolved substance acts as an inert addendum to the system with constant volume. The negative apparent molal compressibility of the dissolved substance is a consequence of this hypothesis, as a little algebra shows at once, utilizing the fact that the compressibility of water decreases with increasing pressure. A second approximation would add to the compressibility of the water at a higher pressure the compressibility of the dissolved substance, but this is small for such typical solutes as NaCl,

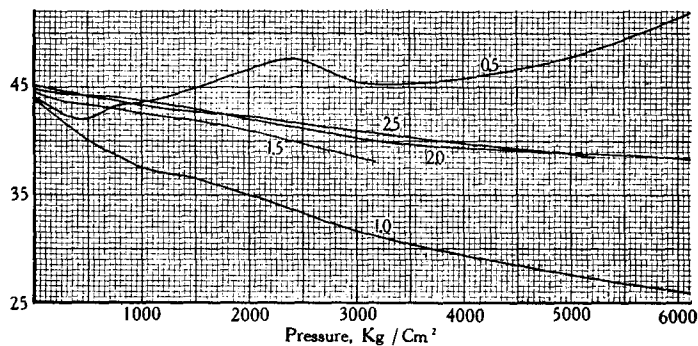


FIG. 1. The apparent molal volumes at 25°C of glycine as a function of pressure. The figures on the curves give the molal concentrations.

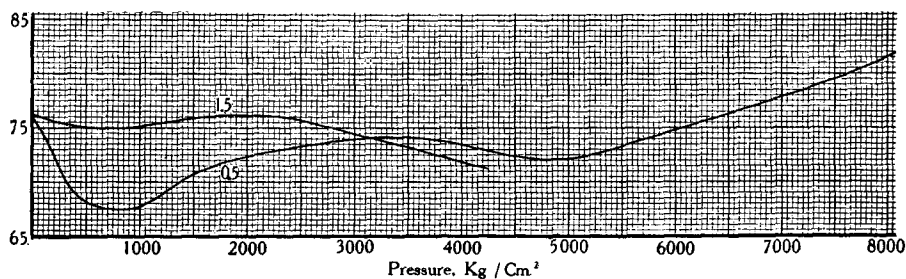


FIG. 2. The apparent molal volumes at 25°C of α-amino butyric acid as a function of pressure. The figures on the curves give the molal concentrations.

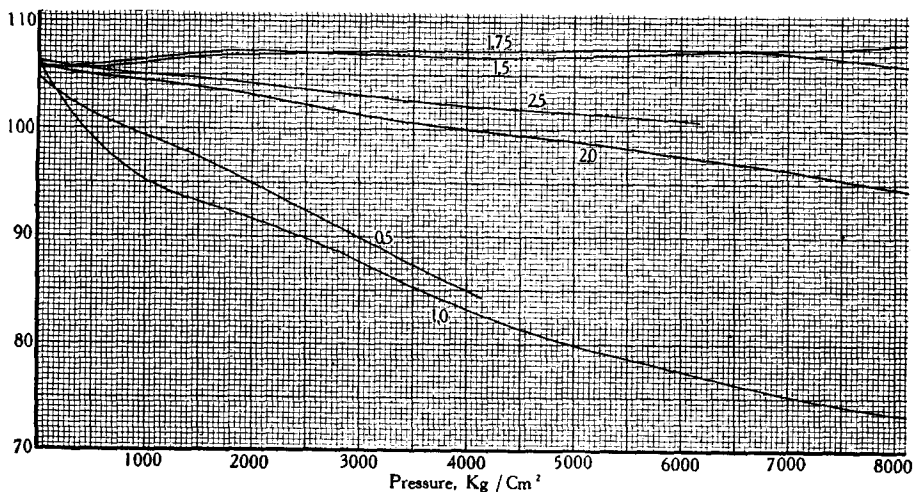


FIG. 3. The apparent molal volumes at 25°C of ε-amino caproic acid as a function of pressure. The figures on the curves give the molal concentrations.

and the situation is dominated by the water.

Contrasted to this almost universal behavior is the behavior of these solutions of Zwitterions. The initial slopes at practically all concentrations of the curves of apparent volume against pressure are negative, that is, the apparent compressibility of the dissolved substance is positive. Expressed in terms of Tammann's theory this would mean that the effect of the dissolved substance is here to *decrease* the internal pressure of the water, instead of to increase it. It seems not unreasonable that such a decrease of internal pressure is to be correlated with the dielectric behavior of these solutions. It has been established by the work of Wyman<sup>4</sup> and others that the dielectric constant of a solution of a Zwitterion in water is higher than the already high dielectric constant of the water. An increase of dielectric constant means a decrease of the intensity of the forces arising from electric charges, and hence a diminution of that part of the internal pressure arising from forces between electric charges separated by distances so great that the intervening medium acts as an approximately homogeneous medium with the mean dielectric constant. This, however, can be only one of the features in the situation, for it is known that solutions of urea, which are unusual in that they increase the dielectric constant of water, are normal in that the urea in solution has a negative, although abnormally low, apparent molal compressibility. Furthermore, the second approximation, which takes account of the compressibility of the dissolved substance, may reasonably be expected to be important when the dissolved molecule is as large as it is here. Unfortunately the compressibility of none of these acids has been determined in the solid state; we may guess that the order of magnitude of the compressibility would not be far different from that of a number of other solid organic compounds, which lose about 1.5 percent in volume at 1000 kg/cm<sup>2</sup>. An effect of this magnitude would account for a large part of the initial slope of the curves for the more concentrated solutions.

At low pressures the behavior of the more concentrated solutions approaches more closely to that of normal electrolytes than does that of the weaker solutions, that is, the apparent molal compressibility of the more concentrated solutions is less strongly positive. At concentrations beyond 1.0 molal there is a striking tendency for the curves of apparent molal volume to become relatively independent of concentration, and in fact to approach the behavior of a system in which there is no interaction between water and acid. But in the concentration range between 0 and 1.0 molal the behavior at constant pressure as a function of concentration is evidently highly complicated. In particular, the volume is very far from being a linear function of  $c^{\frac{1}{2}}$ , and in fact this relation fails even at atmospheric pressure, although the relation is satisfied for practically all other substances. Neither is apparent molal volume any more approximately a linear function of  $c$ . Scatchard and Kirkwood<sup>5</sup> have recently verified the conclusion that in dilute solutions the effect of a Zwitterion should be proportional to the first power of the concentration rather than to its square root.

Resemblances would be expected between the behavior of glycine and  $\alpha$ -amino butyric acid because of the resemblances of structure. A glance at the structural formulas shows that the electrically active parts of the two molecules are identical,  $\alpha$ -amino butyric acid differing from glycine only in that it carries attached to it an inert tail; that is, the polar moments of these two acids must be nearly the same. At the 0.5 molal concentration the similarity in the behavior of these two substances is striking; both curves have a sharp initial drop, a rise to a maximum, followed by a drop to a second minimum, and ultimately at high pressures a continued rise, which means that the apparent molal compressibility ultimately becomes negative, which is typical of other substances. The curves at 1.5 molal, the only other concentration measured for the  $\alpha$ -amino butyric acid, are much more featureless than the curves for 0.5 molal, and differ no more in absolute terms. Contrasted with these, the moment of  $\epsilon$ -amino caproic acid

<sup>4</sup> Jeffries Wyman, Jr., Phys. Rev. 35, 623 (1930); J. Biol. Chem. 90, 434 (1931); J. Am. Chem. Soc. 56, 536 (1934). Jeffries Wyman, Jr., and T. L. McMeekin, J. Am. Chem. Soc. 55, 908, 915 (1933).

<sup>5</sup> G. Scatchard and J. G. Kirkwood, Phys. Zeits. 33, 297 (1932).

must be very materially larger, as shown by its structure, and one would therefore be prepared for qualitative differences in behavior. The most marked difference in behavior is seen to be at the lowest concentration.

Another line of comparison suggests itself. Glycine differs from  $\alpha$ -amino butyric acid only in the presence of a  $C_2H_4$  group. The difference of the molal volumes of corresponding solutions may therefore be described as the contribution to the volume of  $C_2H_4$ , and if the comparison is made at different pressures, the volume of the  $C_2H_4$  group is obtained as a function of pressure. A simple calculation shows that in 0.5 M solution the volume of the  $C_2H_4$  group decreases from 31.91 at atmospheric pressure to 28.41 at 3000 kg/cm<sup>2</sup>, whereas in 1.5 M solution it *increases* from 31.70 at atmospheric to 36.05 at 3000. Similar calculations may be made for other groups of compounds. Thus from the compressibility of the propyl and amyl halides,<sup>6</sup> the volume of the  $C_2H_4$  group may be obtained as a function of pressure by subtraction. It turns out that in these compounds the volume decreases with pressure by roughly the same amount in the chloride, bromide and iodide, which is as one might expect, and surprisingly enough the volumes are about the same as in the 0.5 M solution. From this point of view the 0.5 M solution is therefore more nearly normal than the 1.5 M solution, although the apparent volume curve against pressure of the 1.5 M solution is much more regular than that of the 0.5 M solution.

A study of the thermal expansion discloses only complications which are probably too great to attempt to unravel at present; such complications would be expected in view of the complications already found with respect to pressure. In very broad comment, the thermal expansion shows a very much smaller tendency to become less at high pressures than it does for normal organic substances; this is a property of the water in the solution which was already known.

<sup>6</sup> P. W. Bridgman, Proc. Am. Acad. Sci. **68**, 1 (1933).

Effects as complicated as these obviously demand something more specific in the way of explanation than such general considerations as, for example, the internal pressure in the solution. In fact, from the point of view of internal pressure the variety and magnitude of the effects is very surprising. Thus, to take an extreme case, the initial slope of the curve of apparent volume of 0.5 M  $\alpha$ -amino butyric acid has the largest negative value to be found anywhere in the series. A consideration of numerical magnitudes shows that this means, according to Tammann's picture, that the water in the solution is under a negative pressure of something of the order of 1000 kg/cm<sup>2</sup>. But the internal pressure in water under normal conditions is of the order of 10,000 or 20,000 kg/cm<sup>2</sup>, so that the total internal pressure of the 0.5 M solution is little affected by the dissolved acid. External pressures would not be expected to produce important changes in the properties of such solutions until they become comparable in magnitude with the internal pressures already existing, or in this case, until a pressure is reached comparable with 10,000 kg/cm<sup>2</sup>. But actually an external pressure of only 800 kg/cm<sup>2</sup> acting on this solution reverses the sign of the apparent molal compressibility.

Perhaps something in the nature of specific clustering or hydration effects, involving the possibility of multiple types of approximate order, would be competent to explain the complicated effects. But such effects must be surprisingly sensitive to changes of pressure which would be judged to be comparatively slight from the point of view of other phenomena.

The great complication of these pressure effects suggests that an experimental examination of other phenomena in these solutions might be profitably undertaken. For example, measurements might well be made of the effect of pressure on solubility and on the dielectric constants, on the compressibility of non-aqueous solutions and of solutions of other acids in the series, and of the compressibility of the solid phases of the pure acids.