cates a very definite lowering of the over-all activation energy E', independent of the amount of catalyst, from 22,100 to 19,400 cal./mole. This difference must be due to a lower energy of initial activation; E' of the catalyst–monomer addition complex is only 11,000 cal./mole as compared with 13,700 cal./mole of the simple A* radical. The activation of the catalyst molecule itself requires $E_C = 2600$ cal./mole.

Summary

Macropolymerization is usually explained as a chain reaction which is supposed to be initiated and propagated by radicals produced by the "opening" of the double bond of the monomer. This conception is inadequate for many reasons which are discussed in the paper. It is attempted to interpret macropolymerization and the mechanism of its activation in terms of constitutional changes.

On these premises, two different states of monomeric activation are defined and formulated as virtual free radicals: the form responsible for initial activation of the chain process (prototropic or A* type) and that assumed by the addend molecules (open-bond or B* type). The latter type, without the former, can only effect cyclization. These principles are exemplified within the scope of the paper, but their general validity is implied.

The kinetics of macropolymerization is analyzed in accord with the proposed mechanism of dual activation. The activation energies of the two types of mesomeric radicals are computed from available experimental data on styrene polymerization, and the reaction constants of the main phases of the process are estimated on this basis. The effects of solvents and of catalysts are evaluated.

SHAWINIGAN FALLS, QUEBEC

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Heats of Dilution of Aqueous Solutions of Glycine and Glycolamide, and Other Thermodynamic Properties of Glycine at 25°[1,2]

BY FRANK T. GUCKER, JR., HUGH B. PICKARD AND WILLIAM L. FORD

Introduction

An investigation of the thermodynamic properties of aqueous solutions of non-electrolytes, undertaken in this Laboratory[3] indicates that the limiting slopes of the apparent molal volumes, expansibilities, heat capacities, and heat contents are linear functions of the first power of the concentration, rather than its square root, as in the case of electrolytes. This limiting law is to be expected for dipolar solutes, according to an extension of the theory of Fuoss,[4] and the slopes should be steeper the greater the dipole moment. We are testing these ideas by comparing the properties of the simple amino acids, which occur in aqueous solution chiefly as *zwitterions* with large dipole moments, and their uncharged isomers, which are much less polar.

Studies of glycine, $^{+}H_3NCH_2COO^{-}$, and the isomeric glycolamide, $CH_2OHCONH_2$, have shown[5] that the apparent molal volumes of both are linear functions of the molarity, *c*, at 25°. The apparent molal heat capacities at 5, 25 and 40° become linear in the first power of the concentration in very dilute solutions, although they are quadratic functions of the concentration over a large range. In both cases, the curves for glycine are *lower* than those for glycolamide, apparently because of greater electrostriction, and have *steeper limiting slopes*, which may be attributed to the interaction between the dipolar solute molecules. Now we have measured the heats of dilution of these isomers, which are published and compared in the present article.

Materials and Solutions.—The glycine used in this work was Eastman Kodak Co. best grade, recrystallized once from 70% alcohol. Conductivity measurements indicated about 0.02% electrolyte calculated as sodium chloride.

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[1] The material in this paper was presented before the Division of Physical and Inorganic Chemistry: the work on glycine at the Baltimore Meeting of the American Chemical Society, April 5, 1939, and that on glycolamide at the Cincinnati Meeting, April 10, 1940.

[2] This work was supported by grants from the Penrose Fund of the American Philosophical Society and from the Committee on Research of the Graduate School of Northwestern University.

[3] Gucker, *et al.* (a) THIS JOURNAL, **59**, 447 (1937); (b) **59**, 2152 (1937); (c) **60**, 2582 (1938); (d) **61**, 459 (1939); (e) **61**, 1558 (1939); (f) **62**, 1464 (1940).

[4] Fuoss, *ibid.*, **58**, 982 (1936).

[5] Gucker, Ford and Moser, *J. Phys. Chem.*, **43**, 153 (1939).

Some of the glycolamide, which had been used in the work on heat capacities and densities, was reclaimed as previously described.[5] Additional amide was prepared by passing dry ammonia into freshly distilled ethyl glycolate. The yield was larger than that obtained previously with an alcoholic solution of the ester and the reaction was more rapid. The electrolytic impurity was approximately 0.001%.

The laboratory distilled water, with a specific conductance of 4 × 10^{-6} reciprocal ohm or less, was employed in this work.

The solutions used in experiments 1–9, 12, 17, 24, 28, 33, 37–39, 42, 46, 47, 51–54, 64 and 73–77 were made up determinate. Those used in the remaining experiments were the products of previous dilutions.

Experimental Methods.—We measured the heats of dilution with the twin-calorimeter apparatus, sensitive to one microdegree, which has been described previously.[3d] Again two types of experiment were carried out, one in which the molality of a relatively large amount of solution was decreased only slightly and one in which a large amount of water was added to a small volume of solution, causing a large decrease in concentration.

When the volume of air in the dilution pipet was large, appreciable evaporation or condensation accompanied the dilution. This necessitated a correction to q, the observed heat change, calculated as before.[3f] The necessary vapor pressures of the glycine solutions were obtained from the values of the osmotic coefficients of Smith and Smith[6] at 25° which, as we shall show later, are confirmed by the work of M. M. Richards.[7] Since no measurements of the vapor pressure of solutions of glycolamide were found in the literature, values were calculated from Raoult's law. These undoubtedly were adequate for our purpose, since the amide seems to form more nearly perfect solutions than the glycine.[5]

Experimental Results.—The experimental results for glycine, numbered chronologically, are summarized in Table I. The calorie defined as 4.1833 International joules is used here and throughout this article. Of the eighty-two dilutions, thirteen were discarded. In nine of these, very small heat effects indicated that the dilution pipet had leaked or had been opened accidentally in assembling the calorimeter. Consistently low results were obtained with one of the solutions made up for experiment 33, and used also in 34, 35 and 36. This probably was due to an error in making up the solution, since the density of the 1.50 m solution after experiment 36 was found to be 0.03% low. The results of later experiments covering this range of concentration agreed with the tabulated values of experiments 33–36 and led us to discard the four low results.

TABLE I

HEATS OF DILUTION OF GLYCINE AT 25°

Expt.	Initial concn., m_1	Final concn., m_2	10^3 q in cal. (obsd.)	10^3 q in cal. (calcd.)	$10^3 \Delta q$ (obsd. − calcd.)	ΔH cal./mole	$-\Delta H/\Delta m$
45	0.0940	0.0880	50	51	− 1	0.61	102
22	.1000	.0940	58	55	+ 3	.65	108
23	.1000	.0940	60	55	+ 5	.67	112
44	.1000	.0940	63	57	+ 6	.69	114
20	.1060	.1000	66	61	+ 5	.66	110
21	.1060	.1000	69	62	+ 7	.68	113
43	.1060	.1000	61	60	+ 1	.63	105
18	.1120	.1060	68	64	+ 4	.65	108
19	.1120	.1060	63	64	− 1	.61	101
42	.1120	.1060	59	61	− 2	.59	99
17	.1180	.1120	68	67	+ 1	.62	103
	.1180	.1120	67	67	0	.61	102
16	.1600	.1500	140	142	− 2	1.00	100
	.1600	.1500	141	142	− 1	1.00	100
15	.1700	.1600	156	152	+ 4	1.04	104
	.1700	.1600	156	152	+ 4	1.04	104
11	.1800	.1700	160	163	− 3	0.99	99
14	.1800	.1700	161	162	− 1	1.00	100
	.1800	.1700	166	163	+ 3	1.03	103
10	.1900	.1800	176	170	+ 6	1.04	104
13	.1900	.1800	172	170	+ 2	1.05	105
	.1900	.1800	175	170	+ 5	1.03	103
9	.2000	.1900	185	189	− 4	0.98	98
12	.2000	.1900	192	189	+ 3	1.01	101
	.2000	.1900	188	189	− 1	0.99	99
27	.3000	.2900	263	263	0	.96	96
	.3000	.2900	263	262	+ 1	.97	97
26	.3100	.3000	272	272	0	.96	96
	.3100	.3000	267	273	− 6	.94	94
25	.4000	.3900	338	342	− 4	.92	92
	.4000	.3900	338	343	− 5	.92	92
24	.4100	.4000	367	370	− 3	.92	92
32	.6100	.6000	465	472	− 7	.854	85.4
	.6100	.6000	467	470	− 3	.860	86.0
31	.8000	.7900	561	553	+ 8	.821	82.1
	.8000	.7900	547	551	− 4	.803	80.3
30	.8100	.8000	557	566	− 9	.793	79.3
	.8100	.8000	570	576	− 6	.797	79.7
29	1.0000	.9900	642	653	−11	.742	74.2
	1.0000	.9900	640	654	−14	.739	73.9
28	1.0100	1.0000	665	666	− 1	.750	75.0
	1.0100	1.0000	630	661	−31	.716	71.6
36	1.5100	1.5001	876	873	+ 3	.628	62.2
50	1.9900	1.9800	884	874	+10	.549	54.9
49	2.0001	1.9900	935	921	+14	.554	54.9
35	2.0099	2.0001	969	950	+19	.540	55.1
34	2.5000	2.4900	1014	1008	+ 6	.476	47.6
33	2.5100	2.5000	1054	1037	+17	.479	47.9
47	2.5100	2.5001	996	980	+16	.473	47.8
41	2.5100	2.5001	986	978	+ 8	.469	47.4
	2.5100	2.5001	1016	984	+32	.480	48.5
40	2.9950	2.9849	1007	1043	−36	.420	41.6
39	3.0100	3.0001	1028	1068	−40	.408	41.2
	3.0036	2.9950	900	909	− 9	.364	42.3
1	0.0999	0.0050	57	49	+ 8	11.6	
2	.0999	.0050	68	49	+19	13.8	
3	.0999	.0050	45	49	− 4	9.1	
4	.0999	.0050	57	49	+ 8	11.6	
46	.0999	.0050	55	49	+ 6	11.2	
	.0999	.0050	59	49	+10	12.0	
6	.2000	.0050	101	99	+ 2	20.5	
8	.2000	.0050	103	99	+ 4	21.0	
	.2000	.0050	103	99	+ 4	20.9	
5	.2000	.0100	190	193	− 3	19.3	
	.2000	.0100	196	193	+ 3	19.9	
37	1.000	.0100	848	844	+ 4	89.5	
	1.000	.0100	851	841	+10	90.2	
38	2.000	.0100	1564	1569	− 5	152.4	
	2.000	.0100	1573	1569	+ 4	153.3	

The equation for the slope, ΔH/Δm, which we obtained from the short-chord experiments is

$$\Delta H/\Delta m = -106.8 + 36.60\, m - 5.09\, m^2 \quad (1)$$

The coefficients were determined by the method of least squares. The curve of this equation is

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[6] Smith and Smith, *J. Biol. Chem.*, **117**, 209 (1937).

[7] M. M. Richards, *ibid.*, **122**, 727 (1938).

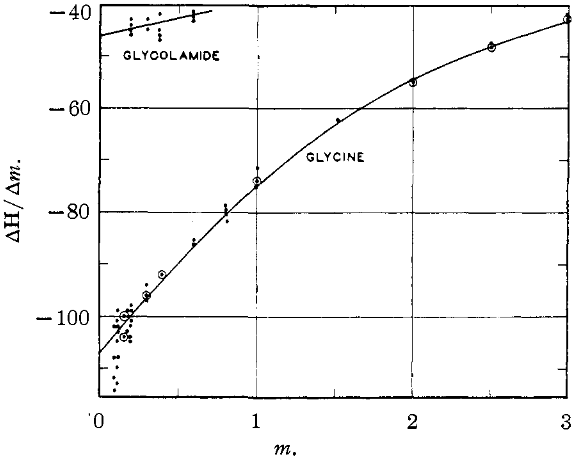

Fig. 1.—Slopes of dilution curves for glycine and glycolamide at 25°.

plotted in Fig. 1, with the experimental values of the chords shown as points, since they represent a change of only about 0.01 in *m*. By integrating equation (1) we obtained the expression for the apparent relative molal heat content

$$\Phi L_2 = \Phi H_2 - \Phi H_2^0 = -106.8\,m + 18.30\,m^2 - 1.70\,m^3 \qquad (2)$$

From this equation we calculated the values of *q* which are given in column 5 of Table I. This equation, the plot of which is shown in Fig. 2, represents the experimental data up to 1.51 *m* with an average deviation of ±4.9 microdegrees, and up to 3.01 *m* with an average deviation of ±7.1 microdegrees.

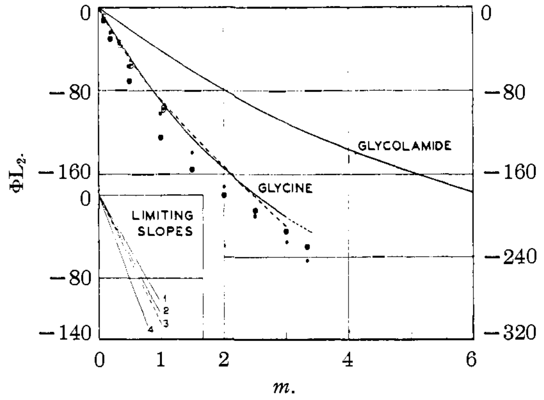

Fig. 2.—Apparent relative molal heat contents of glycine and glycolamide at 25°: ○, Naudé; ●, Zittle and Schmidt; •, Zittle and Schmidt, recalculated; dashed line, Sturtevant. Limiting slopes: 1, this research; 2, Sturtevant; 3, Zittle and Schmidt, recalculated; 4, Schmidt's equation.

Previous work in this Laboratory[3] has fixed the apparent molal heat capacity of glycine as a function of concentration at 5, 25 and 40°. By combining these results, we have obtained the apparent relative molal heat capacity as a function of temperature and concentration. Integration as described in a previous article[3f] gave the difference between the apparent relative molal heat content at any temperature between 5 and 40°, ΦL_2, and that at 25°, $\Phi L_2''$ as

$$10^3\,(\Phi L_2 - \Phi L_2'') = (4570\,m - 470\,m^2)\,(t - 25) - (73.0\,m - 12.1\,m^2)\,(t - 25)^2 + (1.30\,m - 0.26\,m^2)\,(t - 25)^3 \qquad (3)$$

By combining (2) and (3) we can calculate heats of dilution at any temperature between 5 and 40°, although (3), based on heat capacity measurements, is considerably less precise than (2).

Fifty-eight dilutions of solutions of glycolamide were carried out. Eighteen of these were spoiled by leaking or premature opening of the pipets, and in four cases the time–temperature drift was too erratic to allow satisfactory extrapolation. The thirty-six successful experiments, numbered chronologically, are recorded in Table II.

TABLE II

HEATS OF DILUTION OF GLYCOLAMIDE AT 25°

Expt.	Initial concn., m_1	Final concn., m_2	$10^3\,q$ in cal. (obsd.)	(calcd.)	$10^3\Delta q$ (obsd. − calcd.)	ΔH cal./mole	−ΔH/Δm
78	0.2000	0.1870	100	98	+ 2	0.59	46
	.2000	.1870	94	97	− 3	.56	43
79	.2000	.1870	99	97	+ 2	.59	45
	.2000	.1870	97	98	− 1	.58	44
77	.3006	.2900	128	132	− 4	.45	43
	.3010	.2900	139	136	+ 3	.49	45
60	.3800	.3698	143	146	− 3	.43	42
68	.3800	.3700	144	139	+ 5	.45	45
	.3800	.3700	146	140	+ 6	.45	45
59	.3898	.3800	150	143	+ 7	.44	45
58	.4000	.3898	162	149	+13	.48	47
66	.4000	.3900	156	146	+10	.46	46
	.4000	.3900	151	146	+ 5	.45	45
56	.5799	.5700	204	203	+ 1	.421	42.4
55	.5900	.5800	216	214	+ 2	.422	42.0
	.5900	.5799	217	214	+ 3	.427	42.5
65	.5900	.5800	220	212	+ 8	.433	43.4
	.5900	.5800	218	212	+ 6	.429	42.9
64	.6000	.5900	221	219	+ 2	.424	43.7
51	.2001	.0100	88	87	+ 1	8.7	
	.2001	.0100	90	86	+ 4	9.0	
70	.3700	.0100	150	153	− 3	15.7	
	.3700	.0100	147	153	− 6	15.5	
72	.3700	.0100	152	153	− 1	16.0	
52	.4999	.0100	214	213	+ 1	22.2	
53	.5000	.0103	204	209	− 5	21.1	
69	.5800	.0100	234	235	− 1	24.9	
	.5800	.0101	233	234	− 1	24.9	
73	.9999	.0100	374	375	− 1	41.8	
	.9999	.0100	371	373	− 2	41.6	
74	2.000	.0100	768	767	+ 1	78.7	
	2.000	.0100	762	771	− 9	77.7	
76	4.003	.0100	1379	1376	+ 3	136.3	
	4.003	.0100	1356	1360	− 4	135.6	
75	6.004	.0100	1734	1734	0	178.0	
	6.004	.0100	1778	1778	0	178.0	

Since the heat of dilution curve for glycolamide is more nearly linear than that for glycine, it was fixed by a slightly different experimental procedure. The short-chord dilutions were made only from 0.2 to 0.6 *m*, in order to help fix the limiting slope. The long-chord dilutions covered the rest of the range of concentration. The final equation for the apparent relative molal heat content was

$$\Phi L_2 = \Phi H_2 - \Phi H_2^0 = -46.00\,m + 3.52\,m^2 - 0.134\,m^3 \quad (4)$$

This equation is plotted in Fig. 2, and the corresponding slope curve is given in Fig. 1. Values calculated from this equation reproduce the experimental results with an average deviation of ±3.6 microdegrees, as shown in the sixth column of Table II.

As in the case of glycine, we combined heat capacity measurements on glycolamide[8] to determine the change of the apparent relative molal heat content with temperature. The resulting equation was

$$10^3\,(\Phi L_2 - \Phi L_2'') = (720\,m - 30\,m^2)(t - 25) - (24.0\,m - 1.9\,m^2)(t - 25)^2 + (0.48\,m - 0.03\,m^2)(t - 25)^3 \quad (5)$$

The partial relative molal heat content of solute and solvent, $\overline{L}_2$ and $\overline{L}_1$, may be calculated from equations 2–5, by the usual methods.[9]

Comparison with Previous Work.—We could find no measurements of the heats of dilution of glycolamide in the literature, but found several studies of glycine. Naudé[10] used one of the first microcalorimeters to measure nine heats of dilution from 1 *M* to 0.0006 *M* at temperatures near 18°. A comparison between his results, calculated to 25° by means of our equation (3), and the corresponding heat effects calculated from our equation (2), are given in Table III. His results agree excellently with ours at low concentrations, but show a slightly greater absorption of heat at higher concentrations. The average deviation is the same as in the case of urea.[3f] Since this comparison involves our heat capacity data as well as our heats of dilution, the agreement is quite satisfactory. Values of ΦL_2 at 25°, calculated from the results of Naudé at all but the two lowest concentrations, are shown in Fig. 2.

TABLE III[a]

THE HEATS OF DILUTION OF GLYCINE AT 25°, CALCULATED FROM THE RESULTS OF NAUDÉ, COMPARED WITH THOSE OF THIS RESEARCH

m_1	m_2	m_3	ΔH in cal. Naudé	ΔH in cal. Eq. (2)	Diff.	10^6 δT
0.020	0	0.0006	0	1.2	−1.2	−1
.033	0	.001	2	3.4	−1.4	−1
.101	0	.003	8.6	10.3	−1.7	−5
.339	0	.0067	35.6	33.5	2.1	14
.339	0.0067	.0133	32.8	32.1	0.7	5
.513	0	.01	54.4	49.0	5.4	54
.513	0.01	.02	51.1	47.0	4.1	41
1.049	0	.02	95.2	91.8	3.4	68
1.049	0.02	.04	90.5	87.6	2.9	58

[a] m_1 is the molality of the original solution, m_2 that of the diluent and m_3 that of the final solution. ΔH is the heat change per mole of glycine in the *original solution.*

Zittle and Schmidt[11] carried out a series of short-chord dilutions of glycine solutions, with a thermometric sensitivity of 0.0001°, and tabulated the relative molal heat content of the water. By extrapolating to zero concentration and graphical integration, they obtained values of $\overline{L}_2$ and ΦL_2 which they also tabulated. We have plotted these values as the larger closed circles in Fig. 2. Schmidt[12] later published the following equation for the apparent relative molal heat content of glycine

$$\Phi L_2 = -162.2\,m + 47.4\,m^2 - 5.8\,m^3 \quad (6)$$

We have recalculated the work of Zittle and Schmidt and obtain a somewhat different result. Plotting the value of $\overline{L}_1$ given in Table I of Zittle's Dissertation[13] against *m*, we drew a smooth curve through the points. From the equation for this curve, we calculated the equation for the apparent relative molal heat content

$$\Phi L_2 = -121.6\,m + 22.6\,m^2 - 2.40\,m^3 \quad (7)$$

Values of ΦL_2 calculated from our equation (7) are shown in Fig. 2 as the small closed circles. They lie along a flatter curve, with a considerably smaller initial slope. Up to about 1 *m* they are in substantial agreement with our results, although at higher concentrations they are appreciably lower. Above 2 *m* the recalculated results fall lower than the values given by Zittle and Schmidt.

Very recently Sturtevant has carried out a series of long-chord dilutions of glycine solutions over the range from 1.14 *m* to 0.036 *m*. He has been kind enough to send us his results.[14] The equation which he used to represent them is

$$\Phi L_2 = \frac{-115.9\,m}{1 + 0.395\,m} - 5.66\,m^2 \quad (8)$$

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[8] Gucker and Ford, to appear in *J. Phys. Chem.*, **44** (1940) or **45** (1941).

[9] *Cf.* ref. 3f, equations 10–13.

[10] Naudé, *Z. physik. Chem.*, **135A**, 209 (1928).

[11] Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

[12] Schmidt, "The Chemistry of the Amino Acids and Proteins," Charles C. Thomas, Springfield, Illinois, 1938, p. 839.

[13] Zittle, Dissertation, University of California (1934).

[14] Now published in THIS JOURNAL, **62**, 1879 (1940).

This equation, shown by the dashed line in Fig. 2, agrees closely with our equation over the whole range, even when it is extrapolated far beyond 1.14 *m*. It is slightly lower up to about 1 *m*, then crosses our line and is somewhat higher until it crosses again at about 2.2 *m*. Beyond this point it falls appreciably lower. Sturtevant's results are reproduced by his equation with an average deviation of ±40 microdegrees. They average about 120 microdegrees less than the values calculated from our equation (2). The limiting slope of his equation is 8.5% steeper than that of our equation (2), while that of equation (7), from the recalculation of the data of Zittle and Schmidt, is 14% steeper. These limiting slopes agree satisfactorily with our result, which also is confirmed by the data of Naudé at low concentrations. Schmidt's value, from equation (6), which is 53% higher than ours, seems definitely too great. A graphical comparison of these slopes is inserted at the lower left-hand corner of Fig. 2.

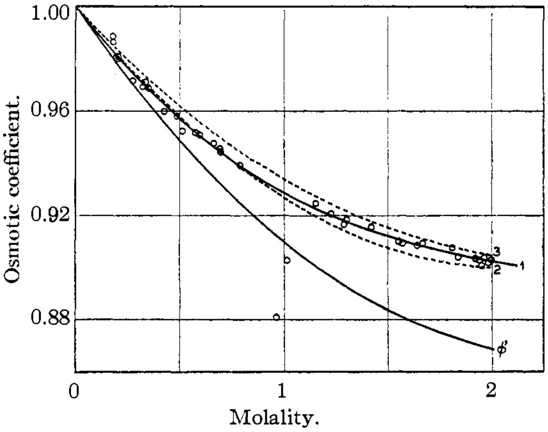

Fig. 3.—Osmotic coefficients of glycine at the freezing point and at 25°. Lower full curve marked φ' was determined by Scatchard and Prentiss at the f. p.; dashed curves (2) and (3), respectively, show the same results calculated to 25° from the thermal data of Zittle and Schmidt, and from those of this research; upper full curve (1) given by Smith and Smith; ○, represents data of M. M. Richards.

Discussion of Heats of Dilution.—Both glycine and glycolamide *absorb* heat upon dilution, like urea[3f] but unlike sucrose,[3d] which *liberates* heat at all concentrations. For all of these solutes, the apparent relative molal heat content is a linear function of the concentration, as predicted by the theory of Fuoss.[4] However, as we expect to show in more detail elsewhere, the theory predicts that in dilute solutions all solutes in water should *liberate* heat, and that the slope should be greater the larger the dipole moment of the solute particle. Exactly the opposite result is found in this case, since the limiting slope for glycolamide is 43% of that for glycine, and it absorbs about half as much heat over the whole range of concentration. Apparently some other factor, beside the dipolar interaction, must be at work in this case.

The Osmotic Coefficient of Glycine at 25°.—Our thermal data allow the calculation of osmotic coefficients at 25° from those determined at the freezing point, and a comparison with the results of vapor pressure measurements.

Smith and Smith[6] used the isotonic method at 25° to compare the vapor pressures of solutions of glycine with those of sucrose, which they took as a standard. They derived[15] an equation for the osmotic coefficient

$$\phi = 1 - 0.105\, m + 0.040\, m^2 - 0.0058\, m^3 \qquad (9)$$

In Fig. 3, this is plotted up to 2 *m*, which is as far as the freezing-point measurements can be carried.

M. M. Richards[7] also employed the isotonic method at 25°, comparing the vapor pressures of solutions of glycine and of potassium chloride. She listed the concentrations of isotonic solutions but not the osmotic coefficients. Using the values of Scatchard, Hamer and Wood[16] for the osmotic coefficient of potassium chloride, we calculated corresponding values for the osmotic coefficient of glycine, up to 2 *m*. These are shown as open circles in Fig. 3. These results agree closely with the curve of Smith and Smith, with an average deviation of ±0.0015 except for two results which, for some unknown reason, are 0.025 and 0.050 low.

Scatchard and Prentiss[17] determined φ', the osmotic coefficient of glycine at the freezing point. They gave the equation

$$\phi' = 1 - 0.1141\, m + 0.02432\, m^2 \qquad (10)$$

from which the average deviation of their 32 experimental results was 0.0008. This equation is plotted in Fig. 3, for comparison with the results at 25°. Cohn, McMeekin, Ferry and Blanchard[17a] have published an equation for the activity coefficient of glycine at 25°, calculated

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[15] Smith and Smith, *J. Biol. Chem.*, **121**, 607 (1937).

[16] Scatchard, Hamer and Wood, THIS JOURNAL, **60**, 3061 (1938), Table II.

[17] Scatchard and Prentiss, *ibid.*, **56**, 1486 (1934).

[17a] Cohn, McMeekin, Ferry and Blanchard, *J. Phys. Chem.*, **43**, 169 (1939).

from the freezing point data of Scatchard and Prentiss and the thermal data of Zittle and Schmidt. By standard methods[3f] the corresponding equation for the osmotic coefficient is found to be

$$\phi = 1 - 0.09632\, m + 0.02313\, m^2 \qquad (10a)$$

This equation, plotted as the dashed curve (2) in Fig. 3, is almost identical with that of Smith and Smith up to 0.75 *m*, and no more than 0.005 lower at the higher concentrations.

From the equations of Scatchard and Prentiss, we calculated values of ϕ' at a series of concentrations and used their equations (13) and (15) to compute the corresponding freezing points. From our thermal data, we then calculated the change of the osmotic coefficient from the freezing point to 25°, using the method described in a previous paper.[3f] The contributions of the $\overline{L}_1''$, $\Delta\overline{C}_{p_1}''$, and the higher terms $\overline{\overline{P}}_1$ and $\overline{\overline{Q}}_1$ are about 54, 34, 9 and 3%, respectively, over the whole range of concentration. The resulting curve for the osmotic coefficient at 25°, as shown by the dashed line (3) in Fig. 3, is slightly higher and flatter than the curve of Smith and Smith. If the difference is due to the thermal terms, one or both of the curves of the apparent relative molal heat content and heat capacity at 25° should be flatter than our work indicates. However, the difference averages only about 0.004 over the whole range, which seems quite satisfactory agreement, considering the different factors involved in the calculations. From all of these results, the osmotic coefficient of glycine at 25° seems to be fixed within ±0.002. Our thermal data can be used to calculate values of the osmotic coefficient at any other temperature between 5 and 40°. The activity coefficient can be calculated from the osmotic coefficient by standard methods.[3f] A comparison of previous results in terms of activity coefficients is contained in the article by Cohn, McMeekin, Ferry and Blanchard, to which reference has been made before.[17a] They also give an interesting calculation of the activity coefficient from the change in the dielectric constant of the solution with concentration.

Heat, Entropy and Free Energy of Formation of Glycine at 25°.—Taking the value of −232.57 kcal./mole for the heat of combustion of glycine,[18] and −68.313 and −94.030 kcal./mole for the heats of combustion of hydrogen and of graphite,[19] respectively, we find a value for the standard heat of formation of solid glycine which is 0.42 kcal./mole less than that given by Huffman, Fox and Ellis, because of the difference in the heat of combustion of graphite.

The entropy of solid glycine has been determined from heat capacities by Parks, Huffman and Barmore,[20] and the standard entropy of formation was calculated by Huffman and Ellis.[21] Using their value and the thermodynamic equation

$$\Delta F = \Delta H - T\Delta S \qquad (11)$$

we found for the standard free energy of formation a value 0.43 kcal. greater than that given by Huffman and Ellis, because of the difference in ΔH and our use of 298.16° for the absolute temperature. These values are collected in Table IV, along with the corresponding values for the hypothetical 1 molal solution (aq.).

TABLE IV

STANDARD HEAT, FREE ENERGY AND ENTROPY OF FORMATION, AND ENTROPY OF SOLID AND AQUEOUS GLYCINE AT 298.16°

	$\Delta H°$ kcal./mole	$\Delta F°$ kcal./mole	$\Delta S°$ E. U.	S E. U.
Solid	−126.27	−88.52	−126.6	26.1
Aqueous	−122.51	−89.05	−112.2	40.5

From equation (9) of Smith and Smith for the osmotic coefficient, we calculated the corresponding equation for the activity coefficient by standard methods.[3f] Taking the solubility of glycine as 3.330 *m*[22] at 25°, we calculated the value of $\gamma = 0.729$ in the saturated solution, and the change in free energy on dilution to a solution of unit activity as

$$\Delta F = -RT \ln \gamma m = -525 \text{ cal.}$$

From this we found the free energy of formation of glycine in the solution at unit activity.

Zittle and Schmidt[11] determined the heat of solution of solid glycine in a 0.1 *m* solution. Making the slight correction for the heat of dilution, we found the relative heat content of the solid, $L_2(s) = -3765\ (\pm 15)$ cal., from which the standard heat of formation in solution was determined. The standard entropy of formation in solution was then found by means of equation (11). The entropy of glycine in the hypothetical 1 molal solution was calculated similarly.

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[18] Huffman, Fox and Ellis, THIS JOURNAL, **59**, 2144 (1937).

[19] Rossini and Jessup, *Bur. Standards J. Research*, **21**, 491 (1938); **22**, 1192 (1939).

[20] Parks, Huffman and Barmore, THIS JOURNAL, **55**, 2733 (1933).

[21] Huffman and Ellis, *ibid.*, **59**, 2150 (1937).

[22] Cohn, McMeekin, Edsall and Weare, *ibid.*, **56**, 2270 (1934).

The heat of solution of solid glycine in the saturated solution is

$$\Delta H = \bar{L}_2 \text{ (satd.)} - L_2(s) = -354 + 3765 = 3411 \text{ cal.}$$

whence the entropy of solution in the saturated solution is

$$\Delta S = 3411/298.16 = 11.4 \text{ E. U.}$$

Summary

We have measured the heats of dilution of aqueous solutions of glycine from 3 *m* to 0.005 *m* and of glycolamide from 6 *m* to 0.01 *m*. The apparent relative molal heat content in each case may be represented satisfactorily by a cubic equation in the molality. From the heat capacity data we have obtained equations for the apparent relative molal heat contents as cubic functions of the temperature.

We have used these data to calculate ϕ, the osmotic coefficient of glycine at 25°, from freezing point measurements and find that these values agree within about 0.004 with the results of precise vapor pressure measurements at 25°.

From known values of the heats of combustion and entropy of glycine we have calculated the standard heat, entropy and free energy of formation of glycine in the solid state and also in the hypothetical 1 *m* solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Reducibility of Quadrivalent Zirconium[1]

BY A. W. LAUBENGAYER AND R. B. EATON

Although the normal valence for elements of the fourth periodic group is four, titanium and zirconium have been shown to form compounds in which they exhibit a lower state of oxidation. Compounds of trivalent titanium have been obtained under both aqueous[2] and anhydrous[3] conditions, and compounds of divalent titanium, anhydrously prepared, have been found[4] to be relatively stable in water. For zirconium, however, the oxidation states of +2 and +3 have been obtained[5,6] only in the absence of water.

No thorough study has been reported concerning the reduction of zirconium in aqueous solution, with special reference to intermediate valence states. Such investigations among elements closely related to zirconium have provided interesting and valuable information. This paper discusses electrolytic and polarographic investigations upon the reducibility of quadrivalent zirconium in aqueous solution.

Experimental

Materials.—Zirconyl chloride was purified by recrystallization from hydrochloric acid solution until spectroscopic analysis showed no metals other than hafnium to be present. Zirconium tetrachloride was prepared by passing a dry mixture of chlorine and carbon monoxide over anhydrous zirconyl chloride or zirconium dioxide, heated to around 450°. The tetrachloride was purified by resublimation in a slow stream of nitrogen. Analysis indicated less than 1% of hafnium in the zirconium preparations.

Electrolysis of Zirconium Solutions.—For the study of the reduction of quadrivalent zirconium by simple electrolysis, solutions and conditions were so chosen as to avoid, so far as possible, hydrolysis and the formation of stable oxy-ions of zirconium. In some cases organic solvents were used in the hope of approaching the normal Zr^{+4} ion. Electrolyses were carried out in the usual manner, with a glass cell and protecting the main body of the solution to be reduced from anodic oxidation products by an unglazed porcelain cup which enclosed the platinum anode. To take advantage of the differences in hydrogen overvoltage, platinum, lead and mercury were used successively as cathodes. The solutions and any products of electrolysis were examined for reducing properties at intervals during the electrolysis. Measurements of current and applied voltage were made with standard equipment.

The solutions studied by electrolysis were the following: zirconium acetate in glacial acetic acid; zirconuim sulfate in both concentrated and dilute sulfuric acid; zirconium fluoride in hydrofluoric acid; and zirconium chloride in water, concentrated and dilute hydrochloric acid, hydrochloric acid saturated with hydrogen chloride at 0°, methyl alcohol, ethyl alcohol and pyridine. These solutions were electrolyzed for from one to fifteen hours at a potential sufficient to produce a steady slow discharge of hydrogen. Reduction of the zirconium to a state of di- or trivalency was not obtained in any case, although in the case of the sulfate solutions, metallic zirconium deposited at the platinum electrode. This metal deposition from

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[1] Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Cincinnati, Ohio, April, 1940.

[2] Diethelm and Foerster, *Z. physik. Chem.*, **62**, 129 (1908).

[3] Ruff and Neumann, *Z. anorg. allgem. Chem.*, **128**, 81 (1923).

[4] Forbes and Hall, THIS JOURNAL, **46**, 385 (1924).

[5] Ruff and Wallstein, *Z. anorg. allgem. Chem.*, **128**, 96 (1923).

[6] Young, THIS JOURNAL, **53**, 2148 (1931).