in non-enzymatic hydrolyses: these are usually about −15 cal./deg./mole (*cf.* Table VII of ref. 4). In view of this, and of the fact that it is highly probable that the big substrate molecule is attached to the enzyme molecule at not more than three or four places[7] (thus necessitating the removal of not more than a few water molecules), the proposal of structural change within the enzyme molecule on complex formation seems to be the more plausible.

Because of the scarcity of data, any discussion along these lines must necessarily be considered as extremely tentative, subject to revision in the light of further experimental evidence. However, the idea of a structural change in the enzyme molecule is attractive when it is remembered that in biological systems enzymes appear to be responsible for the conversion of chemical energy into mechanical work.

Thanks are due to Drs. Rufus Lumry and E. L. Smith for suggestions relative to this paper.

Summary

1. The pepsin-catalyzed hydrolyses of carbobenzoxy-l-glutamyl-l-tyrosine and of its ethyl ester have been investigated over a range of temperature and of substrate concentrations.

2. The results have been analyzed on the basis of a simple model involving complex formation between substrate and enzyme. Values have been calculated for the heat of formation of this complex, ΔH, of the heat of activation for its decomposition, ΔH_0^*, and of the heat of activation in going from the reactants to the activated complex, ΔH^*. The corresponding entropy values (ΔS, ΔS_0^* and ΔS^*) have also been obtained. It is found that ΔS is positive for both systems, that ΔS_0^* is negative, and that ΔS^* is positive.

3. These results are found to fall into line with those for the urea–urease system, and also with those for the reactions investigated by J. A. V. Butler, on the basis of a new interpretation of Butler's results. All of these investigations are discussed tentatively in the light of the proposal that a structural change occurs in the enzyme molecule during the process of complex formation.

WASHINGTON, D. C. RECEIVED JULY 25, 1949

[CONTRIBUTED FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Electromotive Force Studies in Dilute Solutions of Hydrochloric Acid in Aqueous Ethylene Glycol at 25°

BY H. D. CROCKFORD, SAMUEL B. KNIGHT AND HELEN A. STATON

Knight, Masi and Roesel[1] determined the activity coefficients of hydrochloric acid in 10, 20, 40 and 60% by weight aqueous ethylene glycol solutions by electromotive force measurements at 25°. From their data they calculated the values of the ion size parameter for hydrochloric acid in these solutions and noted the fact that these values were not satisfactory inasmuch as they were greater than 4.3 Å. in the two higher concentrations and lower than this value in the two smaller concentrations.

The purpose of the work presented in this paper was to expand the electromotive force measurements to the 5, 15 and 30 weight per cent. solutions and from the data to determine the value of the ion size parameter for the purpose of clearing up the lack of constancy found by Knight, Masi and Roesel[1] in their values.

For this purpose the same cell used by Knight Masi and Roesel[1] was employed.

H_2 | HCl(m), Ethylene glycol (x) H_2O (y) | AgCl–Ag

Electromotive force measurements were made with 5, 15 and 30 weight per cent. of the glycol and over an acid range extending to 0.01 m. The standard potentials of the cell at the various ethylene glycol concentrations, the ion size parameter, and the mean activity coefficients of hydrochloric acid in the various mixtures were calculated from the data obtained.

Experimental

The methods of purification of the chemicals, the preparation of the electrodes, and the experimental procedures were the same as those used by Knight, Masi and Roesel.[1]

Density measurements were made on all solutions at 25°. The vapor pressures used were from the data of Trimble and Potts[2] and the dielectric constant values are from Akerlof.[3]

The electromotive force values reported are the average of at least three checks agreeing within ±0.05 mv. Such checks were easy to obtain. All values are corrected to 1 atm. of hydrogen.

Calculations

Calculations were made by use of the equation

$$E' = E + 0.1183 \log m - \frac{0.1183A\sqrt{c}}{1 + aB\sqrt{c}} - 0.1183 \log (1 + 0.002mM_{xy}) = E^0_m + f(m) \quad (1)$$

in which E is the observed electromotive force corrected to 1 atm. of hydrogen, m is the molality. A and B are the Debye–Hückel constants, a is the ion size parameter, c is the concentration of the hydrochloric acid in moles per liter, and M_{xy} is the mean molecular weight of the solvent. The values of A, B, M_{xy}, along with the values

---

[1] S. B. Knight, J. F. Masi and D. Roesel, THIS JOURNAL, **68**, 661 (1946).

[2] H. M. Trimble and W. Potts, *Ind. Eng. Chem.*, **27**, 66 (1935).

[3] G. Akerlof, THIS JOURNAL, **54**, 4125 (1932).

for the dielectric constant, are given in Table I. Also included in this table are the densities for the three series. These values were constant throughout the acid range of the series.

TABLE I

CONSTANTS OF EQUATION (1)

	A	$B \times 10^{-8}$	M_{xy}	D	
5% ethylene glycol	0.5255	0.3321	18.68	76.9	1.002
15% ethylene glycol	.5544	.3381	20.17	74.2	1.016
30% ethylene glycol	.6077	.3486	22.89	69.8	1.035

The E^0_m values of the solutions and the magnitude of the ion size parameter were determined by solving for E' in Equation (1) for various values of a. The values used ranged from 4.0 to 5.0 Å. The E' values were plotted against the molality. The proper value gives a zero slope for such a curve. These curves also give the values of E^0_m, the standard electrode potentials. From E^0_m the values of E^0_c and E^0_N were calculated from the equations

$$E^0_N = E^0_m - 0.1183 \log (1000/M_{xy}) \qquad (2)$$

$$E^0_c = E^0_m + 0.1183 \log d \qquad (3)$$

The activity coefficients were computed from the electromotive force data by Equation (4)

$$\log y_{\pm} = (E^0_m - E)/0.1183 - \log m \qquad (4)$$

The activity coefficients were also calculated by the Debye–Hückel relationship given in Equation (5)

$$\log y_{\pm} = -A\sqrt{c}/(1 + aB\sqrt{c}) - \log (1 - 0.002M_{xy}m) \qquad (5)$$

Data and Results

The data secured were utilized by calculating the E' values by means of Equation 1. The plots of these values as calculated for various values of ion size parameter when plotted against the molalities established very accurately the values of E^0 to 0.05 mv. While the slopes of the curves were small, it was very apparent that the proper value for the ion size parameter was 4.3 Å.

The results are presented by means of the curves in Figs. 1 and 2. In Fig. 1 are plotted the E' values of the various molalities studied in the 5% series as determined for ion size values of 4.0, 4.3 and 4.6 Å. In Fig. 2 are plotted the E' values for the various molalities for the 15% and 30% ethylene glycol solutions and the ion size value of 4.3 Å.

Copies of the complete data may be secured by writing the senior author.

Since we found satisfactory values of 4.3 Å. for the ion size parameter in the three solutions studied, the original data of Knight, Masi and Roesel were critically examined. The data they plotted in Fig. 1 of their paper was for concentrations below 0.005m. A plot of their original data at higher concentrations showed the same typical curve of zero slope for a parameter of 4.3 Å. This value is in agreement with that found by Harned and Thomas[4] for 10% and 20% methanol solutions and by Harned and Ehlers[5] using pure water as the solvent. The replotted data gave an E^0_m value somewhat higher than those reported for the 10% and 20% solutions. The values found by us at 5, 15 and 30% ethylene glycol, those calculated by us from the data of Knight, Masi and Roesel for the 10 and 20% solutions, and those found by these investigators at 40% and 60% are given in Table II. Also included in this table are the values for E^0_c and E^0_N for the various solutions as calculated by equations (2) and (3).

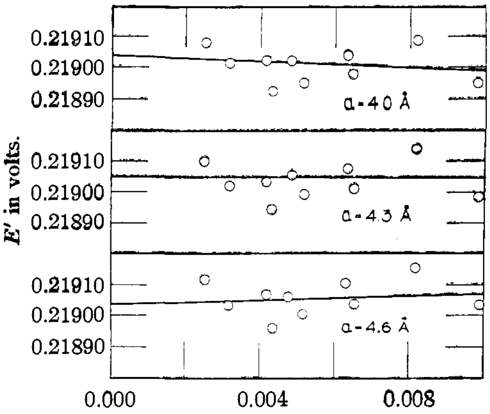

Fig. 1.—Molality data for 5% ethylene glycol solutions.

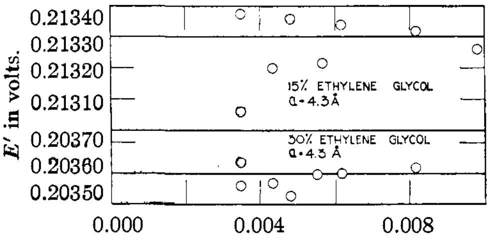

Fig. 2.—Molality data for 15 and 30% ethylene glycol solutions.

TABLE II

STANDARD POTENTIALS

Ethylene glycol–water	E^0_m	E^0_c	E^0_N
5%	0.21905	0.21915	0.01455
10%	.21635	.21684	.01380
15%	.21330	.21412	.01275
20%	.21020	.21137	.01177
30%	.20360	.20537	.00955
40%	.19720	.19968	.00800
60%	.18070	.18437	.00285

A further check was made on the values for E^0_m for the 10 and 20% ethylene glycol solutions by plotting the standard electrode potentials of

---

[4] H. S. Harned and H. C. Thomas, THIS JOURNAL, 57, 1666 (1935).

[5] H. S. Harned and R. W. Ehlers, *ibid.*, 55, 2179 (1933).

Table II against the reciprocal of the dielectric constant. A smooth curve was obtained upon which the recalculated values fitted nicely. These two values have an accuracy of ±0.1 mv. The others have an accuracy of ±0.05 mv.

The mean activity coefficients for the acid in the various solutions were calculated from the experimental data by Equation (4). These values were plotted on a large graph and the rounded values at 0.002, 0.005 and 0.01 m determined. These are given in Table III. The values calculated by Equation (5) agree almost exactly with those determined from the experimental data. The greatest variation was 0.003.

TABLE III

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ETHYLENE GLYCOL–WATER MIXTURES AT 25°

Molality	Weight per cent. ethylene glycol, % 5	15	30
0.002	0.950	0.944	0.940
.005	.925	.918	.913
.010	.898	.895	.886

Summary

1. The values of the electromotive force at 25° of cells of the type $H_2|HCl$ (m), ethylene glycol (x), water (y) $|AgCl–Ag$ were determined for acid concentrations up to 0.01 m and for 5, 15 and 30 weight per cent. of ethylene glycol.

2. From the data obtained the standard electrode potentials for these solutions were determined.

3. It was found that the value of the ion size parameter for hydrochloric acid in the solutions studied is 4.3 Å.

UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

RECEIVED APRIL 25, 1949

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, NEW YORK]

Carbon Vapor Pressure and Heat of Vaporization

BY A. L. MARSHALL AND F. J. NORTON

The values of these important physical properties, in particular, the heat of vaporization of carbon, have been in dispute in the literature for a number of years. The experimental difficulties in this high temperature field are great, and there has been a paucity of detailed direct experimental measurements. The present authors[1] have published a brief report on the heat of sublimation of carbon based on vapor pressure measurements. The recent determinations of Brewer, Giles and Jenkins[2] makes it desirable to have recorded additional complete experimental detail in the literature. In brief, the data of Brewer, *et al.*, give a value of $\Delta H_0° = 170.39$ kilocalories per mole, in excellent agreement with our value of $\Delta H_0^0 = 175.2$ kilocalories for the heat of sublimation. Further, their values for vapor pressure, obtained by an equilibrium effusion method, lie very close indeed to our experimental points, obtained from rate of evaporation of graphite rings in a vacuum.

The relation between rate of evaporation and vapor pressure, is given in the equation of Langmuir[3] derived from kinetic theory

$$m = \alpha(M/2\pi RT)^{1/2} P \qquad (1)$$

where m = rate of evaporation
α = accommodation coefficient
M = molecular weight
R = gas constant
T = absolute temperature
P = vapor pressure

Expressing P in atmospheres, m as grams per square centimeter per second evaporating, $R = 83.15 \times 10^6$ erg deg.$^{-1}$ mole^{-1} and $M = 12$ for monatomic carbon, the equation becomes, using $\log_{10}$

$$\log P = \log m + {}^1/_2 \log T - 2.187 \qquad (2)$$

The factor α is taken as unity, and this is justified in the subsequent discussion. The fact that the carbon evaporates predominantly in the monatomic form is supported by these and other experiments discussed later.

Apparatus and Technique

The vapor pressure was determined from the loss in weight of rings of graphite, of measured gross surface area, heated by high frequency in a very good vacuum, varying times, at various temperatures.

The rings were turned from Acheson graphite, 2.22 cm. outside diameter, 1.11 cm. inside and of various thicknesses, from 0.21 cm. to 0.39 cm., giving 8.0 cm.^{2} to 9.85 cm.^{2} total area from which evaporation takes place. The evaporation from the interior edge of the ring is subject to a very small correction due to the fact that with straight line evaporation some atoms strike the opposite surface, but this is equivalent to only about 2% reduction in area which is negligible compared to other errors.

These rings rested upon carbon prongs, held in a carbon support. A hole in the bottom of the support served as a socket for a 60 mil. tungsten wire, sealed into the bottom of the containing vessel, a graded seal connecting hard glass to quartz.

---

[1] Marshall and Norton, THIS JOURNAL, **55**, 431 (1933).

[2] Brewer, Giles and Jenkins, *J. Chem. Phys.*, **16**, 797 (1948). This appeared also as U. S. Atomic Energy Commission Report MDDC-1575.

[3] Langmuir, *Phys. Rev.*, **2**, 329 (1913).