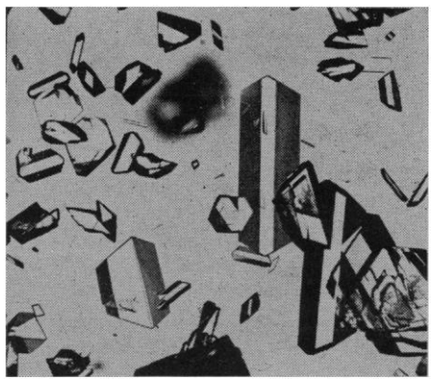

Fig. 1. Human lysozyme chloride; *p*H 10.5; 6 days at 25°C.

I now report the crystallization of human lysozyme chloride. The procedure was essentially identical to that described by Alderton, Ward, and Fevold (*2*, *3*) for the crystallization of hen's egg-white lysozyme chloride. The enzyme was isolated from the urine of patients with monocytic leukemia by its adsorption to bentonite and elution with 5 percent aqueous pyridine adjusted to *p*H 5.0 with sulfuric acid. After exhaustive dialysis against distilled water, the solution of amorphous enzyme was lyophilized. It was then dissolved to a concentration of 50 mg/ml in 5 percent sodium chloride solution adjusted either to the isoelectric region (*p*H 10.5) with sodium hydroxide or to *p*H 4.5 with hydrochloric acid. When cooled to 9°C, copious crystallization in the form of needles occurred within a few hours at both *p*H 10.5 and *p*H 4.5. The needle-like crystals at *p*H 4.5 were randomly dispersed, whereas those at *p*H 10.5 were grouped in bundles resembling wheat sheaves (see cover). After several days at 9°C, the needles of lysozyme chloride at *p*H 10.5 developed into hexagonal prisms up to 2 mm in length. When crystallization from these solutions proceeded more slowly at room temperature (23° to 25°C), polygonal plates and polyhedrons formed with a preponderance of hexagonal prisms, particularly at *p*H 10.5 (Fig. 1). These hydrated crystals were birefringent; but, after drying, this property was lost, concomitant with the appearance of transverse fractures.

The sheaves of needle-like crystals of human lysozyme chloride formed in the cold at *p*H 10.5 resemble those of hen's egg-white lysozyme chloride developed under similar conditions (*3*). The polyhedral and hexagonal prismatic forms of the crystallized human enzyme, however, are distinct from the first-order tetragonal bipyramidal and second-order short prismatic forms of egg lysozyme chloride (*3*, *4*) and are consistent with the previously noted structural and chemical differences between these two enzymes. Detailed optical and x-ray crystallography studies of the human enzyme, similar to those carried out on egg-white lysozyme (*4*, *5*) should provide useful information on the comparative structures of two different enzymes with very similar substrate specificities.

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4 January 1967

Activity Coefficients of Aqueous Potassium Chloride Measured with a Potassium-Sensitive Glass Electrode

Abstract. *Values of $\gamma_{\pm KCl}$ over temperature and molality ranges of 10° to 50°C and 0.01 to 1.0 molal were determined with an electromotive-force cell: potassium-sensitive glass electrode, KCl (molality), Ag–AgCl. A more satisfactory method than is commonly employed was devised for treating the experimental measurements of potential.*

One of the many applications of the recently developed cation-sensitive glass electrodes is to determine mean activity coefficients, $\gamma_{\pm}$, of salts, singly or in mixtures, in aqueous solution. At least for monoelectrolyte solutions of univalent-cation salts, we believe that the accuracy of such values thus derived rivals that by more classical methods. Moreover, the cation-sensitive glass electrode stands alone in convenience. We now report $\gamma_{\pm}$ values for KCl at 10°, 18°, 25°, 38°, and 50°C. Our purpose is twofold: to check the accuracy of the technique at 25°C (at which temperature, data by classical methods are plentiful) and to present values for $\gamma_{\pm KCl}$ at other temperatures, at which earlier data are more meagre.

Our cell is without liquid junction and consists of a potassium-sensitive glass electrode, the aqueous KCl solution to be measured, and a Ag–AgCl electrode; it is represented as:

K-sensitive glass electrode, KCl (molality, m), Ag–AgCl

The potassium-sensitive electrode used was a Beckman 39137, the glass membrane of which has the recommended composition (*1*). The Ag–AgCl electrode was produced by electrolytic deposition of chloride on a silver-billet electrode (*2*).

Potential measurements were made with a vibrating-capacitor, high-impedance electrometer (Vibron 33B) and a potentiometer. Solutions were maintained to within 0.1°C of the desired temperature in a constant-temperature bath and were stirred magnetically. Individual measurements of potential were read to within 0.02 mv.

The potential developed by our cell may be expressed as:

$$E = E' + S(T) \log (\gamma m) \qquad (1)$$

where $(\gamma m) = (\gamma_{\pm} m_{\pm})_{KCl}$, $S(T) = 2(2.303\ RT)/F$, R is the gas constant, T is the absolute temperature, F is the Faraday, and m is the molality of the KCl solution. The quantity E' is a complex function of the glass and the particular construction of the K-sensitive electrode, and of the Ag–AgCl electrode. By comparing the potential E_s of a standard solution, of molality m_s and of known γ_s, with the potential E_x of a solution of molality m_x to determine γ_x, E' may be eliminated, and Eq. 1 yields

$$[(E_x - E_s)/S(T)] - \log (m_x/m_s) + \log \gamma_s = \log \gamma_x \qquad (2)$$

This method, which is analogous to that employed in determinations of *p*H, was used (*1*) to determine $\gamma_{\pm NaCl}$ over a molality range of approximately 0.13 to 6.1; 1.0-molal NaCl was used as the standard solution.

In deriving Eq. 2 one assumed that E' is constant; however, the value of E'

does not remain constant for long periods or for a wide range of solution concentrations; it can be treated accurately as a constant only in successive measurements of potential on solutions of relatively small incremental differences in concentration. Our treatment, which follows, recognizes these factors explicitly.

For successive potential measurements E_{n-1} and E_n, on solutions of concentration m_{n-1} and m_n, Eq. 1 leads, on elimination of E', to

$$[(E_n - E_{n-1})/S(T)] - \log(m_n/m_{n-1}) = \log \gamma_n - \log \gamma_{n-1} \quad (3)$$

or

$$(\Delta \log \gamma)_{n,\,n-1} = [\Delta E_{n,\,n-1}/S(T)] - (\Delta \log m)_{n,\,n-1} \quad (4)$$

Experimental values of m_n and E_n and the derived quantities $(\Delta \log \gamma/\Delta m)_{n,\,n-1}$ obtained by us appear in Table 1.

Our procedure was to plot each set of experimental values of $-(\Delta \log \gamma/\Delta m)_{n,\,n-1}$ for a given temperature as chords of length $\Delta \log m_{n,\,n-1}$, against $\log m$. The resulting plot was then differentiated graphically, by use of the "chord–equal area" method (*3*), to yield the continuous curve $-(d \log \gamma)/dm$ versus $\log m$. This method utilizes all the experimental data and is based on only the assumption that Eq. 4 is correct. The experimental curve for each temperature was extrapolated from approximately $\log m = -1.7$ to $\log m = -2.0$, by use of the Debye-Hückel expression in the form (see Eq. 6)

$$-[(d \log \gamma)/(dm)] = A/[2m^{1/2}(1 + aBm^{1/2})^2] = S_{D\text{-}H} \quad (5)$$

Values of $-\log \gamma$ were obtained from each curve by graphical integration, by use, as the constant of integration, of the value of $-\log \gamma$ at 0.01 m (Table 2), calculated from the Debye-Hückel expression:

$$-\log \gamma = Am^{1/2}/(1 + aBm^{1/2}) \quad (6)$$

Details of the entire graphical procedure will be given elsewhere.

Values of A and B on a molal basis, consistent with the form of Eqs. 5 and 6, were obtained from those listed by Robinson and Stokes (*4*) by multiplying their values by $d_w^{1/2}$, d_w being the density of water (*5*). We used $a = 4.0$ Å (*6*), which value leads to

$$\gamma_{25°}(0.01\ m\text{KCl}) = 0.901$$

which is identical with the "best" experimental value (*5*). Values of A, aB, and d_w used, and values of

$$-(d \log \gamma)/dm = S_{D\text{-}H}$$

at 0.01 m KCl (calculated from Eq. 5), are listed in Table 1.

In Table 2, the $\gamma_{\pm KCl}$ determined by us are compared with values from the literature. Several of the reported determinations were for temperatures a few degrees different from those used by us; in such instances we interpolated or extrapolated the data to our temperatures. The 25°C values of Lewis and Randall (*5*) summarize the best earlier values; from theirs we calculated the $\gamma_{\pm KCl}$ for other temperatures (Table 2), using the formula suggested by them (*7*). At 25°C our values agree closely with those of Hornibrook *et al.* (*6*) and Lewis and Randall (*5*). The average differences in $\gamma_{\pm}$ values are 0.0006 and 0.0007, respectively; the difference never exceeds 0.0015. The values of Hornibrook *et al.* tend to be slightly higher than ours, chiefly because they employed slightly different constants for A and B (Eq. 5) in extrapolating to infinite dilution. Agreement with the values of Harned and Cook (*8*) is not quite so good (average difference in $\gamma_{\pm}$ is 0.0015), while comparison with the values of Caramazza (*9*) shows an average difference of 0.0022, individual

Table 1. Measured potential differences (ΔE) at various temperatures for KCl solutions of various molalities (m), and the corresponding values of $(-\Delta \log \gamma/\Delta m)$ from Eq. 4. Values of constants* used in Eqs. 4–6.

m	ΔE (mv)	$-\Delta \log \gamma/\Delta m$	m	ΔE (mv)	$-\Delta \log \gamma/\Delta m$
Temperature, 10°C			*Temperature, 38°C*		
0.0111			0.0227		
.0323	48.57	1.456	.0349	21.45	1.059
.0509	21.08	0.550	.0535	21.13	0.757
.1095	34.23	0.483	.0814	20.87	0.469
.2418	34.83	0.257	.1206	19.10	0.413
.4960	31.12	0.138	.1845	20.51	0.289
.8572	23.60	0.076	.2773	19.55	0.200
Temperature, 18°C			.4140	19.24	0.134
0.0293			.5638	14.81	0.095
.0482	22.83	0.960	.8364	19.03	0.063
.0773	21.87	0.534	0.0300		
.1250	21.95	0.401	.0437	18.77	0.840
.1978	20.70	0.276	.0650	19.27	0.781
.3091	20.18	0.173	.0948	†	
.5024	21.77	0.116	.1415	19.21	0.398
.8118	21.70	0.066	.2099	19.02	0.250
Temperature, 25°C			.3167	19.99	0.156
0.0336			.4828	20.28	0.114
.0519	21.00	0.659	.6532	14.35	0.089
.0788	19.61	0.565	*Temperature, 50°C*		
.1234	20.93	0.404	0.0295		
.1863	18.86	0.310	.0521	28.97	0.947
.2872	19.73	0.211	.0932	29.70	0.504
.4542	20.98	0.130	.1547	25.57	0.338
.7181	20.95	0.083	.2680	27.46	0.217
0.0106			.5024	31.70	0.110
.0171	23.27	1.781	.8873	28.44	0.066
.0259	20.08	1.220	0.0425		
.0386	19.30	0.821	.0631	20.18	0.673
.0577	18.95	0.747	.0944	20.12	0.572
.0850	18.10	0.545	.1386	19.10	0.405
.1278	†		.2084	20.58	0.240
.1862	17.40	0.283	0.1067		
.2692	16.77	0.219	.2681	46.75	0.220
.3956	17.55	0.150	.3829	18.15	0.116
.5212	12.62	0.104	.5672	19.75	0.090
			.7916	16.57	0.069

*Constants.

Temp. (°C)	A	aB	d_w	$S(T)$	S_{D-H} (m, 0.01)
10	0.4988	1.305	0.9997	56.18	1.952
18	.5050	1.310	.9986	57.77	1.974
25	.5107	1.314	.9970	59.16	1.988
38	.5224	1.322	.9930	61.74	2.037
50	.5341	1.330	.9881	64.12	2.080

†Discarded as unstable.

Table 2. Comparison of our determinations (*10*) of $\gamma_{\pm KCl}$ with values from the literature. In parentheses is γ calculated by Eq. 6 and used in integration constant. Our intermediate values of $\gamma_{\pm KCl}$.

Ref.	Molality of KCl solution									
	0.02	0.03	0.05	0.07	0.10	0.20	0.30	0.50	0.70	1.00
					Temperature, 10°C					
10	.872$_0$	.850$_0$	.819$_5$	.797$_5$	.772$_5$	.720$_0$	.689$_0$	.649$_0$	.623$_5$	.597$_5$
*6**	.872$_0$	.850$_5$	.819$_5$	.797$_0$	.772$_0$					
7	.873	.851	.821	.799	.774	.720	.686	.644	.616	.588
8					.769	.718	.687	.648	.623	.598
9†			.817	.795	.769	.717	.686	.648	.623	.598
					Temperature, 18°C					
10	.870$_5$	.848$_5$	.817$_5$	.795$_0$	.769$_5$	.717$_5$	.687$_0$	.649$_0$	.624$_5$	.601$_0$
6†	.871$_0$	.849$_5$	.818$_5$	.796$_5$	.771$_0$					
7	.870	.848	.818	.797	.772	.719	.687	.648	.623	.598
8†					.769	.719	.688	.651	.627	.603
9			.815	.793	.768	.717	.686	.649	.626	.602
					Temperature, 25°C					
10	.869$_0$	.847$_5$	.816$_5$	.794$_5$	.769$_5$	.718$_0$	.688$_0$	.650$_0$	.626$_0$	.602$_0$
5	.868	.846	.816	.794	.769	.718	.687	.649	.626	.603
6	.870$_0$	.848$_0$	.817$_0$	.794$_5$	.770$_0$					
8					.769	.719	.688	.651	.628	.606
9			.813	.792	.767	.716	.686	.649	.626	.604
					Temperature, 38°C					
10	.866$_5$	.844$_0$	.813$_0$	.790$_0$	.765$_5$	.714$_5$	.685$_0$	.649$_0$	.626$_5$	.603$_0$
6†	.867$_0$	.845$_0$	.813$_5$	.791$_0$	.765$_5$					
7	.863	.840	.810	.788	.763	.712	.682	.647	.627	.607
8†					.766	.716	.683	.647	.626	.604
9†			.809	.787	.763	.713	.682	.646	.624	.603
					Temperature, 50°C					
10	.864$_0$	.841$_0$	.809$_0$	.786$_5$	.761$_5$	.711$_5$	.682$_5$	.647$_5$	.624$_5$	.602$_0$
*6**	.864$_0$	.841$_5$	.810$_0$	.787$_0$	.761$_5$					
7	.858	.835	.804	.781	.756	.705	.675	.641	.621	.603
9			.804	.783	.759	.709	.678	.643	.621	.600

Our intermediate values.

Temp. (°C)	Molality				
	0.01	0.015	0.04	0.15	0.40
10	(.9035)	.886$_0$	.833$_5$	.742$_5$	.666$_0$
18	(.9025)	.884$_5$	.831$_5$	.739$_0$	.665$_5$
25	(.9010)	.883$_0$	.830$_5$	.739$_5$	.666$_5$
38	(.8990)	.881$_0$	.827$_0$	.736$_0$	.664$_5$
50	(.8970)	.878$_5$	.823$_5$	.732$_5$	.662$_5$

*Extrapolated. †Interpolated.

differences being as great as 0.005. Caramazza's values tend to be distinctly lower than the others in the molality range 0.05 to 0.2. Calculated values from Lewis and Randall tend to diverge from other values at 38° and 50°C, and at 10°C for molality higher than 0.2. We believe that at 18°C our values for $\gamma_{\pm KCl}$ are probably about 0.001 too low in the molality range 0.05 to 0.3. This belief derives both from comparison with the values of Hornibrook *et al.* and of Lewis and Randall and, more importantly, from the way in which the $\gamma_{\pm KCl}$ change with temperature as a function of molality. For all temperature pairs, except the 18° and 25°C pair, the molality at which the $\gamma_{\pm}$ become identical is 0.4, or greater; for the 18° and 25°C pair, this molality is 0.09 (Table 2).

Our study is confined to the concentration range 0.01 to 1.0 molal KCl, but we would expect no difficulty in extending the method to higher concentrations. The precision to be expected at molality lower than 0.01 depends mainly on the nature of the particular glass electrode used, including its sensitivity to H^+, and cannot be predicted in the absence of experiment.

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$$4.5758 \log \gamma = (L_I/T) - 2.303\, \bar{J} \log T + \gamma_{25°C}$$

Values for $\gamma_{25°C}$ and L_I and $\bar{J}$ are listed in Lewis and Randall (*5*, p. 643).
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25 November 1966

Baja California: Late Cretaceous Dinosaurs

Abstract. *Late Cretaceous dinosaurs have been discovered along the Pacific margin of Baja California. The presence of* Hypacrosaurus *sp. is suggestive of correlation with the Upper Edmonton Formation, Alberta. Dissimilarities between the Baja California fauna and those from contemporary units along the eastern trend of the Rocky Mountains suggest that Baja California was ecologically separated from mainland Mexico during late Campanian and early Maastrictian time.*

The Los Angeles County Museum of Natural History is investigating the early Tertiary and late Cretaceous vertebrate faunas in Baja California (with permission of the Mexican Government). I previously reported newly discovered Paleocene localities (*1*). During the summer of 1966, I collected specimens of late Cretaceous dinosaurs in the vicinity of El Rosario, Baja California (30°N, 115°45′W). The beds containing dinosaur bones extend about 25 km along the Pacific Coast and about 33 km inland along the Arroyo Del Rosario.

The fauna is the only one from the Pacific margin of the continent where dinosaurian materials are abundant. In addition, the similarities and differences