

Table 1

Complexing carboxylic ions	Band shift from 5760 Å.	Energy difference $V \times 10^{-5}$	$\log \bar{K}$
Monobasic			
Formic	10	0.41	5.9
Acetic	60	2.48	6.6
Propionic	80	3.31	6.4
Butyric	100	4.14	6.3
iso-Butyric	80	3.31	6.2
Valeric	120	4.97	5.0
Caprylic	130	5.38	4.4
Capric	140	5.80	4.0
α-Carboxyl			
Glyoxalic	40	1.66	6.8
Pyruvic	90	3.73	6.1
Dibasic			
Oxalic	50	2.07	11.9
Malonic	40	1.66	9.1
Succinic	10	0.41	8.1
Glutaric	0	0	6.9
Unsaturated dibasic			
Fumaric	50	2.07	7.5
Hydroxy			
Glycollic	40	1.66	7.1
Lactic	50	2.07	8.0
Malic	60	2.48	8.4
Tartaric	60	2.48	9.0
Citric	70	2.90	11.1
Amino			
Glycine	80	3.31	11.4
Alanine	80	3.31	11.9
'Trilo'	90	3.73	11.0
'Enta'	120	4.94	16.8

with increasing values of $\log \bar{K}$. This effect is not one of momentary observation but one which has been continuously checked and noted through a series of some 800 observations. Further examination of the data obtained is being made in an attempt to elucidate this fundamental variation.

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¹ Tevebaugh, A.E.C.D.2749 (1949). Meeller and Brantley, *J. Amer. Chem. Soc.*, **72**, 5447 (1950); *Anal. Chem.*, **22**, 1393 (1950). Vickery, *J. Chem. Soc.*, 421 (1952); 385 (1954); "Chemistry of the Lanthanons" (Butterworth, London, 1953).

Dioxanates of Cadmium Chloride

DIOXANATES of cadmium chloride were precipitated from a solution of the anhydrous salts (certified purity) in acetal-free dioxane, prepared from Eastman Kodak technical 1,4-dioxane by the method of Eigenberger¹. The crude dioxanate (that is, wet with dioxane) was placed in the bulb of the isotenscope of Smith and Menzies², and oil of paraffin, U.S.P., was employed as the levelling liquid. The isotenscope was immersed in a water-bath maintained at $25.5 \pm 0.1^\circ \text{C}$. The system was evacuated and the pressure values were taken continuously until the lowest value was obtained. The pressures were read on a Zimmerly gauge by means of a cathetometer.

Constant vapour pressure-levels were obtained at the values: 36.80, 28.55, 25.40, 23.70, 19.10 mm. mercury and a lower level ranging from 15.00 to 16.90 mm. mercury. The experimental vapour pressure of pure dioxane at the temperature under study was found to be 37.08 ± 0.02 mm. mercury.

Two stable dioxanates have previously been reported^{3,4}: $\text{CdCl}_2 \cdot \text{dioxane}$ and $\text{CdCl}_2 \cdot \frac{1}{2} \text{dioxane}$. Interpretation of the constant pressure-level based on Gibbs's phase rule indicates the existence of at least four stable or metastable dioxanates. It is apparent thus that two or more dioxanates of

cadmium chloride exist other than those previously reported. The lower pressure-levels, 15.00–16.90 mm., correspond to the vapour pressures of solid dioxane crystallized in the iced vapour trap used in the system.

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¹ Eigenberger, E., *J. prakt. Chem.*, **130**, 75 (1931).

² Smith, A., and Menzies, A. W. C., *J. Amer. Chem. Soc.*, **32**, 1413 (1910).

³ Juhasz, R., and Yntema, T. F., *J. Amer. Chem. Soc.*, **62**, 3522 (1940).

⁴ Rheinboldt, H., Luyken, A., and Schmittman, H., *Chem. Abs.*, **31**, 6615 (1937).

Compressibilities of Sodium and Potassium Hydroxides

GUCKER¹, on the basis of the Debye-Hückel theory, found that the apparent molar compressibility of aqueous solutions of electrolytes conforms to the relation $\varphi(k_2) = \varphi^0(k_2) + S_k C^{1/2}$, where $\varphi(k_2)$ is the apparent molar compressibility at molar concentration C and $\varphi^0(k_2)$ at infinite dilution. S_k is a constant. Similarly, the adiabatic compressibility was found to follow the relation $\beta = \beta_0 + AC + BC^{3/2}$ (Bachem²), where β is the adiabatic compressibility at molar concentration C and β_0 is that of water, while A and B are constants.

Using the optical diffraction method, ultrasonic velocities in aqueous solutions of sodium hydroxide and potassium hydroxide have been determined in the frequency range 5–30 Mc./s. Adiabatic and apparent molar compressibilities are computed using the equations:

$$\beta = 1/V^2 d \quad (1)$$

and

$$\varphi(k_2) = \frac{100\beta}{C} - \frac{\beta_0}{d_0} \left\{ \frac{1,000 d}{C} - M_2 \right\} \quad (2)$$

where V is the ultrasonic velocity, d the density of the solution, d_0 the density of water and β_0 the compressibility of water and M_2 the molecular weight of the solute.

Ultrasonic velocity, V , and adiabatic compressibility, β , as functions of concentration C are represented in Fig. 1.

Sodium hydroxide. Ultrasonic velocity is a linear function of concentration in the range 0–6.3 moles/litre. The variation of adiabatic compressibility shows a peculiar behaviour. The entire range can be divided into two regions, each one following Bachem's relation with different sets of constants. One set of constants ($A = -9.38 \times 10^{-6}$; $B = 2.22 \times 10^{-6}$) satisfies the relation from 0 to 1.5 moles/litre and another set ($A = -8.21 \times 10^{-6}$; $B = 1.69 \times 10^{-6}$) holds good in the range 1.5–6.4 moles/litre. In spite of this, the apparent molar compressibility satisfies Gucker's relation with one set of constants.

Potassium hydroxide. In this case, ultrasonic velocity exhibits a peculiarity. The graph of velocity against concentration consists of two straight lines with slightly different gradients: one in the region 0–4.23 moles/litre and the other in the range 4.23–8.0 moles/litre. The difference in the gradients is quite definite though small.