phenylhydrazone) in 100 ml. of dry chloroform was brominated with 2.00 ml. of 1.02 N bromine in chloroform. After two minutes water was added. The aqueous phase contained 10.7 ml. of 0.10 N Br$^-$. A second wash with water after five minutes contained 0.3 ml. of 0.10 N Br$^-$. The chloroform phase was filtered through a pad of anhydrous sodium sulfate; $\lambda_{max.}^{chloroform}$ 364 mμ; ϵ 23,600.

Methyl 3,11-Diketo-12(α)-bromo-Δ^4-cholenate-3-(2,4-dinitrophenylhydrazone).—Chloroform was removed under reduced pressure from a half of the solution. The residue was dissolved in 10 ml. of acetic acid and 5 ml. of acetic anhydride under carbon dioxide. Red crystals which separated within five minutes were filtered after three hours. This material (276 mg., 84% yield; m. p. 237–239°) was identical with a sample of the Δ^4-hydrazone. Admixture with this sample did not depress the melting point; $\lambda_{max.}^{chloroform}$ 387 mμ; ϵ 30,200.

Chloroform was removed from the remaining half of the solution and the residue was dissolved in 15 ml. of acetic acid under carbon dioxide. Yellow crystals which separated after twelve minutes were filtered after three hours. The material weighed 298 mg. and was a mixture of the Δ^4-hydrazone and its hydrobromide salt; $\lambda_{max.}^{chloroform}$ 387 mμ; $E_{1 cm}^{1\%}$ 402. Eighty-three per cent. of the theoretical amount of hydrogen bromide was present in the aqueous phase after distribution of 71 mg. of the crystals between water and chloroform. From the organic phase, after displacement with acetic acid, red crystals (43 mg., m. p. 237–238°) of the Δ^4-hydrazone were separated. Admixture with a sample of this hydrazone did not depress its melting point; $\lambda_{max.}^{chloroform}$ 387 mμ; ϵ 30,100.

This hydrobromide was also prepared from 264 mg. of the Δ^4-hydrazone in 1.60 ml. of chloroform with 0.40 ml. of 2.08 N hydrobromic acid in acetic acid and 16 ml. of acetic acid. After fifteen minutes the yellow crystals were filtered under carbon dioxide and placed in a vacuum desiccator over sodium hydroxide. The wet crystals turn red if exposed to moisture. After drying, the yellow crystals (140 mg.) became red when heated to 130° and melted at 241–242°; $\lambda_{max.}^{chloroform}$ 387 mμ; $E_{1 cm}^{1\%}$ 417. After distribution between chloroform and water, the aqueous phase contained 85% of the theoretical amount of hydrogen bromide.

Methyl 3,11-Diketo-4,12(α)-dibromocholanate-3(2,4-dinitrophenylhydrazone).—Bromination of 2 millimoles of methyl 3,11-diketo-12(α)-bromocholanate-3(2,4-dinitrophenylhydrazone) was carried out as described. The chloroform was removed under reduced pressure to 10 ml., and 120 ml. of absolute ether was added. Canary yellow crystals separated, and three further crops were obtained by concentration of the mother liquor and the addition of ether. The total yield was 80%. An analytic sample was prepared by recrystallization of the first crop from chloroform–ether. When heated, the yellow crystals became red and melted at 134–137°; $\lambda_{max.}^{chloroform}$ 364 mμ, ϵ = 24,500. Calcd. for $C_{31}H_{40}O_7N_4Br$: C, 50.28; H, 5.45; Br, 21.59. Found: C, 50.07; H, 5.57; Br, 21.64; $[\alpha]_D$ −169 ± 2° (29.6 mg. in 3 ml. CHCl$_3$).

With another sample $[\alpha]_D$ −181 ± 2° (31.5 mg. in 3 ml. CHCl$_3$). After four hours and forty-five minutes this solution had become red, $[\alpha]_D$ −113 ± 2°. This indicates loss of hydrogen bromide in the chloroform solution.

The crystals of the 4-bromohydrazone were converted into the Δ^4-hydrazone in two ways. A. The bromohydrazone (148 mg.) was dissolved in 20 ml. of acetic acid at room temperature in an atmosphere of carbon dioxide. The yellow hydrobromide of the Δ^4-hydrazone separated after ninety minutes. The hydrogen bromide was removed by solution of the crystals in acetic acid and chloroform and concentration of the solvents under reduced pressure. The red Δ^4-hydrazone separated in 80% yield; m. p. 238–239°; $\lambda_{max.}^{chloroform}$ 387 mμ; ϵ = 29,400. B. One hundred ten milligrams of bromohydrazone was dissolved in 5 ml. of acetic anhydride and 10 ml. of acetic acid at room temperature in an atmosphere of carbon dioxide. After three hours the solution was concentrated under reduced pressure and the red Δ^4-hydrazone was ob-

tained in 85% yield; m. p. 238–239°, $\lambda_{max.}^{chloroform}$ 388 mμ, ϵ = 30,900.

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Cation Exchange Equilibria at Constant Ionic Strength

BY STANLEY W. MAYER

The theory of cation exchange equilibria has been developed to the stage at which activity quotient relationships have been formulated.[1] Unfortunately, serious uncertainty with regard to the mixed electrolyte activity coefficients in the resin, as well as in the aqueous phase,[2] has negated attempts to develop simple formulations for the equilibrium concentrations of the electrolytes in both phases.

Extensive investigations have shown that very frequently,[3] in a mixture of electrolytes at constant total ionic strength, the logarithm of the activity coefficient of an electrolyte varies linearly with its ionic strength, even when the solvent is a mixture of organic and inorganic molecules. When the ions involved in an exchange are of equal charge, the total ionic strength remains constant. For such exchanges, the principle of linear variation has been empirically applied in this note to develop a simple relationship for the equilibrium concentrations in both phases.

The exchange between two ions of equal charge, n, can be written as
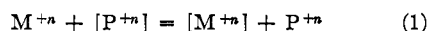
$$M^{+n} + [P^{+n}] = [M^{+n}] + P^{+n} \qquad (1)$$

where the bracket signifies that the ion is in the resin phase. Following the development of Connick and Mayer[2]

$$K = \frac{m_{[M^{+n}]}\, m_{P^{+n}}}{m_{M^{+n}}\, m_{[P^{+n}]}} \cdot \frac{\gamma_{[M^{+n}]}\cdot\gamma_{P^{+n}}}{\gamma_{M^{+n}}\cdot\gamma_{[P^{+n}]}} \cdot \frac{\gamma_{[X^-]}^n\cdot\gamma_{X^-}^n}{\gamma_{X^-}^n\cdot\gamma_{[X^-]}^n} \qquad (2)$$

$$K_m = K \frac{\gamma_{\pm MXn}^{n+1}\, \gamma_{\pm [PXn]}^{n+1}}{\gamma_{\pm [MXn]}^{n+1}\, \gamma_{\pm PXn}^{n+1}} \qquad (3)$$

where K_m is the concentration quotient $m_{[M^{+n}]}\cdot m_{P^{+n}}/m_{M^{+n}}\cdot m_{[P^{+n}]}$.

$$\log K_m = \log K + (n+1)\,(\log \gamma_{\pm 1} + \log \gamma_{\pm [2]} - \log \gamma_{\pm [1]} - \log \gamma_{\pm 2}) \qquad (4)$$

where electrolyte 1 is MX$_n$, electrolyte 2 is PX$_n$.

For those electrolytes which follow the law of linear variation at constant total ionic strength (employing the notation of Harned and Owen,[3] p. 459)

$$\log \gamma_{\pm 1} = \log \gamma_{(0)1} + \alpha_{12}\,\mu_1 \qquad (5)$$

$$\log \gamma_{\pm [2]} = \log \gamma_{[2](0)} - \alpha_{[21]}\,\mu_{[1]} \qquad (6)$$

$$-\log \gamma_{\pm [1]} = -\log \gamma_{(0)[1]} - \alpha_{[12]}\,\mu_{[1]} \qquad (7)$$

$$-\log \gamma_{\pm 2} = -\log \gamma_{2(0)} + \alpha_{21}\,\mu_1 \qquad (8)$$

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(1) Boyd, Schubert and Adamson, THIS JOURNAL, **69**, 2836 (1947).

(2) Connick and Mayer, *ibid.*, to be published.

(3) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 454 ff.

Noting that the first term of each of the right hand members of equations (5)–(8) is constant

$$\log K_m = \log K + (n + 1)k_1 -$$
$$(n + 1)(\alpha_{[21]} + \alpha_{[12]})\mu_{[1]} + (n + 1)(\alpha_{12} + \alpha_{21})\mu_1 \quad (9)$$

The α's of equation (9) are constant at any given total ionic strength. Combining the constants of equation (9)

$$\log K_m = k_2 + k_3\mu_{[1]} + k_4\mu_1 \quad (10)$$

Noting that the ionic strength of an electrolyte is proportional to its molality

$$\log K_m = k_2 + k_5m_{[1]} + k_6m_1 \quad (11)$$

The concentration of electrolyte 1 in the resin phase is proportional to the quantity that has been absorbed from the solution. Or

$$m_{[1]} = W(m_1^0 - m_1)/R = W m_2/R \quad (12)$$

where m_1^0 is the concentration of electrolyte 1 in the aqueous phase before equilibration; $W =$ grams of water involved in the equilibration; $R =$ grams of resin involved in the equilibration. Consequently

$$\log K_m = k_2 + k_5Wm_2/R + k_6m_1 \quad (13)$$

Equation (13) can be tested by using the data of Boyd, Schubert and Adamson[1] (Table IV) for sodium–hydrogen equilibrations at constant total ionic strength. It was found that the equation

$$\log K_m = 0.413 - 0.110Wm_{H^+}/R \quad (14)$$

fits the data for samples 7–9 within an average deviation of 0.3%. The data for samples 1–5 show an average deviation of 1.3% from the equation

$$\log K_m = 0.137 + 0.114Wm_{Na^+}/R \quad (15)$$

If sample 4 were omitted from consideration, the average deviation would be 0.2%. (The average deviation obtained by Boyd, et al.,[1] without making the complete correction for mixed electrolyte activity coefficients, was 4.4%.)

It is known that $(\alpha_{12} + \alpha_{21})$ for sodium chloride and hydrochloric acid mixtures is small.[3] When the concentrations of sodium chloride and hydrochloric acid are not high, the product $(\alpha_{12} + \alpha_{21})m_1$, does not vary sufficiently to cause significant change in the calculated values of K_m. For that reason, equations (14) and (15) are accurate, notwithstanding the omission of the m_1 variable.

The observation of Tompkins and Mayer[4] that K_m is constant for exchange between $< 10^{-4}$ m cerous ion and 0.5 M ammonium ion can be explained on the basis of the considerations in this note. The concentration of cerous ion varied through the range of 10^{-10} m to 10^{-4} m; however, the total ionic strength of the solution did not vary significantly. Accordingly, equation (9) can be applied, with $Ce(ClO_4)_3$ as electrolyte 1. Because μ_1 and $[\mu_1]$ are very small, the terms

(4) Tompkins and Mayer, THIS JOURNAL, **69**, 2859 (1947).

containing μ_1 and $[\mu_1]$ become negligible. Accordingly, $\log K_m$ must be constant in the range below 10^{-4} m cerous perchlorate.

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Precise Measurement of Polarographic Half-Wave Potentials

BY LOUIS MEITES

The recent polarographic literature contains many examples of half-wave potential measurements apparently accurate to ± 5 mv. or better. Because of the increasing interest in refined polarographic measurements, a method has been developed which yields values with a probable error of about ± 0.2 mv.

The residual current is measured at 10-mv. intervals over a range including the previously determined approximate value of the half-wave potential in question, and also at several points corresponding to the plateau of the wave. The reducible material is added and its diffusion current secured from the average of several measurements on the plateau. The applied potential is then adjusted so that the measured diffusion current is roughly half that on the plateau, and the current is measured at 1-mv. intervals on either side of this potential. After correction for the (interpolated) residual current at this potential, the half-wave potential (including, of course, the IR drop in the cell circuit) is most easily found by a short linear interpolation.

The application of the method is illustrated by the data on the tetrammino-cadmium(II) complex given in Table I. The ammonia solution was standardized against recrystallized sodium tetraborate decahydrate *via* perchloric acid. Volumetric equipment was calibrated by standard methods. Polarographic measurements were made with

TABLE I

HALF-WAVE POTENTIAL OF CADMIUM IN 0.812 F AMMONIA–0.10 F POTASSIUM NITRATE

The cadmium concentration was 0.65 millimolar. Measurements were made at 25.00 $\pm$ 0.01°

Ed.e. vs. S. C. E., volt	i_r	Microamperes $i_1 + i_r$	
−0.770	0.522		
− .775		2.458	
− .776		2.546	2.020
− .777	(0.526)	2.641	2.115
− .778		2.727	
− .780	.528		
− .950	.653	4.738	4.085 ⎫
−1.000	.688	4.776	4.088 ⎬ 4.086

$$E'_{1/2} = -0.776 - \left(\frac{2.043 - 2.020}{2.115 - 2.020}\right)(0.001) = -0.7762 \text{ v.}$$

$$E_{1/2} = E'_{1/2} + \frac{i_d R}{2} = -0.7762 + (2.034 \times 10^{-5})(210)$$

$$= -0.7758 \text{ v.}$$