

The Acid Decomposition of Dilute Sodium Thiosulfate

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IN a recent letter, Kerker¹ reports a marked effect of the concentrations of acid and thiosulfate on the optical density characteristic of the termination of the "induction period" (i.e., t_B , the time required for the appearance of colloidal sulfur). His explanation is that the optical density at t_B is due not only to the critical supersaturation concentration of dissolved sulfur, which must be practically constant, but also to tetra- and pentathionates produced in amounts which depend on the concentrations of acid and thiosulfate.

Kerker fails to point out that the contribution of polythionate to the optical density is important only when the concentrations of these reactants, particularly the acid, are sufficiently high.² La Mer and co-workers restricted their studies to that range of low concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ (0.001 to 0.003 M) and HCl (0.001 to 0.006 M) in which monodispersed sulfur hydrosols are produced. Over thirty experiments yielded an average of 0.020 ± 5 percent for $\log(I_0/I)$ at t_B .³ This in turn is responsible for an average deviation of 5 percent in the rate constant calculated for the homogeneous formation of sulfur. These small variations in $\log(I_0/I)$ and the demonstrable absence of a trend with concentration of reactants was taken as indirect evidence that no appreciable concentrations of polythionates are present at t_B in these dilute solutions. This view has been confirmed by Dinegar, Smellie, and La Mer⁴ by an independent method. Their chemical analyses of acidified solutions of thiosulfate (in the range of low concentrations described above) show that the rate of formation of polythionates is exceedingly small compared with that of sulfur. Polythionates are present in the early stages of the reaction (e.g., at t_B) in trivial amounts only.

Further evidence comes from Smellie's findings⁵ based on electrophoretic studies that the micelles in monodispersed sols in these dilute ranges are positively charged, whereas those in sols prepared from more concentrated solutions are negatively charged. The addition of very small amounts of polythionate ion (2×10^{-5} molar) to dilute sols reverses the sign of charge.

¹ M. Kerker, *J. Chem. Phys.* **19**, 1324 (1951).

² For a summary of relevant work by Bassett and Durant, Janickis, and others, see D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry of the Fifth- and Sixth-Group Nonmetallic Elements* (Prentice-Hall, Inc., New York, 1944), pp. 387-398.

³ E. M. Zaiser and V. K. La Mer, *J. Colloid Sci.* **3**, 571 (1948), Table II.

⁴ Dinegar, Smellie, and La Mer, *J. Am. Chem. Soc.* **73**, 2050 (1951).

⁵ R. H. Smellie, dissertation, Columbia University (May, 1951).

The Shape of the Coexistence Curve in the Critical Region

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IN a recent communication Rowden and Rice¹ reported data on the coexistence curve of aniline and cyclohexane and stated that six mixtures of different compositions in the neighborhood of the critical point all separated into two phases within 0.003° of the same temperature. From this they concluded that the coexistence curve had a flat top. However, if one attempts to fit their data by the equation

$$T_c - T = 60(x' - x'')^3, \quad (1)$$

where T is the temperature, T_c the highest temperature at which phase separation occurs, and x' and x'' are the mole fractions of the two phases coexisting at T , it is found that the curve passes within 0.003° of all the six mixtures nearest the critical point and in addition fits the mixtures of extreme composition. Hence, we conclude that these data are as consistent with the existence of a cubic coexistence curve as with a flat-topped coexistence curve.

A cubic curve has been found also in the two-liquid system

of carbontetrachloride-perfluoromethylcyclohexane² and for the liquid-gas coexistence curve of a number of gases.³ Guggenheim³ has found that the gas-liquid data may be represented over a wide range by an equation of the form

$$(T_c - T)/T_c = [k(\rho_l - \rho_g)/\rho_c]^3, \quad (2)$$

where ρ_g is the density of the gas, ρ_l the density of the liquid, and ρ_c the critical density. Equation (1) may be expressed in this form if x replaces ρ , and x_c , the critical mole fraction, is replaced by 0.5, its average value for the two components. When this is done, the constant k requires the value 0.3 in order to represent Rowden and Rice's data, 0.32 for the carbontetrachloride-perfluoromethylcyclohexane case, while Guggenheim used a value of $2/7$ or 0.286 for the rare gases. It is remarkable that this constant is so nearly the same for such diverse systems.

¹ R. W. Rowden and O. K. Rice, *J. Chem. Phys.* **19**, 1423 (1951).

² B. H. Zimm, *J. Phys. and Colloid Chem.* **54**, 1306 (1950).

³ E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

The Kinetics of the Exchange of Tritium between Hypophosphorous Acid and Water

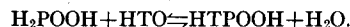
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BECAUSE the reactions of phosphorus and its compounds have long been a source of fundamental interest and even affectionate regard to chemists, to physicists, and to those delving into the chemistry of plant life and because, in particular, the oxidation kinetics of aqueous hypophosphorous acid present some very puzzling features, it was deemed important to approach the kinetics problem from a fresh point of view.

We have, therefore, measured the rates of exchange of radioactive hydrogen (tritium) between tritiated water, HTO, and the two "undissociable" hydrogens of monobasic hypophosphorous acid, H_2PO_2



Exchange runs were carried out as follows: stock solutions of hypophosphorous acid and tritiated water were mixed in a thermostat. Samples were withdrawn from time to time and quenched by neutralizing them with thalious hydroxide. (Preliminary experiments showed that the exchange reaction does not take place in neutral solution.) The resulting solution was then evaporated at room temperature in vacuum to obtain solid thalious hypophosphite. Circular, flat planchets were then filled with the thalious hypophosphite and inserted into a windowless, Q -gas flow, Geiger-Müller counter for tritium assay. The background count of this counter is 36-38 c/m; sample activities ranged from 300 to 1800 c/m. About 45 runs were made at 16 different concentrations to determine the order and the values of the catalytic coefficients (rate constants) given in the following. All runs were carried out in duplicate or triplicate; the average reproducibility of a given run was about 2 percent.

It was found that the kinetics of this exchange in acid solution follow the equation

$$R = k\text{H}(\text{H}^+)(\text{H}_3\text{PO}_2) + k\text{H}_3\text{PO}_2(\text{H}_3\text{PO}_2)^2, \quad (1)$$

when H^+ and H_3PO_2 are the only acids present in the system. R is the rate at which the exchange of one "undissociable" hydrogen atom per acid molecule takes place.¹ Experiments in which other acids were added to the system showed that (1) is a special case of the general rate equation

$$R = (\text{H}_3\text{PO}_2) \sum_a (\text{HA})_a k_a, \quad (2)$$

that is, the reaction is subject to general acid catalysis in the Brönsted sense.

At 30.0° the values of the catalytic coefficients in (1) are

$$k\text{H} = 3.3 \pm 0.15$$

$$k\text{H}_3\text{PO}_2 = 2.9 \pm 0.14$$

in units of liters per mole hour.

Studies by several investigators^{2a-2e} on the rate of oxidation of aqueous hypophosphorous acid to phosphorous acid by various oxidizing agents (Br_2 , Cl_2 , I_2 , HgCl_2 , CuCl_2 , IO_3^-) have shown that the rate law, and under certain conditions, the rate constants are the same for all of these oxidation reactions irrespective of which oxidizing agent is used. In acid solution the oxidation reaction follows the rate law

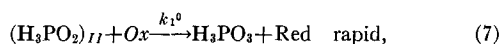
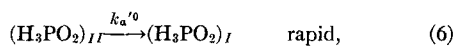
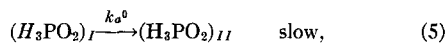
$$R^0 = \frac{(\text{H}_3\text{PO}_2)\sum_a k_a^0(\text{HA})_a}{1 + [\sum_a (\text{HA})_a k_a^0 / k_1^0(\text{Ox})]} \quad (3)$$

where R^0 is the rate at which hypophosphorous acid is oxidized to phosphorous acid, (Ox) is the concentration of the oxidizing agent, and k_1^0 is a constant which varies with the oxidizing agent. When the concentration of the oxidizing agent is made about 0.1*f* or greater, (3) reduces to

$$R^0 = (\text{H}_3\text{PO}_2)\sum_a (\text{HA})_a k_a^0, \quad (4)$$

that is, the rate becomes independent of the concentration and nature of the oxidizing agent. This happens because under these conditions, reaction (5) below becomes rate determining.

The mechanism proposed to explain this oxidation rate law is as follows:



where $(\text{H}_3\text{PO}_2)_I$ denotes the concentration of the "normal" form of hypophosphorous acid in solution, and $(\text{H}_3\text{PO}_2)_{II}$ denotes the concentration of an "active" form. It is assumed that the oxidizing agent reacts only with the active form to produce phosphorous acid, and that both reactions (5) and (6) are subject to general acid catalysis. The further assumption of a small, steady-state concentration of the active form leads to the aforementioned rate laws, (3) and (4).

The values of the catalytic coefficients for H^+ and H_3PO_2 found at 30.0° for the oxidation reactions are^{2c}

$$\begin{aligned} k_{\text{H}^+} &= 21 \\ k_{\text{H}_3\text{PO}_2} &= 7.6 \end{aligned}$$

in units of liters per mole hour.

The exact correspondence between the rate laws (1) and (4) and the close correspondence between the values of the catalytic coefficients k_a and k_a^0 for the two acid catalyzed reactions shows that the exchange reaction takes place *via* the equilibrium expressed by reactions (5) and (6). Furthermore, it seems quite likely that the normal and the active forms differ in the position of a hydrogen atom on the H_3PO_2 molecule. The difference between the numerical values of k_a and k_a^0 is a result of isotope effects.

Thus the results of the exchange experiments serve to verify the presence of two tautomeric forms of hypophosphorous acid in aqueous solution and the essential validity of the mechanism of the oxidation reaction originally suggested by Mitchell.^{2a} Moreover, a clue emerges regarding the more precise nature of the two tautomeric forms. A detailed account of this research will be published later.

We wish to acknowledge with thanks the helpful discussions with Professor Ernest Swift and Dr. Norman Davidson. The research was supported in part by a grant from the Research Corporation for which we are grateful.

¹ J. N. Wilson and R. G. Dickson, *J. Am. Chem. Soc.* **59**, 1358 (1937). R. B. Duffield and M. Calvin, *J. Am. Chem. Soc.* **68**, 557 (1946). Friedlander and Kennedy, *Introduction to Radiochemistry* (John Wiley and Sons, Inc., New York, 1949), p. 288.

² a. A. D. Mitchell, *J. Chem. Soc.* **117**, 1322 (1920); **119**, 1266 (1921); **121**, 1624 (1922). b. R. O. Griffith and A. McKeown, *Trans. Faraday Soc.* **30**, 530 (1934). c. Griffith, McKeown, and Taylor, *Trans. Faraday Soc.* **36**, 752 (1940). d. P. Nylen, *Z. anorg. u. allgem. Chem.* **230**, 385 (1937). e. P. Hayward and D. M. Yost, *J. Am. Chem. Soc.* **71**, 915 (1949).

Change in Thermodynamic Properties Along Isentropes at the Coexistence Line Far from the Critical Point*

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THE isentropic curve on a p - v diagram for a single component substance undergoes an abrupt change in slope on passing through the coexistence line.¹ It does not seem to have been noticed that in the region of volumes much larger than critical, the amount of this change can be calculated with a degree of approximation usually employed in analyses of this type.

In the coexistence region the slope of the isentropic is given by

$$(\partial p / \partial v)_S = -T(\partial p / \partial T)_v^2 / C_v. \quad (1)$$

Using the Clausius-Clapeyron equation, and assuming that the specific volume of the condensed phase can be neglected compared to that of the vapor and that the specific heat L is constant, is equivalent to taking for the vapor pressure an equation of the type $\ln p = A - B/T$, with A and B constants. At the coexistence line

$$C_v = C_{c, \text{sat.}} + (L^2 / RT^2 - 2L/T), \quad (2)$$

and

$$(\partial p / \partial v)_S = -p^2 / RT(1 - 2RT/L + C_{c, \text{sat.}} RT^2 / L^2)^{-1}, \quad (3)$$

where $C_{c, \text{sat.}}$ is the specific heat of the saturated condensed phase. For those substances having $C_{c, \text{sat.}} RT^2 / L^2 \ll 1$, Eq. (2) reduces to

$$(\partial p / \partial v)_S = (-p^2 / RT)(1 - 2RT/L)^{-1}. \quad (2')$$

It is interesting to compare this with the slope along the coexistence line

$$(\partial p / \partial v)_{\text{coex.}} = (-p^2 / RT)(1 - RT/L)^{-1}. \quad (4)$$

Evidently for such substances the saturate disentrope is always steeper, at the coexistence line, than the coexistence line itself.

A calculation for several substances for which virial coefficient data are available indicates that only a very small error will be made if, in computing the slope up to the coexistence line, the perfect gas equation of state is used. Using the perfect gas equation it follows that

$$(\partial p / \partial v)_{S, \text{vap.}} = -\gamma p^2 / RT. \quad (5)$$

An example of the abrupt change in slope occurs with nitrogen at 65°K where the slope at the coexistence line decreases sharply by about 10 percent. Equally sharp decreases occur for the related adiabatic compressibility and sound speed defined as $(\partial p / \partial p)_S$.²

Illuminating discussions on this problem with Dr. K. F. Herzfeld are gratefully acknowledged.

* Some of this material was reported at the New York meeting of the American Physical Society, February 1-3, 1951.

¹ F. Bosnjakovic, *Technische Thermodynamik I* (Edwards Brothers, Ann Arbor, 1944), p. 188.

² Wegener, Reed, Jr., Stollenwerk, and Lundquist, *J. Appl. Phys.* **22**, 1077 (1951).

Erratum: On the Energetic Treatment of Non-Isothermal Processes

[(*J. Chem. Phys.* **19**, 519-25 (1951))]

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TEXT to Fig. 1, 350°C should be 327°C; text to Fig. 2, 327°C should be 350°C; the line just after Eq. (21), cation should be anion; and sixth line after Eq. (32), Eq. (8) should be Eq. (32).