

Fig. 5.

for higher values. This rise is also observed from the very beginning for the 2nd and 3rd sets of data, while theory predicts a continuous, although very slow drop in $[M]$ as $[X_0]$ increases (Fig. 6). At very high values of $[X_0]$ the experimental values for $[M]$ again show a slight drop.

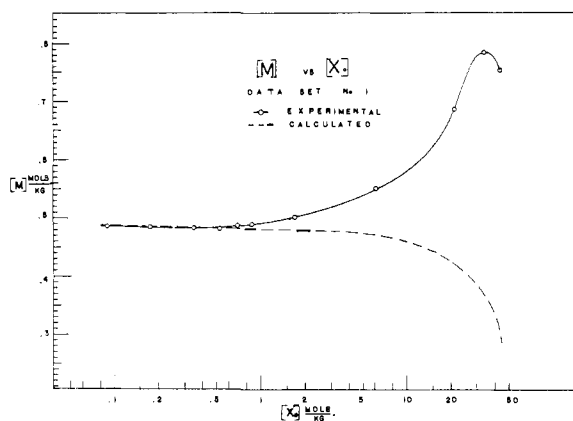


Fig. 6.

The availability of equilibrium constants for three different temperatures suggests the possibility of finding by interpolation of those values (on a $\log K$ vs. $1/T$ graph) the values for the constants at in-

t , °C.	220	230	240	250	260
K	0.00254	0.00266	0.00279	0.00291	0.00304
K_3	1.97	1.79	1.63	1.49	1.36
$[M_{X_0} \rightarrow 0]$	0.508	0.559	0.614	0.671	0.735

termediate temperatures. These values are shown in Table V, together with $[M_{X_0} \rightarrow 0]$, which is the theoretical equilibrium monomer concentration as $[X_0]$ approaches 0.

Graphs of P vs. $[X_0]$ calculated from the above data are shown in Fig. 7. On a log-log scale, linearity is observed for $0.1 < [X_0] < 2.0$ in the tem-

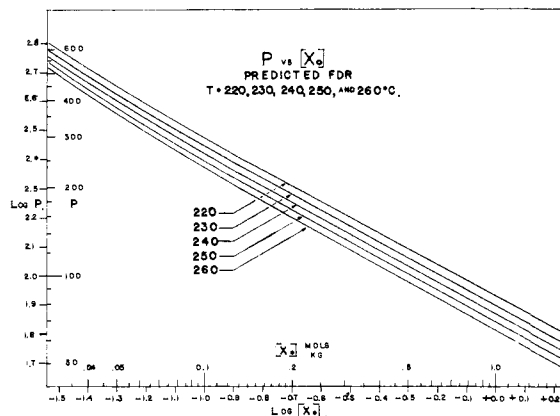


Fig. 7.

perature range investigated, suggesting a single formula which would define the P for any $[X_0]$ in this linear range. The constants A and B corresponding to the equation $\log P = A + B \log [X_0]$ were determined for each temperature, and since an apparently linear relationship exists between these constants and the temperature ($A = 2.456 - 0.00241t$; $B = -0.4365 - 0.000465t$, where t is the temperature in °C.), the required formula is

$$\log P = (2.456 - 0.00241t) - (0.4365 + 0.000465t) \log [X_0] \quad (11)$$

This formula should be also of practical interest since the range of linearity corresponds to the commercially employed range of P values.

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[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, DEPAUW UNIVERSITY]

The Potential of the Tellurium-Tellurium Dioxide Electrode as a Function of pH

By JOHN A. RICKETTS AND LOUIS W. TRESSELT

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The electromotive force of the electrochemical cell, $\text{Te}(s)/\text{TeO}_2(s)$ buffer solution//saturated calomel electrode, is determined as a function of pH, at a temperature of 25°. The variation can be represented by the relationship $E = 0.349 - 0.0469\text{pH}$ for the pH range 2.2 to 8.0. In addition the tellurium electrode is shown to be a suitable indicator electrode in acid-base titrimetry.

The reversible oxidation potential E of a metal electrode in contact with a solution that is saturated with a sparingly-soluble oxide of the metal is expressed by the equation

$$E = E^{\circ'} + \frac{2.303RT}{F} \text{pH} \quad (1)$$

provided that the only source of metal ions in solution is through ionization of the oxide. $E^{\circ'}$ is a constant characteristic of the electrode reaction and the other terms have their usual significance.¹ The

(1) See, for example, G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier Publishing Company, New York, N. Y., 1951, p. 293.

only such system that has been studied extensively is the antimony-antimony oxide electrode.² The purpose of this investigation was to determine the suitability of the tellurium-tellurium oxide electrode for the potentiometric measurement of hydrogen ion activity in aqueous solutions.

Experimental

The electromotive force of the galvanic cell

Te(s)/TeO₂(s) buffer soln./satd. calomel electrode
 was measured using a Leeds and Northrup Type K-2 Potentiometer coupled with a General Electric portable, high sensitivity galvanometer. All measurements were made at 25 ± 0.1°. The e.m.f. of each galvanic cell was determined twice using duplicate saturated calomel electrodes which were prepared from triply distilled mercury, thrice recrystallized KCl and C.P. calomel (low SO₄⁻² and Hg⁺²). These calomel half cells had potentials that differed by no more than 0.0001 v. when checked against each other. They were not checked against a standard hydrogen electrode. The liquid junction was established with saturated KCl solution through an asbestos wick sealed through the end of a side arm extending from the calomel electrode vessel. The latter dipped into a beaker containing the buffer and the tellurium electrodes.

MacIlvaine citric acid-disodium phosphate buffer solutions covering the pH range, 2.2 to 8.0 were prepared immediately before they were used from C.P. reagents.³ Each buffer was saturated with C.P. TeO₂ which seemed to expedite the establishment of a stable potential. As measured with a Beckman Model G pH meter, those buffer solutions that contained no TeO₂ and those that were saturated with the compound had the same pH. In buffer systems that contained potassium acid phthalate the tellurium electrodes failed to reach stable potentials.

C.P. tellurium, further purified by electrodeposition,⁴ was used to prepare the indicator electrodes. Spectroscopic analysis of the electrodeposited metal showed it to be free from selenium. Slugs 3 to 4 cm. long were prepared by repeated vacuum casting in 7 mm. Pyrex tubing until no further distillation of volatile matter from the molten metal was observed. Copper leads were soldered to the electrodes with Wood's metal. The electrodes were then cemented into glass tubing; all joints were covered with paraffin to prevent possible contamination of the buffer solutions. The electrodes were mirror-polished using graded metallographic emery papers, given various etching treatments in mineral acids, thoroughly rinsed and then placed in the buffer solution. Although in many instances the system appeared to reach a stable potential, this potential could not be reproduced—a condition previously reported by Tomíček and Poupe.⁵ The most reproducible results were obtained by scratching the polished electrodes with 1/0 emery paper immediately before use; consequently, this treatment was adopted. Observations were made 15 minutes after immersion in the solution.

Although cast electrodes were mainly employed, some experimentation was made using platinum foil or wire electrodes upon which an apparently amorphous, adherent coating of tellurium had been electrodeposited. The bath was a 2% sodium carbonate solution saturated with TeO₂. A tellurium slug was used as anode. A potential difference of 1.5 v. applied to the cell (the current density was not measured) gave a satisfactory coating. Because this coating reacted with concentrated H₂SO₄ to give the red TeSO₃, it was assumed to be elemental tellurium.⁶

Results and Discussion

Table I summarizes those observations deemed the most reliable. Since some of the brittle elec-

(2) For a review see J. Stock, W. Purdy and L. Garcia, *Chem. Revs.*, **58**, 611 (1958).

(3) N. Lange (ed.), "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 5th ed., 1944, p. 1118.

(4) F. Mathers and H. Turner, *Trans. Am. Electrochem. Soc.*, **54**, 293 (1928).

(5) O. Tomíček and F. Poupe, *Collection Czechoslov. Chem. Commun.*, **8**, 520 (1931).

(6) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green and Co., London, 1931, p. 116.

TABLE I
 THE VARIATION OF THE E.M.F. OF THE CELL Te(s)/TeO₂(s) BUFFER SOLN./SATD. CALOMEL ELECTRODE^a

pH	Electrode A		Electrode B				Electrode C				Electrode D								
	Run 1	Run 2	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
2.2	0.2419	0.2436	0.2406	0.2461	0.2425	0.2355	0.2402	0.2418	0.2376	0.2376	0.2407	0.2381	0.2468	0.2444	0.2449	0.2446	0.2426	0.2419	0.2377
3.0	.2019	.2098	.2022	.2149	.1928	.1928	.2006	.2193	.2006	.2030	.2030	.1926	.2144	.2022	.2210	.2210	.2048	.2050	.1940
4.0	.1702	.1823	.1658	.1619	.1643	.1611	.1671	.1655	.1663	.1651	.1597	.1510	.1779	.1658	.1665	.1679	.1622	.1559	.1510
5.0	.1179	.1387	.1163	.1310	.1193	.1313	.1193	.1302	.1294	.1167	.1088	.1088	.1251	.1149	.1261	.1251	.1245	.1135	.1099
6.0	.0721	.0714	.0705	.0807	.0642	.0783	.0746	.0753	.0668	.0760	.0669	.0638	.0736	.0684	.0741	.0654	.0716	.0657	.0645
7.0	.0186	.0166	.0203	.0233	.0365	.0365	.0240	.0218	.0311	.0311	.0170	.0060	.0201	.0183	.0164	.0164	.0286	.0160	.0121
8.0	-.0369	-.0315	-.0923	-.0178	-.0345	-.0139	-.0272	-.0249	-.0352	-.0208	-.0380	-.0121	-.0358	-.0349	-.0218	-.0378	-.0289	-.0390	-.0404

^a The negative sign signifies that the polarity of the tellurium electrode was negative with respect to the calomel electrode.

trodes fractured in repolishing, all could not be used for the same number of runs. The results of each determination were given equal weight, the Pierce-Chauvenet Criteria⁷ being used to decide whether an observation was to be rejected. Treatment of the data by the method of least squares gives the relationship

$$E = 0.349 - 0.0469pH \quad (2)$$

The probable deviation of any single result from the value predicted by (2) is less than 0.005 volt.

If the contribution of the saturated calomel electrode and associated liquid junction is assumed to be -0.244 v. (oxidation potential),⁸ the reduction potential for the tellurium—tellurium oxide couple becomes

$$E' = 0.593 - 0.0469pH \quad (3)$$

At 20° in the pH range 0 to 9 Tomíček and Poupe⁶ report

$$E' = 0.603 - 0.058pH \quad (4)$$

These workers employed mechanically polished tellurium electrodes and oxygen-saturated buffer solutions. If, in oxygen saturated solutions, tellurium behaves as an oxygen electrode, the theoretical slope would be 0.059 at 25°. Preliminary measurements do indicate a positive oxygen effect; the e.m.f. of the cell does increase when oxygen is bubbled through the system. Passage of nitrogen has negligible effect on the e.m.f. of the cell.

The lack of agreement of potential-pH relationships of metal-metal oxide electrodes among vari-

(7) T. Crumpler and J. Yoe, "Chemical Computations and Errors," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 190.

(8) H. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., A.C.S. Monograph 95, Reinhold Publ. Corp., New York, N. Y., 1950, p. 320.

ous workers is well known. Tourky and Moussa⁹ have summarized the relationships from twenty-five investigations of the antimony-antimony oxide electrode; the slopes and intercepts ranged from 0.043 to 0.0647 and from 0.151 to 0.290, respectively.

Brief studies of the suitability of both the cast and the electroplated amorphous tellurium electrodes in acid-base titrimetry also were made. In the titration of HCl or acetic acid with NaOH, the equivalence points obtained, respectively, with the glass and the tellurium electrodes agreed to $\pm 0.5\%$. Contrary to the findings of Brouwer¹⁰ and Bravo¹¹ who claimed that potential stabilization of the tellurium-calomel couple was not attained for two or three hours after each addition of base, our electrodes stabilized in a few minutes. At a pH greater than 10, however, stability could not be realized.

In solution tellurium dioxide is a weak ampholyte; its isoelectric point occurs at a pH of 4.2.¹² Thus the dissociation of the basic form is not the simple $\text{Te}(\text{OH})_4 = \text{Te}^{+4} + 4\text{OH}^-$ as postulated by Kasarnowsky.¹³ A calculation of the standard electrode potential of the Te/TeO₂ half cell cannot be made satisfactorily. Further studies of this electrode system are being made using cells without liquid junction.

Acknowledgments.—The authors wish to thank the Research Corporation of America for the funds that were used to support this work.

(9) A. Tourky and A. Moussa, *J. Chem. Soc.*, 752 (1948).

(10) St. de Brouwer, *Bull. soc. chim. Belg.*, 48, 158 (1938).

(11) A. Bravo, *Ann. chim. applicata*, 26, 162 (1936).

(12) I. Assa and S. Awad, *J. Phys. Chem.*, 58, 948 (1954).

(13) J. Kasarnowsky, *Z. physik. Chem.*, 109, 287 (1924).

GREENCASTLE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Studies. LIV. Methanol Vapor¹

BY RAYMOND P. PORTER AND W. ALBERT NOYES, JR.

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The principal products of the photochemical decomposition of methanol vapor at wave lengths below 2000 Å. are hydrogen, formaldehyde, ethylene glycol together with small amount of carbon monoxide and methane. By use of scavengers and by study of deuterated methanol, CD₃OH, it is shown that there are at least two primary processes, one of which must be $\text{CH}_3\text{OH} + h\nu = \text{CH}_3\text{O} + \text{H}_2$. One process must give hydrogen atoms. Secondary reactions are discussed.

The thermal decomposition,² the direct photochemical decomposition,³ and the mercury sensitized decomposition⁴ of methanol vapor have been studied. Patat and Hoch³ concluded that the

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(2) W. A. Bone and H. Davies, *J. Chem. Soc.*, 1065, 1691 (1914); E. Peytral, *Compt. rend.*, 165, 703 (1917); J. M. C. Fletcher, *Proc. Roy. Soc. (London)*, 147A, 119 (1934).

(3) F. Patat and H. Hoch, *Z. Elektrochem.*, 41, 494 (1935).

(4) H. S. Taylor and J. R. Bates, *THIS JOURNAL*, 49, 2438 (1927); M. K. Phibbs and B. de B. Darwent, *J. Chem. Phys.*, 18, 495 (1950).

primary process for direct photochemical decomposition was into formaldehyde and hydrogen. Hydrogen and formaldehyde were found to be produced in equal amounts. Rough measurements indicated a quantum yield of 1.1 for hydrogen formation. A heavy wall deposit was formed, however. The results on the mercury sensitized reaction are best explained by the initial formation of CH₂OH radicals and hydrogen atoms.

Fricke and Hart⁵ and Farkas and Hirshberg⁶ found the ultraviolet irradiation of aqueous solutions of methanol to give mainly hydrogen and formaldehyde. Differences in results and in interpretation need not be discussed here.

(5) H. Fricke and E. J. Hart, *ibid.*, 4, 418 (1936).

(6) L. Farkas and Y. Hirshberg, *THIS JOURNAL*, 59, 2450 (1937).