497. *Studies on Some Metal Electrodes. Part IX.* The Temperature Coefficients of the Copper and Antimony Electrodes in Solutions initially Free from Their Ions. The Mode of Oxidation of These Metals.*

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Examination of the temperature coefficients of the copper and the antimony electrode in buffer solutions initially free from the metal ions in and out of contact with air reveals for copper a negligible coefficient between 20° and 47° in air except in solutions of pH ≥ 7 in which it is as high as 3·7 mv/°c from 35° to 47°. Out of contact with air a regular small coefficient of $-1 \pm 0{\cdot}05$ mv/°c is obtained and the potentials correspond closely to the thermodynamic value for the Cu–Cu_2O couple (designated as E_0'). Calculations based on the latter value give for the standard entropy $S^{\circ}_{Cu^+}$ a value of 11 ± 1 cal./°c/g.-ion. Massive and plated antimony electrodes yield in both cases similar E_0'–temperature diagrams characterised by minima and maxima within the range 20—60°. The minima all occur at about 40° and correspond, in absence of oxygen, to the thermodynamic E_0'(Sb–Sb_2O_3). The temperature coefficients vary and are usually high.

The results are discussed in the light of the theory of lattice defects on the basis that whereas cuprous oxide has a metal-deficient lattice and can thicken through the upward diffusion of metal ions leading to a stable system, yet oxygen deposited on antimonous oxide persists as doublets. These are readily desorbed with rise of temperature unless oxygen is re-formed on the surface by some other process. Under conditions favouring the formation of a secondary layer of cupric oxide on copper (pH ≥ 7), the electrode may become passivated by a similar process.

IT is fairly well established that an oxide with a defect-metal lattice such as cuprous oxide thickens through the diffusion of ions and electrons from the underlying metal towards the

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metal oxide–gas interface. At higher temperatures the migration of ions is brought about by thermal diffusion, whereas at lower ones it may be effected through the electric fields operative at the metal–metal oxide–gas interfaces (Wagner, *Z. physikal. Chem.*, 1933, *B*, **21**, 25; 1936, **32**, 447; Wagner and Hammen, *ibid.*, 1938, **40**, 197; Jost, "Diffusion und Chemische Reaktion in festen Stoffen," Dresden and Leipzig, 1937; Ann Arbor, Michigan, 1943, p. 149; Hoar and Price, *Trans. Faraday Soc.*, 1938, **34**, 867). One would therefore expect that oxygen deposited on a copper–cuprous oxide surface would contribute to the thickening of the oxide without persisting as such for long. If this was the case, a Cu–Cu_2O electrode should manifest the thermodynamic E_0' value, and its temperature coefficient should be small and comparable with those of other stable systems. In antimony trioxide, on the other hand, where the lattice defects, as in other metal trioxides, are most probably restricted to oxygen ions (Fischbeck, *Z. Elektrochem.*, 1933, **39**, 316; Jost, *op. cit.*, p. 79; Mott, *Proc. Camb. Phil. Soc.*, 1938, **34**, 568; *Trans. Faraday Soc.*, 1940, **36**, 472; 1947, **43**, 429; Zintl and Croatto, *Z. anorg. Chem.*, 1939, **242**, 79), diffusion of metal ions may not take place and oxygen deposited on the oxide surface from the atmosphere persists as oxygen doublets. Consequently, an Sb–Sb_2O_3 electrode should behave as a metal–metal oxide electrode subject to an oxygen overvoltage effect. Both this and the arsenic system are more correctly designated as metal–metal oxide–oxygen than as metal–metal oxide electrodes (Tourky and Mousa, *J.*, 1948, 750; 1949, 1297). The temperature coefficient of such electrodes should vary, being comparatively large like those usually encountered in overvoltage phenomena (Bürcher and Harkins, *J. Amer. Chem. Soc.*, 1923, **45**, 2890; Hickling and Salt, *Trans. Faraday Soc.*, 1941, **37**, 333; Milton Le-Baron and Choppin, *Trans. Amer. Electrochem. Soc.*, 1940, **77**, 12; Onoda, *Z. anorg. Chem.*, 1927, **165**, 79, 93; Bockris and Parsons, *Trans. Faraday Soc.*, 1949, **45**, 322, 916). The object of the present investigation was to find whether these predictions were borne out by experiment.

Experimental.—The copper electrodes were prepared as described by Tourky and Wakkad (*J.*, 1948, 740). Stick as well as plated antimony electrodes, prepared after Schukoff and Awsejewitsch (*Z. Elektrochem.*, 1930, **35**, 348) by electrodeposition from a 25% solution of antimony trichloride in dry acetone, were used. The buffer solutions used for evaluating the E_0' values were acetic acid–sodium acetate and Clark and Lubs buffers within the pH ranges 5—7·3 for copper and 4—7·5 for antimony. Cells and apparatus were essentially the same as used by Tourky and Mousa (*loc. cit.*). The measurements were carried out in air at temperatures ranging from 20° to 47° or to 60° with the copper and the antimony electrodes, respectively. After the electrodes had been subjected alternately to the action of hydrogen and to high vacuum at 350° and kept out of contact with air, the measurements were performed between 20° and 41° and to 50°, respectively. The potential measurements were accurate to four decimal places.

RESULTS AND DISCUSSION

(A) *Temperature Coefficient of the Copper–Cuprous Oxide Electrode.*—In studying the behaviour of the spongy copper electrode in buffer solutions initially free from copper ions, Tourky and Wakkad (*loc. cit.*) found that the electrode responded to variations in pH from 4·65 to 8·08 in air. The linearity of the potential–pH relation within their experimental range, and the fact that $\Delta E/\Delta pH$ was close to the theoretical value, suggested that the metal functioned as a metal–metal oxide electrode. They found that, when the electrode had been kept out of contact with air and subjected alternately to the action of hydrogen and to high vacuum, it functioned as a metal–metal oxide electrode within the pH range 6—8.

In the present investigation it was found impracticable to extrapolate the E_H–pH plots obtained in air at all applied temperatures to pH = 0. By calculating E_0' for each buffer, values were obtained (see below) which, though showing slight irregularities, exhibited but negligible variations with temperature within the pH range 4·95—6·33. From pH 6·94 to 7·32 they behaved similarly from 20° to 35°, but changed considerably with rise of temperature from 35° to 47°.

Electrodes subjected alternately to the action of hydrogen and high vacuum, yielded E_H values at the steady states which varied linearly and almost theoretically within the pH

Acetic acid–acetate buffers.

t	20°	25°	30°	35°	37·5°	35°	37·5°	47°
pH	5·24	5·20	5·38	5·35	5·35	5·65	5·67	5·55
E_0', v	0·508	0·504	0·510	0·498	0·500	0·526	0·529	0·526
Mean E_0', v			0·504				0·527	

Phthalate–sodium hydroxide buffers.

t	20°	25·2°	30°	35°	37·5°	47°	20°	25·2°	30°	35°	37·5°	47°
pH	4·95	5·11	5·21	5·31	5·34	5·24	6·01	5·97	6·10	6·25	6·33	0·23
E_0', v	0·466	0·476	0·483	0·480	0·481	0·478	0·512	0·511	0·520	0·517	0·517	0·527
Mean E_0', v				0·478						0·517		

Phosphate–sodium hydroxide buffers.

t	20°	26°	30°	35°	37·5°	47°
pH	6·97	6·94	7·06	7·32	7·30	7·20
E_0', v	0·576	0·586	0·576	0·588	0·597	0·630
	Mean E_0', v = 0·582			$\Delta E_0'/\Delta t$ = 0·0037 v/° c.		

range ~5·6—7·3 from 22° to 41°. The linearity could also be traced down to pH 4·90 but only at the initial temperature, 22°. On extrapolation, E_0' values were obtained which are shown in the following table together with their temperature coefficient as determined from the slope of the E_0'–temperature linear plot.

t	22°	25°	30°	35°	41°
E_0', v	0·480	0·477	0·472	0·467	0·462
$\Delta E_0'/\Delta t$, mv/°c.			− 1·0 ± 0·05		

For comparison, the thermodynamic E_0' values for the Cu–Cu_2O and the Cu–CuO couples have been evaluated. Thus, $\Delta G°$ values for Cu_2O and H_2O being taken as −35,150 and −56,690 cal., respectively (Latimer, "Oxidation Potentials," New York, 1938, pp. 304 *et seq.*), the corresponding value for the reaction $Cu_2O + H_2 = 2Cu + H_2O$ is found to be −21,540 cal., from which E_0' (Cu–Cu_2O) = 0·467 v at 25°. Similarly, it can be shown by taking $\Delta G°$ of CuO as −30,400 cal., that E_0'(Cu–CuO) = 0·570 v at 25°. From these values and those obtained experimentally it is found that, with the exception of the E_0' values obtained at about pH 5 in the phthalate buffers, all other values in air are always higher than those obtained out of contact with air; the latter, as well as those obtained in air in the phthalate buffers of pH 5, correspond practically to the theoretical value of the Cu–Cu_2O couple. One may visualise the behaviour of the copper electrode in air in such a manner that on immersion, the electrode is partly covered with a film of cuprous oxide constituting the cathodic area on the metal. By local action, oxygen may not only oxidise the bare metal parts constituting the anodic areas, but it may also receive electrons from dissolved cuprous ions leading thus to the formation of hydroxide and cupric ions. Under conditions favouring the formation of a more or less complete layer of cuprous oxide on the metal, cupric oxide may form a secondary layer on the electrode surface, leading to a drift in potential towards more positive values (Evans, *J.*, 1925, **127**, 2484; Müller, *Z. Elektrochem.*, 1907, **13**, 133; Feitknecht and Lenel, *Helv. Chim. Acta*, 1944, **27**, 775; Gatty and Spooner, "Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions," Oxford, 1938, p. 216; Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529). In the limiting case, the electrode may function, virtually, as a Cu–CuO electrode. This is especially observed at about the neutral point within the pH range 6·94—7·32, the mean E_0' between 20° and 35° being 0·580 v and thus approaching the calculated value for that couple. At higher temperatures E_0' increases rapidly, the coefficient between 35° and 47° being as high as 3·7 mv/°c. It is probable that within the latter temperature range, the outer layer of cupric oxide is completed, rendering the electrode more or less passive. Under such conditions, oxygen deposited from the solution will persist on the surface, subjecting the electrode to an overvoltage effect increasing with rise of temperature and tending to shift the potential towards that of the reversible oxygen electrode.

The Standard Entropy of the Cuprous Ion.—No value has as yet been assigned to the standard entropy of the cuprous ion. Evaluations from electrochemical measurements are complicated by the slight solubility of most cuprous salts and the circumstance that even in more concentrated copper salt solutions of either ionic species in contact with metallic copper, cupric ions predominate (Fenwick, *J. Amer. Chem. Soc.*, 1926, **48**, 860), whereas only in more dilute ones will cuprous ions be present in a comparatively greater amount.

We have evaluated $S°_{\mathrm{Cu}^+}$ by using the relation

$$E_0'(\mathrm{Cu{-}Cu_2O}) = E°(\mathrm{Cu{-}Cu^+}) + (\boldsymbol{R}T/\boldsymbol{F}) \ln S_p/K_w \quad . \quad . \quad . \quad . \quad (1)$$

where S_p is the solubility activity product of cuprous oxide $= a_{\mathrm{Cu}^+} \,.\, a_{\mathrm{OH}^-}$; S_p almost certainly rises with temperature as does K_w, this being a general property of slightly soluble compounds, so that the temperature dependence of their ratio is likely to be smaller than a_{Cu^+} or a_{OH^-} separately; and as a first approximation this ratio may be considered constant. Accordingly, from (1) it follows that :

$$\mathrm{d}E_0'/\mathrm{d}T = \mathrm{d}E°/\mathrm{d}T + 2{\cdot}303\ (\boldsymbol{R}/\boldsymbol{F}) \log S_p/K_w \quad . \quad . \quad . \quad . \quad (2)$$

Taking Feitknecht's value of $1{\cdot}26 \times 10^{-15}$ (*Helv. Chim. Acta*, 1944, **27**, 771) for S_p and using our value $-1 \pm 0{\cdot}05$ mv for the temperature coefficient, we get by substitution in equation (2) :

$$\begin{aligned}\frac{\mathrm{d}E°}{\mathrm{d}T} &= -0{\cdot}001 \pm 0{\cdot}00005 - \frac{2{\cdot}303 \times 1{\cdot}998}{23066} \log \frac{1{\cdot}26 \times 10^{-15}}{10^{-14}} \\ &= -0{\cdot}001 \pm 0{\cdot}00005 + 0{\cdot}0002 = -0{\cdot}0008 \pm 0{\cdot}00005 = -0{\cdot}8 \pm 0{\cdot}05 \text{ mv/°c}\end{aligned}$$

This represents also the temperature coefficient of the cell

$$\mathrm{Cu|Cu^+}\ (a = 1),\ \mathrm{H^+}\ (a = 1),\ \mathrm{H_2}\ (1 \text{ atm.})$$

The standard entropy $S°$ for the cell reaction $\mathrm{Cu^+} + \tfrac{1}{2}\mathrm{H_2} = \mathrm{Cu} + \mathrm{H^+}$ is computed by the use of the relation :

$$\begin{aligned}S°_{298} &= \boldsymbol{F}(\mathrm{d}E°/\mathrm{d}T)_{298} \\ &= -23066 \times (0{\cdot}8 \pm 0{\cdot}05) \times 10^{-3} \\ &= -18{\cdot}45 \pm 1{\cdot}2 \text{ cal./°c/g.-ion}\end{aligned}$$

But since $S° = S°_{\mathrm{Cu}} + S°_{\mathrm{H}^+} - S°_{\mathrm{Cu}} + -\tfrac{1}{2}S°_{\mathrm{H}_2}$, therefore

$$\begin{aligned}S°_{\mathrm{Cu}} &= S°_{\mathrm{Cu}} + S°_{\mathrm{H}^+} - \tfrac{1}{2}S°_{\mathrm{H}_2} - S° \\ &= 7{\cdot}97 + 0 - \tfrac{1}{2} \times 31{\cdot}23 + 18{\cdot}45 \pm 1{\cdot}2 \text{ (Latimer, \textit{op. cit.}, pp. 330 \textit{et seq.})} \\ &= 10{\cdot}8 \pm 1{\cdot}2 \simeq 11 \pm 1 \text{ cals./°c/g.-ion}\end{aligned}$$

(B) *Temperature Coefficient of the Antimony Electrode.*—The influence of temperature on the electrode-potential behaviour of antimony was investigated by previous authors but mainly within the temperature range 10—30°, *i.e.*, that most frequently encountered in measurements with that electrode. Franke and Willaman (*Ind. Eng. Chem.*, 1928, **20**, 87) showed that the potential decreased, but not linearly, with increase of temperature, and Brewer and Montillon (*Trans. Amer. Electrochem. Soc.*, 1929, **55**, 356) stated that it had only a small temperature coefficient. Schukoff and Awsejewitsch (*loc. cit.*), on the other hand, noticed an appreciable variation of E_0' within the range 7° to 30°. Tomiyama (*J. Biochem. Japan*, 1933, **18**, 285) found, after the electrode had been immersed for 30 minutes and kept between 10° and 30°, that the temperature coefficients were 1·5, 2, and 2·5—3 mv/°c within the pH ranges 2—4, 5—7, and 8—11 respectively. Mehta and Kulkarni (*J. Ind. Inst.*, 1935, **18**, *A*, 85) measured the potential of a cast electrode at 25° and 40° and gave two values which indicated a pronounced coefficient. None of the above authors tried to explain the results in terms of temperature effects. Consideration of the results obtained in this investigation reveals that :

(i) The E_{H}–pH plots obtained with the plated electrode in air remain practically linear within the temperature range 20—44°. At higher temperatures the linearity is less pronounced, the curves manifesting smaller or higher slopes than the corresponding, theoretical ones. Linear plots are also obtained with the stick electrodes within the temperature ranges 20—25°, 43—53°, and at 60° in almost all the buffers used. In the absence of atmospheric oxygen, and when the electrode had been subjected alternately to the action of hydrogen and high vacuum, the E_H–pH plots obtained at 25·2°, 30°, and 35° each consist of three straight lines, the first and last of which possess slopes which are respectively smaller and greater than, whereas the middle parts run almost parallel to, the theoretical ones. The deviations from the theoretical slopes usually decrease with increase of temperature, the curves obtained at 37·6° and 42° being almost linear. At higher temperatures, deviations reappear to varying extents.

(ii) By plotting the extrapolated E_0' values against temperature, curves are obtained in air (Fig. 1) and out of contact with air (Fig. 2), which possess the same general shape inasmuch as they pass through minima and maxima within the temperature range used. The temperature coefficients for different parts of these curves are recorded in the following table.

FIG. 1.

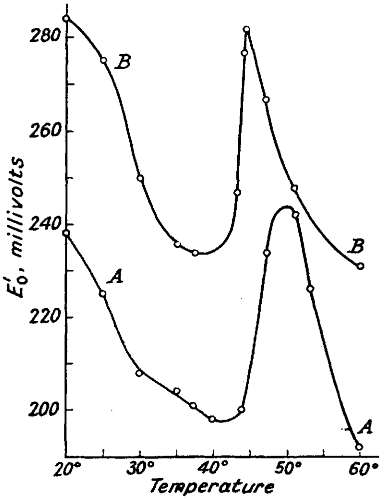
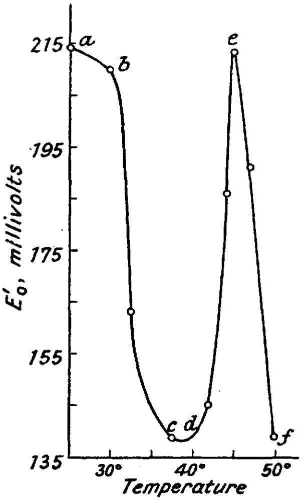


FIG. 2.



		Curve A			Curve B				
Fig. 1	Temp. range	20—30°	30—40°	49—60°	20—25°	25—32°	32—37·5°	44—53°	53—60°
	$\Delta E_0'/\Delta t$, mv/°c	−3	−1	−4	−1·8	−5	−1·5	−5	−1
Fig. 2	Temp. range	25·2—30°	30—37·5°	45—50°					
	$\Delta E_0'/\Delta t$, mv/°c....	−0·8	−7·5	−15					

In interpreting the results obtained with the plated electrodes out of contact with air, one may conceive the charging of the metal to take place by one of the following processes. (α) It may attach water dipoles with subsequent liberation of hydrogen and formation of SbO^+ ions according to

$$Sb + 2H_2O = SbO^+ + 2H^+ + 3e \quad . \; . \; . \; . \; . \quad (3)$$

The SbO^+ ions may then be transformed into the trioxide thus :

$$2SbO^+ + 2OH^- = Sb_2O_3 + H_2O + Q \quad . \; . \; . \; . \; . \quad (4)$$

(β) Alternatively, the metal may either react directly with OH^- ions with the formation of $SbOH^{++}$ or indirectly by promoting the reaction :

$$OH^- + OH^- = H_2O + O + 2e \quad . \; . \; . \; . \; . \; . \quad (5)$$

with subsequent formation of the oxide according to

$$2Sb + 3O = Sb_2O_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

As can be seen in Fig. 2 the E_0' values decrease with rise of temperature within the range 25—39°. The minimum value corresponds to that of the $Sb–Sb_2O_3$ couple (0·152 v at 25°). Since reaction (4) proceeds with evolution of energy, it is probable that the energy absorbed is mainly an activation energy. This is borne out by the fact that, whereas the reaction proceeds comparatively slowly along the line *ab* on the curve, where the E_0' values correspond closely to that of the Sb–SbO$^+$ couple (0·212 v at 25°), it manifests a rapid fall along the line *bc*. Reactions (5) and (6), which are also possible processes catalysed by the bare metal surface, may contribute to the formation of the oxide and probably be favoured by rise of temperature. A plausible explanation for the sudden rise in potential is that, after the oxide has completely developed on the metal surface through self-polarisation which extends within the temperature range from *c* to *d*, oxygen formed by the discharge of hydroxyl ions according to reaction (5) or by any other possible mechanism accumulates on the electrode surface, leading to an overvoltage effect which superimposes the reversible Sb–Sb_2O_3 potential. One may assume that the oxide film initially formed on the metal is not completely impervious to the electrolyte, which thereby comes in contact with the exposed metal. Oxygen discharged on the film surface renders the film cathodic and current will, therefore, flow with cathodic dissolution of oxygen. The equivalent anodic process at the metal surface is probably deposition of oxygen with subsequent formation of the oxide. Any ions formed by the anodic dissolution of the metal will at once be precipitated by the cathodically produced hydroxyl ions migrating inwards through the pores, which will thus be clogged with the oxide. Under such conditions, after self-polarisation, thickening of the oxide layer can only take place if metal ions in the oxide lattice are capable of diffusion towards the metal oxide–gas interface. Since the lattice defects in antimony trioxide are most probably restricted to oxygen ions (*loc. cit.*), diffusion of metal ions will not take place, and oxygen discharged by the above process will persist on the electrode surface, leading to the over-voltage effect. The maximum E_0' attained at point *e* may plausibly be ascribed to the saturation of the free valency bonds through adsorption of oxygen. This is apparently held to the oxide surface by van der Waals forces rather than by chemisorption owing to the much smaller activation energy of the former, and because, otherwise, a higher oxide such as the tetroxide should be formed with subsequent increase of E_0' to that of the Sb–Sb_2O_4 couple, *viz.*, 0·329 v at 25° (Simon and Thaler, *Z. anorg. Chem.*, 1927, **161**, 113; Latimer, *op. cit.*, p. 328). As the temperature rises, owing to the small heat of adsorption, the adsorbed oxygen is removed more or less completely. Accordingly, at temperatures from 44° to 50°, the overvoltage contributed by the presence of adsorbed oxygen is diminished with rise of temperature until the film can no longer persist, the potential corresponding again to that (*f*) of the Sb–Sb_2O_3 couple. That the gas film is merely adsorbed on the oxide surface by van der Waals molecular forces is further substantiated by the difference in potential between the minimum at *c* and the maximum at *e*, *i.e.*, 75 mv, which corresponds to 6900 cal./mole. As is well known in the two distinct types of adsorption, the van der Waals and the chemisorption, the heats of adsorption in the former type are usually of the same order of magnitude as the heats of condensation of gases, whereas in the latter they are of the same order as the heats of chemical reactions. The heat of formation of antimony tetroxide from the trioxide and oxygen according to the reaction $2Sb_2O_3(s) + O_2(g) = 2Sb_2O_4(s)$ is 27,900 cal./mole (Simon and Thaler, *loc. cit.*). On the other hand, the heat of liquefaction of oxygen is 1632 cal./mole (I.C.T., 1929, Vol. I, p. 102), a value which is of the same order of magnitude as that experimentally observed.

The results in air are somewhat more complicated. They can be explained on the premise that antimony metal possesses a great tendency to become oxidised to the trioxide ($P_{O_2} = 0{\cdot}2 \times 10^{-68}$ atm.). Owing to the impermeability of the trioxide film to oxygen molecules and to the non-diffusion through it of metal ions, oxygen doublets will tend to persist on the electrode surface for varying periods of time, leading to the observed over-voltage effect which amounts, at the maximum, to about 100 and 140 mv for the plated and the stick electrodes, respectively. Such values correspond to only a small fraction of the surface being covered with oxygen. The quantity of electricity necessary to establish oxygen over-voltage per 100 mv is 11×10^{-6} as compared with the value of 6×10^{-7} coulombs for hydrogen overvoltage (Bowden, *Proc. Roy. Soc.*, 1929, *A*, **125**, 446). The former quantity corresponds approximately to 1/15 of the surface being covered with oxygen if the true and the apparent surface are identical, a condition found to be valid only for liquid metals (Bowden and Rideal, *ibid.*, 1928, *A*, **120**, 59). For other metals, including antimony, the ratio of the true to the apparent surfaces is identical with that between the quantity of electricity necessary to contribute an overvoltage of 100 mv and the quantity 11×10^{-6} coulombs. For the same quantity of electricity the overvoltage on a smooth surface is accordingly greater than that on a spongy one. This is believed to explain the fact that the overvoltage effect acquired by stick electrodes is always greater by ~40 mv than that manifested by the plated ones, the spongy nature of the latter being more effective in increasing the true surface than the alternative effect of polishing on the former.

The decrease of the E_0' values obtained for the two types of electrode as the temperature is raised from 20° to 39°, may be ascribed to the partial dissolution of the trioxide with subsequent depolarisation of some of the oxygen doublets. A state of considerable stability is notably achieved with plated electrodes along the range 30—39°, manifesting itself in the small temperature coefficient (−1 mv/°c). It is probable that at this stage portions of the bare metal become exposed to the solution, leading to the formation of SbO^+ ions. The potential, which approaches that of the Sb–SbO^+ couple, corresponds at the same time to a metal–metal oxide potential governed by a certain oxygen overvoltage effect. This follows in accordance with the principle that when at a given electrode two distinct electrochemical processes can take place corresponding to two different potentials, a reaction will tend to occur between the substances concerned of such a sort as to equalise the two potentials (Lewis, *J. Amer. Chem. Soc.*, 1906, **28**, 158). It may be duly recognised that oxygen formed by the discharge of hydroxyl ions should contribute to the redevelopment of the oxide and thus tend to counteract the depolarising effect of increasing temperature. When a more or less complete layer of the oxide is formed, oxygen will accumulate on its surface, leading to the sudden rise in potential above 39°. As already pointed out, adsorbed oxygen is loosely held to the oxide surface by molecular forces. This explains the considerable fall in potential observed as the temperature is slightly raised above 49° and 44° for the plated and the stick electrodes, respectively, a process which may ultimately lead to the attainment of the metal–metal oxide potential.

A remarkable feature of the results obtained with both types of electrode in and out of contact with air is that the minima on the curves followed by sudden rise in potential occur almost at the same temperature of ~40°. This temperature lies within the range of temperatures at which the rate of thermal decomposition of hydrogen peroxide is a maximum, *i.e.*, at 35—45° in the presence and at 45—50° in the absence of a catalyst (Galecki and Jerke, *Rocz. Chem.*, 1927, **7**, 1; Eizi Suito, *Rev. Phys. Chem. Japan*, 1941, **15**, 1). This seems to be consistent with the hydrogen peroxide theory of electrolytic oxidation (Glasstone and Hickling, *Chem. Reviews*, 1939, **25**, 407). We are still investigating this point.

Recently, El Wakkad (*J.*, 1950, 2894) questioned whether the behaviour of the antimony electrode in air was governed by an oxygen overvoltage effect which led to its functioning as a metal–metal oxide–oxygen electrode; he inferred "that the irregularities were caused by the gradual formation of a higher oxide (tetroxide) on the electrode and by its exceedingly slow attainment of equilibrium which depends upon the supply of oxygen as well as on the surface of the metal exposed." As was previously shown (Tourky and Mousa, *loc. cit.*), the E_0' values obtained by many previous authors in air fluctuate, under a variety of conditions, within the narrow limits 220—280 mv, so that if a higher oxide is formed, a definite ratio must obtain between the amounts of lower and higher oxide present. The slow formation of a higher oxide requires, further, that the potential initially set should approach the thermodynamic value for the Sb–Sb_2O_3 couple (0·152 v at 25°), then increasing gradually as the presumably higher oxide is progressively formed. No value lower than 220 mv for the massive and the electrodeposited electrodes has ever been reported. The surplus in potential of about 100 mv or more seems to be a general phenomenon manifesting itself in metal–metal oxide electrodes with oxygen-deficient oxide lattices: it has been observed with arsenic (Tourky and Mousa, *loc. cit.*), bismuth and molybdenum electrodes (to be published). In most of these metals higher oxides are either incapable of existing in contact with the metal or cannot be formed under the prevailing conditions on the electrode surface. Under conditions favouring the formation of a layer of hydrogen on the metal or metal oxide surface as with nickel, the potentials set up in air are found to be 100 mv or more lower than the thermodynamic values (to be published). In agreement with Bowden and Rideal's findings (*loc. cit.*) that such changes of electrode potential are associated with the deposition of hydrogen doublets, there is no way of attributing such a decrease except to a certain hydrogen overvoltage effect. Further evidence for the theory of adsorbed gas layers is provided by the present investigation.

The inference (El Wakkad, *loc. cit.*) that the persistence of oxygen doublets on the electrode surface necessitates the formation of a unimolecular layer of the oxide is also untenable, since the theory of lattice defects requires that a well-formed lattice several molecules thick should be formed on the metal. It is only when such a lattice is formed that the rate of oxidation is restricted to either the diffusion or the non-diffusion of metal atoms or ions towards the oxide–gas interface according to the nature of defects in the lattice. Conclusions regarding the thickening of the oxide from polarisation experiments are not in line with the theory, since under such conditions atomic oxygen initially deposited is apt to diffuse through the oxide.

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