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Kinetic study of the copper-iodine reaction by electrical resistance measurements

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Abstract. Kinetics of the reaction between copper and iodine (vapour) have been studied by electrical resistance measurements. A relationship between the change in electrical resistance and thickness of the product film has been formulated. From the data, which follows a parabolic law, values of the specific reaction rate constant have been calculated. The results have been compared with the earlier reported kinetic data of the reaction, measured by the gravimetric method, and are in good agreement.

Keywords. Kinetics; copper; iodine; electrical resistance; gravimetric method; parabolic law.

1. Introduction

In the tarnishing of metals, reaction kinetics is generally determined by measuring the product thickness, change in weight and vapour pressure (Cabrera and Mott 1949; Grimley 1955; Hardel 1972; Bassi and Sharma 1972). All such techniques have inherent practical difficulties. In a tarnishing reaction, metal is consumed with the reaction process and converted into reaction product. Therefore, the thickness of the reacting metal plate decreases. If the electrical conductivities of the other reactant and the product are appreciably low, as compared to that of the metal, the kinetics of the reaction can be measured by following the change in electrical resistance of the metal plate.

The kinetics of the reaction between copper (plates) and iodine (vapour and solid) have been studied by gravimetric method and parabolic growth of the product has been observed (Bassi and Sharma 1977). The reaction product has also been identified. The electrical conductivity of the reaction product is much lower as compared to that of the metal (Mellor 1952). In the present study, kinetics of the reaction have been determined by measurement of the electrical resistance of the metal plate during its reaction with iodine (vapour). The rate constants have been calculated and compared with earlier studies, and show good agreement at low temperatures.

2. Experimental

AnalaR copper metal foil and iodine (BDH) were used. A kelvin bridge which can precisely compare 4-terminal resistance was used for resistance measurements. The

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bridge has a range of 10^{-7} ohm to 1 ohm measurements and an accuracy of 0·50% to 0·20% of the slide wire. The reaction was carried out in a cell so that the area of the copper plate ($4 \times 0{\cdot}5$ cm^2), exposed to iodine at the saturated vapour pressure, remained constant throughout the reaction and the resistance of only that dimension of the plate was measured. Copper plates of fixed size ($8 \times 0{\cdot}5$ cm^2) were cut from the metal foil, treated as described earlier (Bassi and Sharma 1972) and fixed in the reaction cell. The cell was placed in a thermostat set at constant temperature with ± 1°C variation after the necessary connections. For the resistance measurements, 4A DC was passed through the bridge only momentarily to prevent any heating. First, the initial resistance of the metal plate was measured and then the plate was exposed to iodine (vapour). The thickness of the plate decreases with increase in the reaction interval and because of the fact that the high conducting metal was replaced by the reaction product of high resistivity, the kinetics were determined by following the electrical resistance of the plate as a function of time.

3. Results and discussion

The values of change in electrical resistance (ΔR) are plotted against time t in figure 1 and ΔR^2 values vs t are plotted in figure 2.

Consider the metal plate of length L, width W and the thickness d cm reacting with iodine (vapour) and suppose a thickness P of the plate is consumed in time t, giving a product layer of thickness X, then

$$X = PC, \tag{1}$$

where C is the ratio of the molar volumes, product layer to metal. At $t = 0$, the initial thickness of the metal foil is given by

$$R_0 = \rho L/Wd, \tag{2}$$

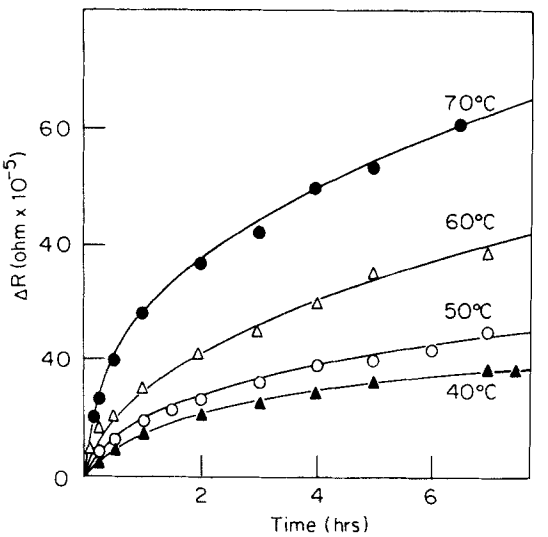

Figure 1. Kinetics of the reaction between copper (plates) and iodine (vapour) by electrical resistance measurements at different temperatures.

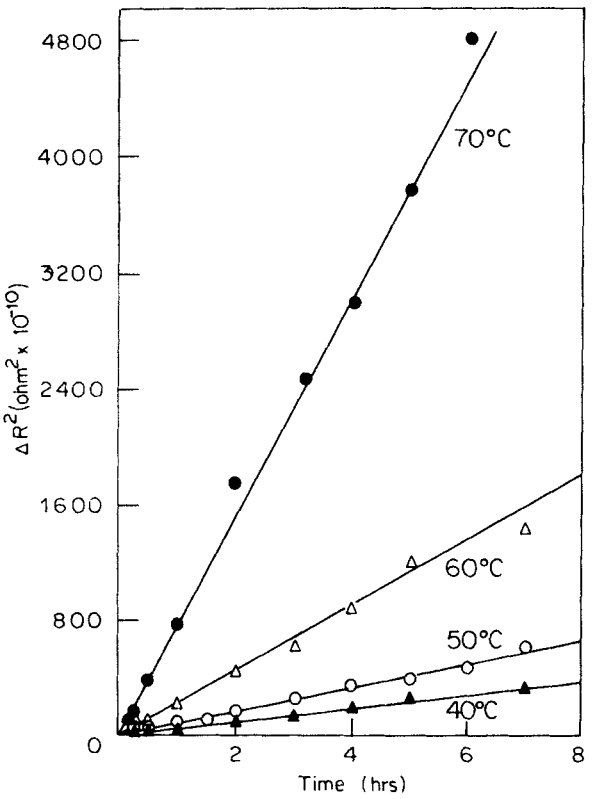

Figure 2. Plots of ΔR^2 *vs* t at different temperatures for the reaction between copper (plates) and iodine (vapour).

where ρ is the resistivity of the metal. Neglecting conduction through the product layer, the resistance of the metal plate exposed to iodine (vapour) for time t is

$$R = \rho L/W(d-P). \tag{3}$$

Eliminating P from (1) and (3)

$$R = \rho L/W(d-X/C). \tag{4}$$

If $R - R_0$, increase in the resistance, is taken as ΔR

$$\Delta R/R_0 = \frac{1}{1-X/Cd} - 1, \tag{5}$$

when the extent of the reaction is small, $X \ll Cd$

$$\frac{\Delta R}{R_0} = \frac{X}{Cd} \quad \text{or} \quad X = \frac{Cd}{R_0}\Delta R. \tag{6}$$

If the iodination reaction is parabolic and obeys the rate equation

$$X^2 = kt, \tag{7}$$

Table 1. Comparison of the specific reaction rate constant (k) values for the copper (plates)-iodine (vapour) reaction, determined by the electrical resistance technique and the gravimetric method (Bassi and Sharma 1977).

Temp. (K)	Slopes of R^2 vs t plots ($\times 10^{-10}$)	R_0 ($\times 10^{-3}$)	Conductivity technique: k ($cm^2\ hr^{-1} \times 10^{-6}$)	Gravimetric method: k ($cm^2\ hr^{-1}/4\ cm^2 \times 10^{-5}$)	Gravimetric method: k ($cm^2\ hr^{-1} \times 10^{-6}$)
313	50·7	1·75	2·69	11·63	2·11
323	84·8	1·84	4·08	21·62	3·92
333	230	1·90	10·41	39·58	7·2
343	769	1·96	32	71·85	13·01

where k = rate constant and t = reaction interval. Substituting the value of X from (6) in (7)

$$[Cd\Delta R/R_0]^2 = kt. \tag{8}$$

When the extent of the reaction is small, d is almost constant and at a constant temperature R_0 is constant. The ratio of the molar volumes (C) is also a constant and its value, as calculated from the literature (Weast 1979), is 4·75 at 25°C. The initial thickness of the metal plate (d) is $8{\cdot}5 \times 10^{-3}$ cm. Therefore, from (8) the plots of ΔR^2 vs t should be straight lines, which is true in this case (figure 2). The slopes of the plots are equal to kR_0^2/C^2d^2.

The k values calculated from the slopes are given in table 1. The k values, calculated by the gravimetric method (Bassi and Sharma 1977) from the plots of w^2 (where w = weight of copper reacted) *vs* time t, are also given in the table. To convert the specific reaction rate constant (k) values in the units of thickness of the product layer, the reported values were multiplied by a factor $(190{\cdot}46/63{\cdot}5)^2 \times (1/5{\cdot}62)^2$, [(mol. wt of CuI/atomic wt of Cu)^2 × (1/density of CuI)^2]. Comparison of the k values, determined by the two methods, gives good agreement between the two at 313 and 323 K. However, at 333 K they do not show much agreement and the difference is more pronounced at 343 K. The deviations at 333 and 343 K are because the condition $X \ll Cd$ is no more valid here. At 343 K, ΔR is $\approx 0{\cdot}6 \times 10^{-3}$ ohm which is about 30% of R_0. The results show that the electrical resistance measurement is a useful technique to determine the reaction kinetics in such reactions at temperatures, where $X \ll Cd$.

References

Bassi P S and Sharma I B 1972 *Indian J. Chem.* **12** 813

Bassi P S and Sharma I B 1977 *Indian J. Chem.* **A15** 649

Cabrera N and Mott N F 1949 *Reports on progress in physics* (London: The Physical Society) Vol. 12 p. 163

Grimley T B 1955 *Chemistry of the solid state* (ed) W E Garner (London: Butterworths) p. 336

Hardel K 1972 *Angew. Chem. Int. Ed. Engl.* **11** 173

Mellor J W 1952 *A comprehensive treatise on inorganic and theoretical chemistry* (London: Longman) Vol. 3 p. 203

Weast R C 1979 *CRC handbook of chemistry and physics* (Florida: CRC Press) B-115