

Oxidation of Metals: Determination of Activation Energies

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A new method is proposed for the determination of energies of activation of oxidation of metals and alloys. Metals are oxidized under conditions of linearly increasing temperature, and the activation energy may be determined from one single oxidation run. In addition the method also gives the approximate temperature regions in which different rate laws of oxidation are found.

The described method has been applied to high-temperature oxidation of nickel, zirconium, copper, and titanium.

In the study of oxidation of metals and alloys the activation energies are of fundamental importance in the consideration of oxidation mechanisms. Hitherto, however, the reported values often show large mutual disagreements for the same metal. A good example is the oxidation of copper, where activation energies ranging from 29.4 to 42 kcal have been reported in the temperature region 500—1 000°C by different investigators.¹⁻⁶

An accurate determination of activation energies involves a large number of isothermal runs at different temperatures. In this communication a faster method is proposed for the determination of activation energies. The metals are oxidized under conditions of linearly increasing temperature, and the method gives the activation energy of oxidation from one single oxidation run, and in addition gives the approximate temperature regions in which different rate laws are found. Although the proposal of oxidizing metals under such conditions is not new,⁷ it is believed that the present treatment of the results provides a new approach for a simple and rapid method for studies of oxidation of metals and alloys.

OXIDATION OF METALS

The oxidation of metals follows different rate laws depending upon the metal, the nature and semi-conducting properties of the oxide formed, and the temperature. At high temperatures (generally greater than 200—300°C) we usually have 1) linear, 2) parabolic, or 3) cubic rate laws, which may be expressed as,

$$\frac{d(m/A)}{dt} = k_1 \quad (\text{Linear}) \quad (1)$$

$$m/A \frac{d(m/A)}{dt} = k_2 \quad (\text{Parabolic}) \quad (2)$$

$$(m/A)^2 \frac{d(m/A)}{dt} = k_3 \quad (\text{Cubic}) \quad (3)$$

In these equations m/A represent gain in weight per unit area at time t , and k_1 , k_2 , and k_3 are the oxidation rate constants for the linear, parabolic, and cubic rate laws, respectively.

The temperature dependence of oxidation reactions may be expressed by the empirical Arrhenius equation

$$k = B \exp(-Q/RT) \quad (4)$$

where k is the rate constant for the oxidation at temperature T , B is a parameter whose dimensions depend on units for k , and Q is the activation energy.

In order to provide a more complete interpretation of B , Gulbransen⁸ applied the absolute reaction rate theory to oxidation reactions obeying parabolic rate laws. The rate constant was accordingly expressed in terms of the entropy and heat of activation and with a preexponential factor proportional to T .

In as much as oxidation processes obey the Arrhenius equation and as also non-parabolic rate laws are included in this treatment, the following approach will be confined to the use of eqn. 4.

Eqns. 1, 2, and 3 may be written as

$$(m/A)^n \frac{d(m/A)}{dt} = k \quad (5)$$

where n is a constant having values of 0, 1, and 2 for the linear, parabolic, and cubic rate laws, respectively.

Oxidizing under conditions with linear increase of temperature, we have

$$T = at + b \text{ or } dT = a dt \quad (6)$$

Substituting (4) and (6) in eqn. 5, we get

$$(m/A)^n \frac{d(m/A)}{dT} = (B/a) \exp(-Q/RT) \quad (7)$$

Taking the logarithm and rearranging, eqn. 7 may be written

$$(n + 1) \ln(m/A) + \ln \frac{d \ln(m/A)}{dT} = \ln B/a - Q/RT \quad (8)$$

According to eqn. 8 a plot of $(n + 1) \ln(m/A) + \ln \frac{d \ln(m/A)}{dT}$ versus $1/T$

should yield a straight line whose slope is equal to $(-Q/R)$ and which permits calculation of the activation energy, Q . The value of the parameter B in eqn. 4 may also be determined by introducing corresponding experimental values of (m/A) , T , and a .

The use of eqn. 8 necessitates the evaluation of $\frac{d \ln(m/A)}{dT}$, and the approximate values for this differential quotient were calculated as

$$\left(\frac{d \ln(m/A)}{dT}\right)_{T = T_j} = \frac{\ln(m/A)_{j+1} - \ln(m/A)_{j-1}}{T_{j+1} - T_{j-1}} \quad (\text{a})$$

Temperature intervals of 25°K were found suitable in the described runs, and a table of the following type was used for each oxidation run:

$T^\circ\text{C}$	$1/T$	$x = m/A$	$\ln x$	$(n+1) 2 \ln x$	$\frac{\Delta \ln x}{\Delta T}$	$\ln \frac{\Delta \ln x}{\Delta T}$
Intervals of 25°K		x_1	$\ln x_1$			
		x_2	$\ln x_2$	z_2	y_2	$\ln y_2$
		x_3	$\ln x_3$	z_3	y_3	$\ln y_3$
		x_4	$\ln x_4$	z_4	y_4	$\ln y_4$

where $z_j = \ln x_{j+1} - \ln x_{j-1}$

and $y_j = z_j/50$

In applying this approach to metals oxidizing according to linear rate laws, it is necessary to plot $\ln(m/A) + \ln \frac{\ln(m/A)}{T}$ versus $1/T$, in the case of parabolic rate laws $2 \ln(m/A) + \ln \frac{\ln(m/A)}{T}$ versus $1/T$, and cubic rate laws $3 \ln(m/A) + \ln \frac{\ln(m/A)}{T}$ versus $1/T$. This treatment of the data should yield

straight lines for the particular rate laws in the corresponding temperature regions. If the oxidation of a metal follows different rate laws in different temperature regions, one should also obtain distinct breaks in the curves at the temperature regions where the oxidation changes rate laws. For example if the oxidation of a metal follows the cubic, parabolic, and linear rate laws successively with increasing temperature, the plotted curve will be a straight line only in the temperature regions where the assumed rate law is valid, while the plotted curve should show a curvature in the temperature regions where the other rate laws are valid. Thus in addition to the activation energy, such a treatment would also give approximate values as to the temperature regions in which the different rate laws may be found.

It should be emphasized that eqn. 8 is valid only under conditions of cubic, parabolic, and linear rate laws. The described approach is thus not applicable for oxidation of metals at low temperatures or at the very beginning of the oxidation at higher temperatures, at which conditions logarithmic and reciprocal logarithmic rate laws are generally obeyed. These latter rate laws may, however, also be treated in the same manner as described above.

EXPERIMENTAL RESULTS

The described method was tried on Ni, Zr, Cu, and Ti, and the experimental results gave activation energies in satisfactory agreement with previously published values obtained from isothermal runs.

The metals were oxidized under conditions with linearly increasing temperature from 400°C to 1 100°C with a temperature increase of either 3.86 or 2.22°C/min. Owing to the small weight gain before 600–700°C during these runs, activation energies could only be determined for temperature regions 700–1 100°C.

The oxidation of titanium has previously been found to obey the cubic (400–600°), the parabolic (600–900°C), an linear rate law (900–1 000°C) in the indicated temperature regions.⁹ With the above mentioned experimental conditions one should consequently obtain a break in the curve corresponding to a transition from the parabolic to the linear rate law region.

In Fig. 1 are shown the data for unannealed van Arkel titanium oxidized under linear temperature increase of 3.86°C/min plotted under the assumption of linear and parabolic rate laws. As seen the parabolic rate law plot yields a straight line between 700°C and 900°C, while the linear rate law plot gives a straight line above 900°C, thus confirming the results obtained from isotherm-

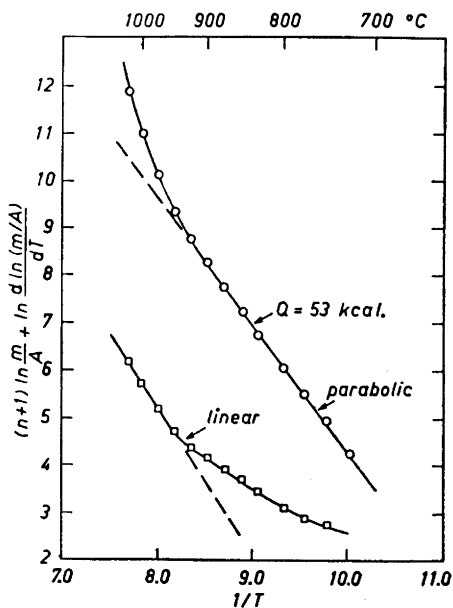


Fig. 1. Oxidation of van Arkel titanium with temperature increase of 3.86°C/min. Data plotted under assumption of linear and parabolic rate laws.

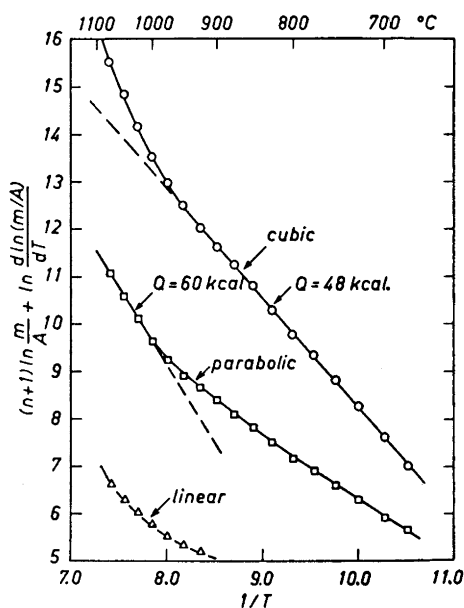


Fig. 2. Oxidation of zirconium (2.22°C/min). Data plotted under assumption of linear, parabolic, and cubic rate laws.

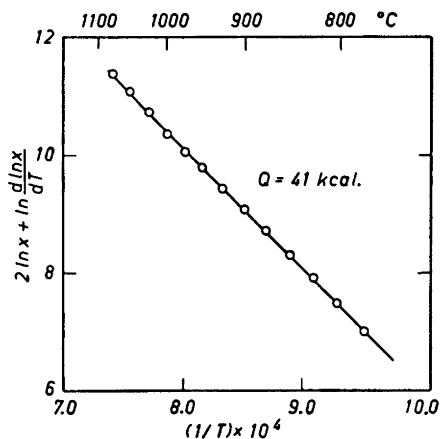


Fig. 3. Oxidation of nickel (2.22°C/min).

al runs. Furthermore, the activation energy in the parabolic rate law region amounts to 53 kcal, which is in excellent agreement with the value of 52 ± 2 kcal, which was obtained by isothermal oxidation of the same metal in this laboratory.

Fig. 2 shows the results on oxidation of zirconium (2.22°C/min) plotted under the assumption of linear, parabolic, and cubic rate laws. As seen the cubic rate law plot yields a straight line between 650 and 950°C giving an activation energy of 48 kcal in agreement with the results of Belle and Mallett,¹⁰ who found that the oxidation of zirconium conformed with a cubic rate law between 400 and 1 000°C and with an activation energy of 47.2 kcal. Furthermore, the plots in Fig. 2 also indicate that the cubic rate law is not conformed with between 950 and 1 100°C, but in this region the parabolic rate law plot yields a straight line and an activation energy of approximately 60 kcal, and thus indicating conformity with the parabolic rate law in this temperature region. Two runs with a temperature increase of 3.86°C/min showed conformity with the cubic rate law between 700 and 1 050°C, and with an activation energy of 46 kcal.

Isothermal oxidation of zirconium by both Cubicciotti¹¹ and Gulbransen¹² has previously been found to obey a parabolic rate law, and the disagreement between these data and those of Belle and Mallett cannot be explained at present. A tentative explanation may be that the amount and type of impurities may have a decisive effect on the rate law observed, as Mallett and Albrecht¹³ showed that 1.5 and 2.5 wt. % Zn—Zr alloys oxidize according to cubic and parabolic rate laws, respectively.

Isothermal oxidation of nickel has previously been found to follow a parabolic rate law at high temperatures, and in accordance with this a parabolic rate law plot yields a straight line between 750 and 1 050°C, as shown in Fig. 3. The activation energy was found to be 41 kcal. As a comparison previously published values range from 34 to 51 kcal¹⁴⁻¹⁷.

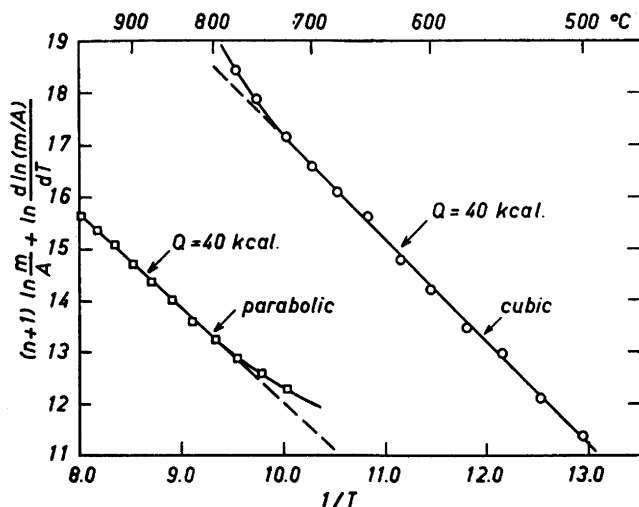


Fig. 4. Oxidation of copper (2.22°C/min). Data plotted assuming parabolic and cubic rate laws.

The results for oxidation of copper for a temperature increase of 2.22°C/min are given in Fig. 4. According to the plots the assumption of a parabolic rate law is only valid in the temperature region 750—1 000°C, while it may be inferred that the oxidation obeys a cubic rate law between 500 and 750°C. The activation energies for the parabolic and the cubic rate law regions was found to be 35 and 40 kcal, respectively. As a comparison previously published values for the parabolic rate law region range from 29.2 to 42.0 kcal¹⁻⁶.

DISCUSSION

The described results indicate that activation energies determined under conditions of linearly increasing temperature are in agreement with corresponding values determined from isothermal runs. Furthermore, the method also gives approximate temperature regions in which different rate laws are found.

While the activation energy found should be independent of the heating rate, it is to be expected that the appearance of different rate law regions are somewhat dependent on the rate of temperature increase, which is also apparent from the present results. The rate law observed in isothermal runs may be dependent upon the thickness of the oxide scale, and a certain rate law may thus be found to extend to higher temperatures for a fast than for a slow rate of temperature increase. This is indicated by the results on zirconium, in which case the cubic rate law was conformed with up to 1 050°C for a temperature increase of 3.86°C/min, but only up to 950°C for a temperature increase

of 2.22°C/min. In the case of oxidation of copper it might seem surprising, when comparing to the isothermal studies, that the cubic rate law is valid up to a temperature of about 700°C. However, in addition to the effect of the relationship between rate of temperature increase, film thickness, and rate law observed, this may be due to the fact that the oxide formed consists both of CuO and Cu₂O, and that their relative amounts changes with temperature. At 500°C the oxide scale consists mainly of CuO, and the relative amounts of CuO decreases with increasing temperature until it at 900°C only accounts for 10 % of the oxide scale⁶. The oxidation of Cu₂O to CuO has previously been¹⁸ found to obey a cubic rate law between 600 and 1 000°C, and it does not therefore seem unreasonable that the cubic rate law is obeyed up to 700°C under the described experimental conditions.

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