

Cubic Press to India

March 1975

Pallet #1

GROSS WT. 7350 lb. / 3334 kg.

NET WT. 6375 lb. / 2892 kg.

W. 64 in. / 163 cm.

L. 66 in. / 167 cm.

H. 55.5 in. / 141 cm.

VOL. 117 cu. ft. / 3.31 cu. m.

III. APPLICATION TO REFRACTORY METAL OXIDATION

A. GENERAL CONSIDERATIONS

Evaporation of oxides is an important feature in the high-temperature oxidation of a number of metals. Among these, tungsten, molybdenum and the platinum group of metals are of special interest due to their many potential uses. At temperatures sufficient to produce a high rate of evaporation, the oxide desorbs from the surface as soon as it is formed, leaving the surface clean at all times. Under these conditions, diffusion of oxygen through an oxide layer no longer plays a role in the oxidation kinetics and the fundamental processes of adsorption, reaction, and desorption determine the nature and rate of the interaction.

Adsorption of oxygen on these clean metal surfaces is non-activated (Reference 11) and has a rate dependent on the rate of oxygen impingement on the surfaces, i.e., the oxygen beam intensity I . Thus, the rate of adsorption r_a is just

$$r_a = 2 I s, \quad (1)$$

where s is the sticking probability.

For simple first order desorption of the surface species A^* to produce the gaseous species A ,



the rate of desorption is given by

$$\frac{-d(A^*)}{dt} = \frac{d(A)}{dt} = k(A^*) \quad (3)$$

This integrates to

$$(A^*) = (A^*)_0 e^{-kt} \quad (4)$$

where $(A^*) = (A^*)_0$ at $t = 0$. Therefore,

$$\frac{d(A)}{dt} = k(A^*)_0 e^{-kt} \quad (5)$$

The rate constant k is the Arrhenius rate constant

$$k = K e^{-E/RT} \quad (6)$$

Thus, the rate of first order desorption decreases exponentially with time, and a semilog plot of $d(A)/dt$ versus t yields a straight line of slope k . Furthermore, k varies exponentially with the inverse temperature ($1/T$), which permits

Pallet no. 2

Gross wt 870 lb / 394 kg
net wt 500 lb / 227 kg

W. 48 in. / 122 cm

L. 50½ in / 128 cm

H. 79 in / 200 cm

Vol 106 cu ft. / 3.02 cu m.

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3 Pallet

W. 39 in / 97 cm,

L. 51 in / 129 cm,

H. 48 in / 122 cm,

VOL 54 cu.ft. / 1.53 cu. m.

GROSS WT. 1260 lb. / 558 kg.

NET WT. 980 lb / 445 kg

To Resident Representative United
Nations Development Program
In India IND 72/058
PO Box 136
New Delhi India

7/11/72

Total for 3 pallets

gross wt 9480 lbs / 4300 kg

net wt 7855 lbs / 3563 kg

Vol 277 cuft / 7.84 cu. m.

evaluation of the activation energy of desorption E through determination of the desorption curve at several temperatures.

For two independent first order processes leading to the same gaseous species A, the observed desorption curve of $d(A)/dt$ versus t is just the sum of the two separate processes. Thus, for



and



we have

$$\begin{aligned} \frac{d(A)}{dt} &= -\frac{d(A^*)}{dt} - \frac{d(A^{**})}{dt} \\ &= k_1(A^*) + k_2(A^{**}). \end{aligned} \quad (9)$$

This leads to

$$\frac{d(A)}{dt} = k_1(A^*)_0 e^{-k_1 t} + k_2(A^{**})_0 e^{-k_2 t}. \quad (10)$$

A semilog plot of $d(A)/dt$ versus t will yield a curve which is the sum of two straight lines of different slope. These two lines can be separated from the experimental desorption curve and treated separately, as above.

Another situation of interest occurs when a given surface species A^* is removed from the surface by two different first order processes resulting in two different gaseous species, A and MA, as in, for example,



Then, if (12) is dependent on (A^*) only, or if (M) is constant,

$$\frac{d(A)}{dt} = k_1(A^*); \quad \frac{d(MA)}{dt} = k_2(M)(A^*) = k_2'(A^*)$$