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Kinetics of the Reaction Between Tungsten Trioxide and Carbon Tetrachloride

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Under proper experimental conditions, tungsten trioxide reacts with chlorine or chloridizing reactants giving two volatile oxichloridized products: WO_2Cl_2 and $WOCl_4$. The former is a light yellow solid melting at 226°C and decomposing before reaching boiling point; the latter melts at 211°C and boils at 227.5°C.

As proposed in the literature (for example, Li and Wang, 1956; Papa, 1968), these reactions could prove to be helpful in the tungsten trioxide purifying processes.

Calderon et al. (1969) studied the kinetics of reaction between tungsten trioxide and chlorine with carbon. Our aim was to investigate the kinetics of the reaction between tungsten trioxide and carbon tetrachloride.

Thermodynamic investigations on the system, carried out by Funaki and Uchimura (1962) and by Castro Luna and Rivarola (1971), show that the main possible reactions are

$$WO_3(s) + CCl_4(g) \rightleftarrows WOCl_4(g) + CO_2(g) \qquad (1)$$

$$2WO_3(s) + CCl_4(g) \rightleftarrows 2WO_2Cl_2(g) + CO_2(g) \qquad (2)$$

$$WO_3(s) + CCl_4(g) \rightleftarrows WO_2Cl_2(g) + COCl_2(g) \qquad (3)$$

The system is very complex, and it is necessary to simplify it in order to elaborate a reasonably simple model. Thus, the three equations shown above can be summed up as

$$A(g) + b\,B(s) \rightleftarrows \text{gaseous products} \qquad (4)$$

THEORY

If we consider that our spherical pellets of WO_3 have an initial porosity ϵ_o, the reaction with CCl_4 vapor will take place simultaneously on the outer and inner surfaces. As the reaction goes on, the porosity and surface areas will change.

The starting point is a mass balance for A and B. Assuming that our solid is isotropic, and considering that we are working with spherical pellets, we get

$$\epsilon \frac{\partial C_A}{\partial \theta} = \nabla (D_A\, \nabla C_A) - r_A \qquad (5)$$

$$-\frac{\partial C_B}{\partial \theta} = b\, r_A \qquad (6)$$

If we assume that under our experimental conditions the reaction is irreversible, the rate equation can be written as

$$r_A = k\, a_i\, C_A{}^{\gamma} \qquad (7)$$

With the following additional hypotheses: the gaseous reactant instantaneously achieves the pseudo steady state, the system is isothermal, and the gaseous reactant is totally consumed near the outer pellet surface, Equations (5), (6), and (7) can be solved as proposed by Williams et al. (1970). Thus, the following equations are obtained:

$$M\,\theta = 3\,(1 - R^*) + 2\,P \ln R^* \qquad (8)$$

$$1 - X_B = R^{*3} - P\,R^{*2} \qquad (9)$$

where

$$M = \left[1 + \frac{1-\alpha_o}{\alpha_o}\,\frac{h^+}{h_o} \right] \frac{b\,k\,C_{As}{}^{\gamma}}{L_o C_{B_o}} \qquad (10)$$

$$P = \frac{\gamma + 1}{2}\,\frac{h^+}{h_o} \qquad (11)$$

and h_o is represented by

$$h_o = L_o \left[\frac{\gamma + 1}{2}\,\frac{k\,a_{i_o}\,C_{As}{}^{\gamma - 1}}{D_{A_o}} \right]^{0.5} \qquad (12)$$

and h^+ is a factor defined by

$$h^+ = \left[(\gamma + 1) \int_0^1 D_A{}^* \, a_i{}^* \, C_A{}^{*\gamma} \, dC_A{}^* \right]^{0.5} \qquad (13)$$

where asterisks represent dimensionless values.

Equations (8) through (13) were applied to our system considering that, as stated by Equation (4), no solid products are produced at our working temperatures.

EXPERIMENTAL

The experimental equipment used and the technique for preparing spherical pellets have been described elsewhere (Papa, 1968).

The WO_3 pellets had a diameter of 1.27 cm, with porosity ranging between 0.45 and 0.49. The specific surface area was determined by the BET method, varying between 12 and 13 m^2/g. Before use, the pellets were sinterized at 500°C.

A high purity WO_3 was used. On analysis it rendered 0.05% chlorides, 0.01% sulfate, 0.001% lead, 0.001% iron, 0.005% calcium, and 0.3% water.

CCl_4 of purity better than 99.5% was used as the gaseous reactant, and nitrogen of 99.6% purity was used as carrier gas. Experiments were performed with gases flowing at high enough rates so that control by mass transport through the limit layer could be neglected.

Experiments were carried out at temperatures between 340° and 448°C and with tetrachloride mole fractions between 0.076 and 0.274. The reaction was followed by recording the weight change of a spherical pellet.

Partially reacted pellets were sectioned and carefully compared with nonreacted ones. It was found that reaction took place through a very shallow outer region, so one hypothesis of the intended model is thus experimentally ascertained. The pseudo steady hypothesis has already been verified by several authors (Bischoff, 1963; Wen, 1968). The isothermicity of the system was checked by means of runs using pellets having thermocouples inserted in them.

Parameters M and P of Equations (9) and (10) were determined for each experimental run minimizing the function

$$\phi = \sum_{i=1}^{n} [X_{B|\exp} - X_{B|\text{model}}]^2$$

with the aid of a computer. The agreement between experimental data and the model prediction was in every case excellent.

A value in the order of 10^2 for $(1 - \alpha_o)h^+/\alpha_o h_o$ can be estimated from the values obtained for P. Thus, the first term inside brackets on Equation (10) can be neglected. Then, introducing Equation (12), we get

$$M = \left[\frac{1 - \alpha_o}{\alpha_o} \right] \frac{b\,h^+}{C_{B_o} L_o{}^2} \left[\frac{2\,k\,D_{A_o}}{a_{i_o}(\gamma + 1)} \right]^{0.5} C_{As}{}^{(\gamma+1)/2} \qquad (14)$$

In Figure 1, Equation (14) is plotted in logarithmic form for runs at 370°C and CCl_4 molar fractions between 0.076 and 0.274. The values obtained by least-squares regression introduced in Equation (14) give

$$M = 0.0182\, C_{As}{}^{0.617}$$

On the other hand, introducing Equation (12) into Equation (11), we get

$$P = \frac{h^+}{L_o} \left[\frac{(1 + \gamma) D_{A_o}}{2\,k\,a_{i_o}} \right]^{0.5} C_{As}{}^{(1-\gamma)/2} \qquad (15)$$

In a similar way (as for M), we get

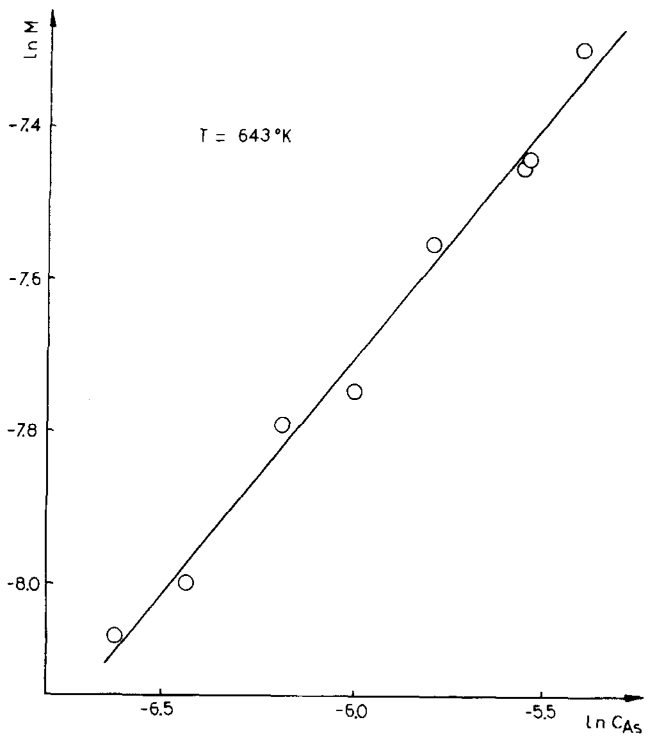

Fig. 1. Reaction rate dependence with outer surface concentration of CCl_4.

$$P = 0.0597\, C_{As}{}^{0.394}$$

The experimental reaction order γ obtained from M is 0.234, while that obtained from P is 0.212. This difference is not significant.

In order to analyze the dependence of reaction rate with temperature, we take

$$k = A' \exp\,(-\,E/RT) \qquad (16)$$

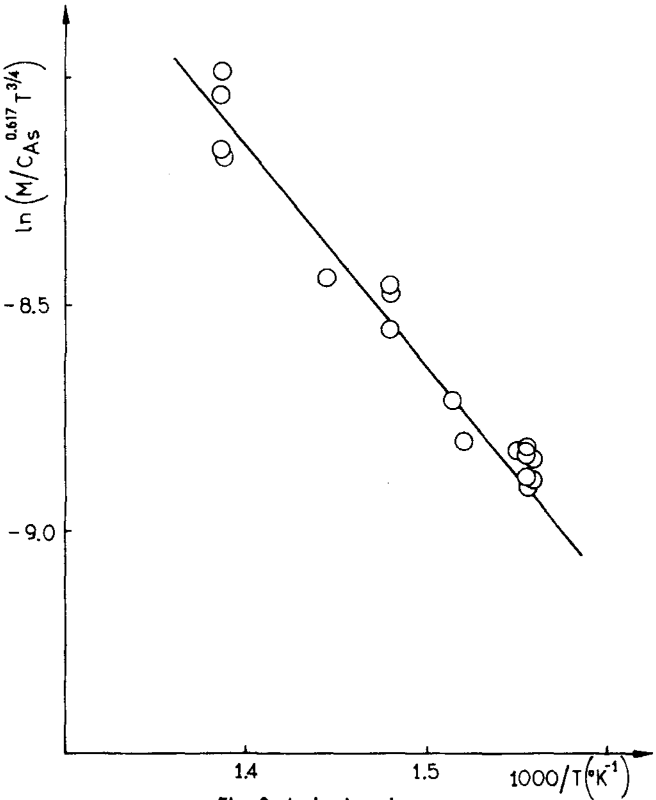

Fig. 2. Arrhenius plot.

$$D_{A_o} = Z\,T^{3/2} \qquad (17)$$

Applying Equations (16) and (17) to (14) and (15), we get

$$M = \frac{1-\alpha_o}{\alpha_o}\;\frac{b\,h^+}{C_{B_o}L_o^2}\left[\frac{2\,A'\,Z}{a_{i_o}(\gamma+1)}\right]^{0.5} C_{A_s}^{0.617}\,T^{3/4}\,e^{-E/2RT}$$

$$P = \frac{h^+}{L_o}\left[\frac{(\gamma+1)\,Z}{2\,a_{i_o}\,A'}\right]^{0.5} C_{A_s}^{0.394}\,T^{3/4}\,e^{E/2RT}$$

The values of $\ln(M/C_{As}^{0.617}\,T^{3/4})$ vs. $1/T$ are plotted in Figure 2. These values can be fitted by a straight line with a correlation factor of 0.982. From the fit we get

$$M = 0.25\,C_{A_s}^{0.617}\,T^{3/4}\,e^{-9\,590/RT}$$

$$P = 0.26 \times 10^{-6}\,C_{A_s}^{0.394}\,T^{3/4}\,e^{9\,590/RT}$$

In order to obtain values for A' and Z, it would be necessary to assign values to h^+ and b. Values for h^+ were computed using Equation (13) and were found to be near unity. It is rather difficult to assign a value to b, although it is known that $1 < b < 2$.

CONCLUSIONS

The kinetics of the reaction between tungsten trioxide and carbon tetrachloride has been interpreted by a diffuse interface model, from which an order of reaction of 0.234 and an activation energy of 19 180 cal/g-mole have been determined.

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NOTATION

A' = constant in Equation (16)

a, a^* = total surface area per unit volume, cm^{-1}, dimensionless value = a/a_o

b = stoichiometric coefficient

C, C^* = molar concentration, g-mole/cm^3, dimensionless value = C/C_o

D, D^* = effective diffusivity, cm^2/s, dimensionless value = D/D_o

E = activation energy, cal/g-mole

h^+ = correction factor, defined in Equation (13)

h_o = generalized Thiele modulus, Equation (12)

k = reaction rate constant per unit surface area

K = equilibrium constant

L = characteristic length, $L = R_p/3$

M = variable defined in Equation (10)

P = variable defined in Equation (11)

r = reaction rate, g-mole/cm^3 s

R_p, R^* = pellet radius, cm, dimensionless radius = R_p/R_o

R = gas constant, cal/g-mole °K

T = temperature, °K

X = conversion

Z = constant in Equation (17)

α = external surface area/total surface area

γ = apparent reaction order

ϵ = porosity

θ = time, s

Subscripts

o = initial value

i = inner value

s = external surface area

A = gaseous reactant

B = solid reactant

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Catalyst Effectiveness Factor and Contacting Efficiency in Trickle-Bed Reactors

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In order to interpret or predict trickle-bed performance, attempts have been made to account for liquid maldistribution, deviation from plug flow, and for incomplete wetting of catalyst particles (Ross, 1965; Cecil et al., 1968; Murphree, 1964; Henry and Gilbert, 1973; Mears, 1974). It has been shown that liquid phase deviation from plug