30. Characteristics of Fluidized Particies

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From the point of view, that there is some resemblance between liquid and fluidized particles, we have investigated the latter viscosity, which is one of the most characteristic properties.

Our empirical equation for the viscosity of fluidized particles as the function of the gas velocity (U), is as follows:

$$\eta = A \exp. (B/U),$$

where A and B are constants relating to the particle diameter, density, and shape.

This formula is analogous to the equation of the liquid viscosity as the function of the temperature (T),

$$\eta = C \exp. (E/RT). \quad \text{(Arrehnieus's, Andrade's equation.)}$$

Furthermore the Batshinski's equation of liquid viscosity,

$$\eta = C/(V - V_0)$$

and the J. Kendahl's equation

$$\log \eta_{12} = V_1 \log \eta_1 + V_2 \log \eta_2$$

are also applicable to the case of the fluidized particle system. The equation,

$$\log (V - V_0) = a - b/U$$

Which is derivated by combining two equations for liquid viscosity, i.e.

$$\log \eta = A + B/RT,$$

and

$$\eta = C/(V - V_0)$$

is applicable for fluidized bed expansion till its volume (V) is 1.5 time larger than its volume of fixed bed (V_0).

From the quasi-crystalline model theory for liquid, we have also obtained the equation,

$$U = C \left\{ 1 - (V_0/V)^{\frac{1}{3}} \right\}^2 + U \min.$$

which agreed with experiments till (V/V_0) becomes 4 or 4.5.

At the range of (V/V_0) larger than 4 or 4.5, the fluidized bed plays as same as the liquid at critical point.

The following equation, which is used empirically in the liquid case, is also applied to the bed expansion till V/V_0 is to 10:

$$V/V_0 = 1 + \beta \dot{U}_{max} - [(U_{max} - U)/(U_{max} - U_{min})]^{\frac{1}{n}}$$

where U_{max} and U_{min} are the maximum and minimum fluidized gas velosity respectively and a, b, C, β, and n, are constants concerning the diameter, density, and shape of particles.

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31. On the Mechanism of Vinyl-Acetate Synthesis

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On the vapor-phase synthesis of vinylacetate, it was found that the reaction velocity was proportional to the partial pressure of acetylene and the chemisorption of acetylene on the catalyst (zinc acetate on the active carbon) was the rate determining step for the reaction. We measured then the velocity of chemisorption of acetylene on the catalyst at the constant pressure of acetylene, raising the temperature at the constant rate. From this experiment, we evaluated the activation energy E, and the constant A of chemisorption according to the following equation ;
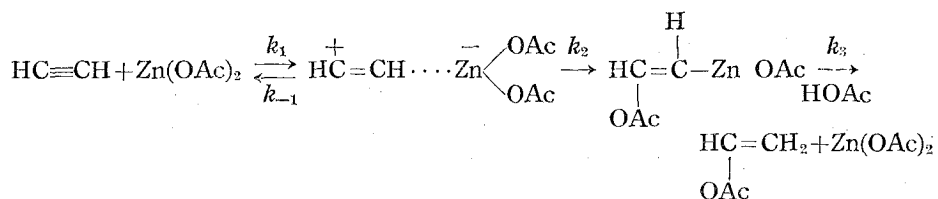
$$\log V = \log A + \log T - \log a - 0434E/RT$$

where V is the volume of acetylene adsorbed at any time or any temperature T, and a is the rate of raising the temperature. The observed activation energy is about 18 to 20 Kcal/mol which is in accordance with the date obtained from the experiment on reaction between acetylene and acetic acid vapor.

The reaction did not occured by zinc acetate or active carbon alone below 240°C.

Zinc chloride had also activity at 250°C, after it had turned to zinc acetate as seen from the analytical date.

From these facts we assumed the following mechanism,

$$HC\equiv CH + Zn(OAc)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \overset{+}{HC}=\overset{-}{CH}\cdots Zn\overset{OAc}{\underset{OAc}{\diagdown}} \overset{k_2}{\longrightarrow} \underset{OAc}{\overset{\overset{H}{|}}{HC=C}}-Zn\ OAc \overset{k_3}{\longrightarrow} HOAc$$

$$\underset{OAc}{\overset{|}{HC=CH_2}} + Zn(OAc)_2$$

where k_1, k_{-1}, k_2 and k_3 are constants of reaction velocity. k_1 will be probably small in comparison with k_2 and k_3 except for the case at high temp. For the latter case k_{-1} predominate and E becomes small.

About the action of active carbon, we regard that the active carbon forms

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