groups face outside and hydrophobic inside.

It is reasonable to consider that the swelling velocity v is a product of the velocity constant of dissolution reaction and the concentration of free water. Hydrophilic substances decrease the free water molecules according to the hydration energy E_{xw} and reduce the velocity approximately in proportion to the molar concentration of the substance x. (cane sugar and methyl alcohol). The substances which are capable to enter the helix and form a complex with starch by their hydrophobic properties make easy the formation of α-form, the intermediate step of dissolution, and decrease the activation energy of swelling E by the energy of complex formation E_{xs}. (nitrobenzen). Swelling velocity in pure water is given as $v_0 = Ae^{-E_0/RT}$ and the relative velocity v/v_0 was given theoretically and experimentally as following, $v/v_0 = e^{Bx}(1-cx)$, where $B = E_{xs}/RT$ (lyophilic property), $c = E_{xw}/RT$ (hydrophilic property). In case of hydrophilicaly and hydrophobicaly balanced substances, both action scompete and the velocity increases below a certain conc. x and decreases above it. This max. point is given as $x_0 = \dfrac{1}{c} - \dfrac{1}{B}$. (Ethyl alc. and propyl alc.) The experimental result for ethyl alc. is $v/v_0 = e^{1\cdot0C}(1-0.88\,C)$, C weight %. If these balanced molecules are too large to enter the helix, they can exhibit only the hydrophilic property (various polythylene glycol ester and ether). The pasting temperature of starch T varies proportionally to the conc. of these substance when they are dilute and $T = T_0 \left\{1 + (E_{xw} - E_{xs})\, x/E_0\right\}$. For potato starch in cane sugar solution, $T = 320 + 0.454\,C$.

---

67. On the Kinetics of the Activated Adsorption. (II)

Noriaki Kadota and *Shinjiro Kodama.*

(Kodama Laboratory)

The rate equation reported by us in the preceding paper (this Bulletin No. 20 p. 57) was found sufficient for the adsorption of hydrogen by copper–kieselguhr catalyst. But generally for other several catalysts, e. g. iron–kieselguhr catalast, the adsorption rate constants which can easily be calculated from the above referred equation by the graphical differentiation of $(dx/dt)^{-1/2}\,t$ curve, do not remain constant. The cause of this deviation might be at first attributed to the neglection of the reverse process. But a mere correction for the reverse process is not enough to explain the deviation. So we come to the point of view that the interactions among absorbed particles should be considered. On this consideration we can deduce an approximate rate equation, which is analogous to what H. Eyring proposed, with an additional term in the exponential from of x, i. e.

$$\frac{dx}{dt} = K_1[G] \; (A_2 - x_2)^2 \, e^{-\alpha x/RT}, \quad \alpha = \mathrm{const} \times E, \quad [G] = \mathrm{conc. \; of \; gas}$$

In this equation x in the exponential term should be rationally written as $f(x)$ instead of αx, but from the observed data of a differential adsorption heat it might be considered not so remote from the linear function of x. The equation can be integrated as,

$$K_1[G]\,t = ae^{aA_2} \left\{ \frac{e^{-a(A_2-x_2)}}{a(A_2-x_2)} - \frac{e^{-aA_2}}{aA_2} + \log\frac{A_2-x_2}{A_2} \right. $$
$$\left. + ax_2 + \frac{a^2(A_2-x_2)^2 - A_2^2}{2 \cdot 2!} + \ldots\ldots + (-1)^n \frac{a^n(A_2-x_2)^n - A_2^n}{n \cdot n!} + \ldots \right\},$$

where

$$a = \alpha/RT$$

But it is not easy to verify this formula directly by the numerical data. So we plot the logarithm to show the relationship between the apparent absorbed volume and the rate constants calculated from the equation which was derived from the foregoing report (ibid). If the linear relationship between these two properties is admitted, we can approximately conclude the existence of repulsive interactions among adsorbed particles. The results for the iron–kieselgur catalyst show that this relation holds stepwise, i. e. the plot comes out in such a way as several straight lines with equal inclination and unequal intercepts are connected by curved parts. And the inclinations of the straight parts are scarcely influenced by the variation of temperature. This reason may be interpreted in various ways, but what we can conclude from those results are the existence of repulsions and that activation energy changes with the increase of adsorbed fraction of the surface.

---

68. Studies on the Velocity of Copolymerization. (II)

On the Phenomena that the Copolymerization Stops at Very Low Conversions.

Seizo Okamura, Takao Yamashita and *Masako Tsuchiya.*

(Sakurada Laboratory)

The purpose of this report is to give the kinetical explanation on the phenomena that copolymerization stops at very low conversions, in the case copolymerization occurs with comonomers where some of them easily and the others hardly polymerize.

In the theoretical studies of Prof. Sakurada and others (cf. " KOJUGOHANNO " p. 29, 1944 or J. Alfrey et al. J. Chem. Phys., 12 205, 321, 1944 etc.), the following relationship was proved.