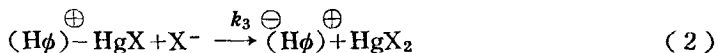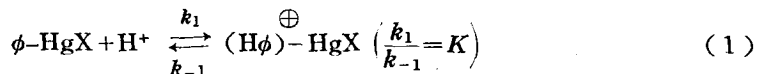reaching a max. value.

k_1' (80°C)   0.00264   0.0067   0.0103   0.0275   0.047   0.050

conc. of Br⁻   0.0287   0.0441   0.0761   0.1011   0.134   0.180

From the above results the mechanism of the decomposition of ϕ–HgX is elucidated as follows:

$$\phi\text{–HgX} + \text{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{H}\phi)^{\oplus}\text{–HgX} \quad \left(\frac{k_1}{k_{-1}} = K\right) \tag{1}$$

$$(\text{H}\phi)^{\oplus}\text{–HgX} + \text{X}^- \xrightarrow{k_3} (\text{H}\phi)^{\oplus} + \text{HgX}_2^{\ominus} \tag{2}$$

$$(\text{H}\phi)^{\overset{\ominus}{\oplus}} \longrightarrow \phi\text{H} \tag{3}$$

$$\text{HgX}_2 + 2\text{HX} \xrightarrow{fast} \text{H}_2\text{HgX}_4 \tag{4}$$

From this mechanism, using the methods of the stationary state, the general rate equation results in the form:

$$\frac{d(a-x)}{dt} = \frac{k_1 k_3 (a-x)(b-3x)(b'-3x)}{k_{-1} + k_3(b'-3)}.$$ If $k_{-1} \ll k_3(b'-3x)$, then the reaction must be second-order, this being the case (I). If $k_{-1} \gg k_3(b'-3x)$, then the reaction must be third-order, this being the case (II). In the case (III) it is believed that the unimolecular decomposition of ϕ–HgBr occurs simultaneously in addition to the second-order reaction at large conc. of Br⁻ according to the following mechanism: ϕ–HgBr $+n\text{Br}^- \longrightarrow \phi + \text{HgBr}_2^{\ominus}...n\text{Br}^-$, $\phi^{\ominus} + \text{H}^+ \xrightarrow{fast} \phi$. The rate determining step in these series of reactions is that of the ionization of ϕ–HgBr. This consideration is reasonable so far as the Hg in ϕ–HgBr has some coordinating power to Br⁻ which is saturated at a certain large conc. of Br⁻. And this is the reason why k_1' reaches a max. value. ($a-x$, $b-3x$ and $b'-3x$ are the conc. of ϕ–HgX, H and X⁻ at time t respectively. The unit of velocity constant is mol/1. min.)

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66. Studies on Solvation. (I)
Swelling Velocity of Starch and Lyophilic Property.

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In swelling or dissolution of raw starch, water molecules diffuse into micells and the micell crystals grow loose and chain molecules of starch begin to expand gradually in randon forms. But at its intermediate step it is probable that the chain molecules take spiral structure of α-form (helix) where their hydrophilic

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 $x_0 = \frac{1}{c} - \frac{1}{B}$. (Ethyl alc. and propyl alc.) The experimental result for ethyl alc. is $v/v_0 = e^{1 \cdot 0C}(1-0.88\,C)$, 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, $T = 320 + 0.454\,C$.

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

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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.