KINETICS OF SOL-GEL TRANSFORMATION

Part III. The Influence of Temperature on the Setting of Some Inorganic Jellies

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Introduction

In two of the previous publications, the authors have made a systematic study of the formation of inorganic gels from sols by bringing out coagulation of the latter. The coagulation velocities of sols giving out lyophobic coagulum have been hitherto studied by authors like Paine and others, but very little attention has been paid to the gelation velocities of lyophilic inorganic sols. It must be mentioned here that no rigid distinction appears to be existing between a lyophobic and a lyophilic sol, especially when one has to deal with inorganic substances. An inorganic sol giving out a jelly is both lyophilic and lyophobic. It is lyophilic so far as its water binding capacity is concerned. It is lyophobic because it is not generally heat-reversible, nor its aged or dehydrated particles show that amount of swelling which one experiences in the case of gelatin, agar agar and other lyophilic organic substances. But the authors have experienced that suitably prepared sols of iron, chromium and aluminium salts or hydroxides exhibit these properties also to some extent.

In his experiments on copper sol, Paine observed that on addition of an electrolyte, there is an initial period in which the sol remains quite clear; when coagulation commences at the end of this period, the speed at which it occurs, diminishes in a continuous manner. For colloidal solutions of different concentrations, the rate of coagulation is proportional to the square of the initial concentration. This, according to Paine, is in agreement to the mass action law and indicates that coagulation is brought about by the mutual attraction of the particles. Paine has also studied the rate of coagulation with respect to the variation of the electrolyte concentration. He finds that the rate of coagulation in case of copper sol is proportional to some power of the concentration of the anion, that is, $R \propto C^p$. Within the limits
of the experimental errors, the value of the index $p$ is the same as the index $n$
 in the adsorption formula $y = aC^n$. Paine also found that $p$ has the same
value for coagulation with ions of different valencies, this agreeing with the
Freundlich’s view of the mode of action of the ions. When equivalent
quantity of ions have been adsorbed, the colloidal particles behave quite
similarly in reference to the process of coagulation.

In the present series of papers, the authors have made an attempt to
see how far the Paine’s expression can be applied to the gelation processes.
In the first paper, they have shown that in the case of the jellies of ferric
arsenate, ceric hydroxide, zirconium hydroxide and chromium arsenate
(positively and negatively charged both), the following expression gives the
relation between the setting time of the jelly ($\theta$) and the concentration of the
electrolyte ($C$):

$$S = \frac{1}{\theta} = RC^p$$

or

$$\log S = \log R + p \log C.$$

In this expression, $S$ denotes the velocity of jelly formation and is equal to
the inverse of the setting time of the jelly. The mechanism of jelly forma-
tion is more complicated than the mechanism of coagulation and as such, it
will be interesting to see that the index $p$ very much differs from the index $n$
of the Freundlich’s adsorption formula.

**Experimental**

We have applied this expression to some more sols as aluminium
hydroxide and ferric phosphate, and have found that it is invariably appli-
cable. We shall give here our results with four different samples of ferric
phosphate sols prepared separately and having different concentrations.

*Ferric phosphate sol I.*—Concentration of the sol $= 42.64$ g. of ferric
phosphate per litre. The sol was prepared by the Holmes's method by
adding potassium dihydrogen phosphate to an excess of ferric chloride solu-
tion and then dialysing the sol thus formed. To three c.c.’s of the sol were
added different amounts of N-potassium chloride solution, making total
volume in each case 5 c.c. The setting time of the jellies was measured
in seconds. The values of $p$ and $\log R$ were calculated out from the two
observed values, and then applied to determine the values of $\log S$ in other
cases. From the two values $S_1$ and $S_2$, corresponding to the concentrations
of electrolyte, $C_1$ and $C_2$,

$$p = \frac{\log S_1 - \log S_2}{\log C_1 - \log C_2}$$

From the value of $p$, $\log R$ is easily determined.