RATE OF FORMATION OF CONDENSATION NUCLEI
IN A SUPERSATURATED VAPOR

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The dynamics of the condensation process are analyzed, and the kinetic equations of phase transformations (transitions) in a supersaturated vapor are derived. The formation of molecular associates is described by means of the well-known chains of A. A. Markov.

1. Statistical Process of the Formation of Molecular Associates

A study of the physical mechanisms underlying the condensation of vapor is of considerable interest in many fields of science and technology. The problem assumes special technological importance in connection with condensation-type steam turbines in which the working substance is water vapor with drops of moisture suspended in it.

Many theoretical and experimental investigations have been devoted to the problem of condensation [1-4]. However, as yet the physical mechanism underlying the condensation process has been inadequately studied, and the problem of constructing a general theory of phase transformations is still a long way from practical solution.

Questions relating to condensation may be approached not only from the phenomenological principles of thermodynamics but also from the physical kinetics of the process.

In this paper we shall make an attempt at deriving the kinetic equations of the phase transformations on the basis of an analysis of the dynamics of the condensation process. We shall assume that the formation of a stable equilibrium complex consisting of g molecules is preceded by the formation of intermediate, unstable associates comprising a smaller number of molecules. The collision of two molecules will be regarded as the initial act. The simultaneous collision of a large number of molecules is an unlikely event. Coagulation as a result of the collision of complexes is neglected.

The stability of the complex being formed is determined by the possibility or otherwise of eliminating the heat of condensation evolved on forming a bond between the molecules. This energy may be carried away, in heterogeneous condensation, by a cold surface, and in homogeneous condensation by collision with other gas molecules.

Let us consider the formation of a liquid phase in an atmosphere of supersaturated (supercooled) vapor, assuming the existence of a Maxwell−Boltzmann velocity distribution of the gas molecules. We shall further assume that the vapor phase is so rarefied that the time of interaction when the molecules collide is small compared with their mean free period. Under these assumptions we may picture the following mechanism for the formation of stable molecular associates.

As a result of the paired collision of molecules, a bond is established between these and an unstable saturated binary complex is formed. The bond energy is concentrated in the colliding molecules in the form of vibrational energy. We shall call the type of molecular complex in which the bond energy is concentrated in this way an activated complex. The lifetime of an activated complex consisting of g molecules we shall denote by τ_g^*. If in the lifetime τ_2^* of an activated complex consisting of two molecules the bond energy is carried away from the complex, the latter will become stable, and we shall then describe it as deactivated.

The binding (bond) energy may be carried away from the activated binary complex by virtue of collision with a third gas molecule (homogeneous condensation) or with a solid surface (heterogeneous condensation). The lifetime of a deactivated complex consisting of g molecules we shall denote by τ_g.

It follows from the kinetic theory of gases that the lifetime of an activated complex τ_g^* (or the activation time of a deactivated associate of molecules) coincides with the time of interaction between two colliding molecules or between a molecule and a complex. The lifetime of a deactivated complex is in turn determined by the time of free flight of the molecules (time between collisions).

The formation of a complex of g molecules may be pictured as a chain of elementary activation and deactivation processes. Using an asterisk to denote the activated state of the complex, we may write this process in the form of a succession of collisions. For the collision of two molecules

$$M_1 + M_1 \rightarrow M_2^* (\tau_2^*). \tag{1}$$

The activated complex M_2^* thus formed may be converted into a stable deactivated complex M_2 if during its lifetime τ_2^* it collides with a third molecule M_1 which removes the bond energy in the complex. We then have

$$M_2^* (\tau_2^*) + M_1 \rightarrow M_2 (\tau_2) + M_1^* . \tag{2}$$

The stable complex M_2 so formed may exist for a period τ_2 before the next collision with a molecule M_1. Then

$$M_2 (\tau_2) + M_1 \rightarrow M_3^* (\tau_3^*). \tag{3}$$

By analogy with (2) we may write the condition for the formation of a stable complex of three molecules in the form

$$M_3^* (\tau_3^*) + M_1 \rightarrow M_3 (\tau_3) + M_1^* . \tag{4}$$

On the basis of the foregoing, we may further write down the condition for the formation of a stable complex of g molecules M_g, which is preceded by an unstable (activated) complex M_g^* with a lifetime τ_g^*:

$$M_{g-1} (\tau_{g-1}) + M_1 \rightarrow M_g^* (\tau_g^*), \tag{5}$$

$$M_g^* (\tau_g^*) + M_1 \rightarrow M_g (\tau_g) + M_1^* . \tag{6}$$

This process will continue until a stable complex is formed, this consisting of such a large number of molecules g_{cr} that any further interaction with the gas molecules will be determined by the character of the heat and mass transfer associated with free molecular flow. This limiting (critical) complex $M_{g_{cr}}$ constitutes a condensation nucleus.

2. Rate of Formation of Condensation Nuclei under Conditions of Dynamic Equilibrium

Using N_2^* to denote the number of two-molecule collisions associated with the thermal motion of the gas molecules, and considering that the probability of the loss (decay) of an activated complex M_2^* is inversely proportional to its lifetime τ_2^*, it is not hard to determine the resultant concentration n_2^* of the unstable activated binary complexes.

Following [5], we may write the differential equation determining the rate of formation of activated complexes in the form

$$\frac{dn_2^*}{dt} = N_2^* - \frac{n_2^*}{\tau_2^*} . \tag{7}$$

The terms N_2^* and n_2^*/τ_2^* on the right-hand side of Eq. (7) respectively characterize the number of generated and eliminated binary complexes per unit volume per unit time.

Analogously for the activated and deactivated complexes of g molecules

$$\frac{dn_g^*}{dt} = N_g^* - \frac{n_g^*}{\tau_g^*}$$

and

$$\frac{dn_g}{dt} = N_g - \frac{n_g}{\tau_g} . \tag{8}$$

Under steady-state conditions of dynamic equilibrium ($dn_g^*/dt = 0$; $dn_g/dt = 0$), the number of generated complexes equals the number of eliminated complexes:

$$n_g^* = N_g^* \tau_g^*,$$
$$n_g = N_g \tau_g. \tag{9}$$

Let us suppose that unit volume of gas contains n_i molecules of radius r_i and n_j molecules of radius r_j. According to the kinetic theory of gases, the number of possible paired collisions between molecules of types i and j per unit time is

$$N_{i+j} = \pi (r_i + r_j)^2 \, n_i n_j \overline{c_{ij}}, \tag{10}$$

where $\overline{c}_{ij}$ is the mean relative velocity of thermal motion of the molecules.

In the vapor-condensation problem under consideration we are concerned with collisions between individual molecules and between single molecules and complexes (activated and deactivated), respectively. Using r_1 to denote the radius of a vapor molecule (i = 1) and r_g for the effective radius of a complex of g molecules, we may convert (10) into

$$N_{1+g} = \pi (r_1 + r_g)^2 \, n_1 n_g \overline{c_{1g}}. \tag{11}$$

Considering that the mass of a complex consisting of g molecules equals the sum of the molecules composing it, we may readily determine the effective radius of the complex

$$r_g = r_1 \sqrt[3]{g}.$$

Then

$$N_{1+g} = \pi r_1^2 \left(1 + \sqrt[3]{g}\right)^2 n_1 n_g \overline{c_{1g}}. \tag{12}$$

The quantity N_{1+g} characterizes the rate of formation of different complexes as a result of paired collisions. Such complexes may be either activated or deactivated.

The formation of activated complexes is always accompanied by the joining of a molecule to another molecule or a deactivated complex. Under these conditions, on the basis of (12), we may write

$$N_{1+g}^* = \pi r_1^2 \left(1 + \sqrt[3]{g}\right)^2 n_1 n_g \overline{c_{1g}}. \tag{13}$$

The formation of a stable deactivated complex, in turn, takes place as the result of a collision between a molecule and an activated complex. The number of molecules in the complex does not change in this process; only deactivation occurs. Under these conditions

$$N_g = \pi r_1^2 \left(1 + \sqrt[3]{g}\right)^2 n_1 n_g^* \overline{c_{1g}}. \tag{14}$$

Denoting

$$W_g = \pi r_1^2 \left(1 + \sqrt[3]{g}\right)^2 n_1 \overline{c_{1g}}, \tag{15}$$

we write (13) and (14) in the form

$$N_{1+g}^* = W_g n_g, \tag{16}$$
$$N_g = W_g n_g^*. \tag{17}$$

In accordance with (9), under steady-state conditions of dynamic equilibrium, the volume concentration of the unstable activated complexes is

$$n_{1+g}^* = N_{1+g}^* \tau_{1+g}^* = W_g n_g \tau_{1+g}^*. \tag{18}$$

The volume concentration of the stable deactivated complexes is

$$n_g = N_g \tau_g = W_g n_g^* \tau_g. \tag{19}$$

As indicated earlier, in the mode of condensation under consideration, a stable two-molecule complex M_2 is formed by the collision of an activated unstable complex M_2^* with a gas molecule M_1. Using (17), we may determine the number of stable binary complexes M_2 formed every second. Taking g = 2 for this case we obtain

$$N_2 = W_g n_2^*. \tag{20}$$

Allowing for (18), we may write

$$N_2 = W_1 n_1 (W_2 \tau_2^*). \tag{21}$$

The volume concentration of stable two-molecule complexes is

$$n_2 = W_1 n_1 (W_2 \tau_2^* \tau_2). \tag{22}$$

Analogously for three- and four-molecule complexes

$$N_3 = W_1 n_1 (W_2^2 \tau_2^* \tau_2) (W_3 \tau_3^*), \tag{23}$$

$$n_3 = W_1 n_1 (W_2^2 \tau_2^* \tau_2) (W_3 \tau_3^* \tau_3)$$

and

$$N_4 = W_1 n_1 (W_2^2 \tau_2^* \tau_2) (W_3^2 \tau_3^* \tau_3) (W_4 \tau_4^*), \tag{24}$$

$$n_4 = W_1 n_1 (W_2^2 \tau_2^* \tau_2) (W_3^2 \tau_3^* \tau_3) (W_4 \tau_4^* \tau_4).$$

For complexes of g molecules

$$N_g = W_1 n_1 (W_2^2 \tau_2^* \tau_2) (W_3^2 \tau_3^* \tau_3) \cdots (W_{g-1}^2 \tau_{g-1}^* \tau_{g-1}) (W_g \tau_g^*), \tag{25}$$

and

$$n_g = W_1 n_1 (W_2^2 \tau_2^* \tau_2) (W_3^2 \tau_3^* \tau_3) \cdots (W_{g-1} \tau_{g-1}^* \tau_{g-1}) (W_g \tau_g^* \tau_g), \tag{26}$$

or

$$N_g = W_1 n_1 (W_g \tau_g^*) \prod_{i=2}^{g-1} (W_i^2 \tau_i^* \tau_i) \tag{27}$$

and

$$n_g = W_1 n_1 (W_g \tau_g^* \tau_g) \prod_{i=2}^{g-1} (W_i^2 \tau_i^* \tau_i). \tag{28}$$

The foregoing model, representing the formation of complexes by the collision of molecules, is based on the assumption that the probability of the formation of a complex of higher order does not depend on the probability of the formation of complexes of the preceding lower orders. We see from (27) and (28) that the process may be described by the well-known chains of A. A. Markov [6].

Using the concepts of the kinetic theory of gases [7] and liquids [3], we may determine the lifetime of the activated and deactivated complexes τ_i^* and τ_i in Eqs. (27) and (28). Taking the lifetime of an activated complex as equal to the time of interaction, we write

$$\tau_{g+1}^* = \tau_0 \exp \left[\frac{U_0}{kT} \right], \tag{29}$$

where the period of natural oscillations of the molecule

$$\tau_0 = \frac{\Delta}{\bar{c}_{1g}}. \tag{30}$$

Here k is Boltzmann's constant; T is the temperature; U_0 is the activation energy of the bond; Δ is the "effective" width of the potential pit (well). In turn

$$\bar{c}_{1g} = \sqrt{\frac{8kT}{\pi} \cdot \frac{m_1 + m_g}{m_1 m_g}}. \tag{31}$$

Substituting $m_g = m_1 g$, we obtain

$$\bar{c}_{1g} = \sqrt{\frac{8kT}{\pi m_1} \left(1 + \frac{1}{g} \right)}. \tag{32}$$

Hence

$$\tau_{g+1}^* = \frac{\Delta}{\sqrt{\frac{8kT}{\pi m_1} \left(1 + \frac{1}{g} \right)}} \exp \left(\frac{U_0}{kT} \right). \tag{33}$$
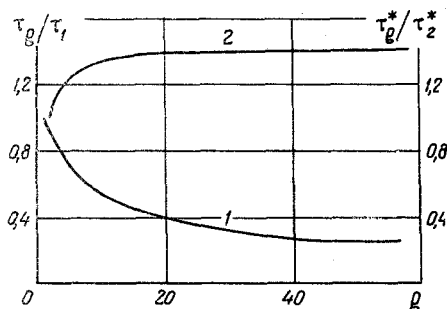
Fig. 1. Activation and deactivation times of a complex as a function of the number of constituent molecules: 1) τ_g/τ_1; 2) τ_g^*/τ_2^*.

If, on the basis of (33), we write down the lifetimes of activated complexes formed by two and g molecules, respectively, we may readily derive the relation

$$\frac{\tau_g^*}{\tau_2^*} = \sqrt{2\left(1 - \frac{1}{g}\right)}. \tag{34}$$

Equation (34) characterizes the relative change in the lifetime of the activated complexes on changing the number of molecules in the complex, expressed in fractions of the lifetime of the original two-molecule complex.

The free flight times of a complex of g molecules and a single molecule, respectively, equal

$$\tau_g = \frac{\lambda_g}{c_{1g}} \text{ and } \tau_1 = \frac{\lambda_1}{c_{1,1}}. \tag{35}$$

Writing down the expression for the free path

$$\lambda_g = \frac{1}{\pi(r_1 + r_g)^2} \cdot \frac{V}{N_1} = \frac{1}{\pi r_1^2 \left(1 + \sqrt[3]{g}\right)^2} \cdot \frac{V}{N_1},$$

we easily find

$$\frac{\tau_g}{\tau_1} = \frac{4}{\left(1 + \sqrt[3]{g}\right)^2} \cdot \frac{\bar{c}_{1,1}}{\bar{c}_{1g}}. \tag{36}$$

Allowing for (32), we finally obtain

$$\frac{\tau_g}{\tau_1} = \frac{4\sqrt{2}}{\left(1 + \sqrt[3]{g}\right)^2 \sqrt{1 + \frac{1}{g}}}. \tag{37}$$

Equation (37) characterizes the relative change in the free flight time as a function of the number of molecules in the complex.

Figure 1 illustrates some curves reflecting the effect of the number of molecules in the complex on its lifetime for both the activated and the deactivated state. The relative lifetime of the activated complexes increases with increasing number of molecules in the complex. This increase appears most markedly in complexes containing less than ten molecules. The lifetime of complexes of higher order is almost independent of the number of molecules in the complex, and exceeds the lifetime of the original two-molecule complex by approximately 40%. For an unlimited increase in the number of molecules in the complex

$$\lim_{g \to \infty} \left| \frac{\tau_g^*}{\tau_2^*} \right| = \sqrt{2}.$$

The relative lifetime of stable deactivated complexes (the period of their free flight), on the other hand, diminishes with increasing number of molecules in the complex. The ratio τ_g/τ_1 tends asymptotically to zero as the number of molecules in the complex increases without limit. The greater the number of molecules in the complex, the shorter is its lifetime τ_g as compared with the lifetime of a molecule τ_1.

Thus, as the number of molecules in a deactivated complex increases, the collision frequency rises sharply, and in the limit of $g \to \infty$ the complex undergoes continuous bombardment by gas molecules. Under these conditions the character of the interaction between the complex and the gas molecules suffers a qualitative change, and becomes analogous to the interaction of gas molecules with a solid surface.

The relationships here obtained enable us to calculate the rate of formation of molecular associates constituting nuclei of the liquid phase in a supersaturated vapor.

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