# Statistical Theory of Condensation Phenomena

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# LETTERS TO THE EDITOR

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## Statistical Theory of Condensation Phenomena

Mayer and his co-workers[1] and subsequently Kahn and Uhlenbeck[2] and Born and Fuchs[3] have developed an interesting theory of condensation phenomena, which, however, because of its mathematical intricacy will hardly appeal to the experimental physicist or chemist.

I wish to show in this note that essentially the same results can be obtained in a quite elementary way with the help of the statistical theory of chemical equilibrium in a gas mixture.

The simplification underlying the application of this theory to the problem of the condensation of a vapor, consists in neglecting intermediary degrees of binding between its atoms (we limit ourselves to the case of a monoatomic substance). These atoms will be considered accordingly either as entirely free, or as bound together into diatomic "molecules," or into triatomic "molecules" and so on. The number of "molecules" consisting of $g$ atoms will be denoted with $N_g$. For sufficiently large values of $g$ these "molecules" will actually behave as small drops of the liquid or small crystals of the solid phase. For the sake of simplicity, the existence of different "isomeric" forms of the same $g$-atomic molecule (differing with respect to shape and size) will be neglected.* If moreover we neglect the mutual action between different molecules and treat the whole system as an ideal gas mixture, the ratios between the numbers $N_g$ can be determined by the ordinary mass action law

$$N_g/N_1{}^g = F_g/F_1{}^g, \qquad (1)$$

where $F_g$ is the partition function for one molecule of the given species. We have

$$F_1 = V\left(\frac{2\pi m_1 kT}{h^2}\right)^{\frac{3}{2}} e^{-U/kT}, \qquad (2)$$

where $V$ is the total volume occupied by the system, $m_1$ is the mass of an atom, and $U$ its potential energy in the free state ($=0$).

We have further $F_g = e^{-\psi_g/kT}$ where $\psi_g$ is the free energy of the molecules of the species $g$ referred to one of them. For very large values of $g$ ($g \sim 10^3$, say) $\psi_g$ must be proportional to $g$, so that we can put in this case $\psi_g = U' \cdot g$ and consequently

$$N_g = \xi^g \qquad (g \gg 1), \qquad (3)$$

where

$$\xi = \frac{N_1}{V}\left(\frac{2\pi m_1 kT}{h^2}\right)^{-\frac{3}{2}} e^{(U-U')/kT}. \qquad (3a)$$

So long as $\xi < 1$ we have to do with an unsaturated vapor of the substance under consideration (contrary to the current opinion, such a vapor in the case of a monoatomic substance consists partially of larger atomic groupings). The case $\xi > 1$ corresponds to an over-saturated vapor. The saturation or condensation point is thus determined by the condition $\xi = 1$. Putting $U' = U_0' - 3kT \lg h\nu/kT$, where $U_0'$ is the energy per atom at $T = 0$ and $\nu$ is an average vibration frequency (this formula can be applied both to liquid drops and to crystals), we can rewrite this condition in the form

$$\frac{N_1}{V} = \left(\frac{2\pi m_1 \nu_1{}^2}{kT}\right)^{\frac{3}{2}} e^{-(U-U_0')/kT}, \qquad (4)$$

which agrees with the usual formula for the concentration of the saturated vapor of a monoatomic substance as a function of the temperature (with the minor difference that $N_1/V$ is not the *total* concentration, but the *partial* concentration of the monoatomic portion of the vapor).

If $g$ is not too large, the surface free energy of the droplets, or crystals, must be taken into account by adding to $\psi_g$ a term proportional to $g^{\frac{2}{3}}$. Denoting the proportionality coefficient with $\alpha$ we obtain instead of Eq. (3)

$$N_g = \xi^g e^{-\alpha g^{\frac{2}{3}}/kT}. \qquad (5)$$

If $\xi < 1$ this expression decreases monotonically with increase of $g$. In the contrary, case ($\xi > 1$) it displays a minimum for a value of $g$ given by

$$\lg \xi = \frac{2}{3} \frac{\alpha}{kTg^{\frac{1}{3}}}. \qquad (6)$$

Since at a given temperature $\xi$, according to Eq. (3), is proportional to the concentration $N_1/V$ and consequently to the pressure $p$ of the vapor (or more exactly to the partial pressure of its monoatomic component) and since $\xi = 1$ corresponds to the saturation pressure $p = p_0$, the preceding formula can be written in the form

$$\lg \frac{p}{p_0} = \frac{2}{3} \frac{\alpha}{kTg^{\frac{1}{3}}}. \qquad (6a)$$

In the case of a spherical droplet it reduces to the well-known Thomson formula for the vapor pressure over the surface of a droplet as a function of its radius (which is proportional to $g^{\frac{1}{3}}$).

Substituting the expression (6) into (5) we obtain for the minimum value of $N_g$

$$N_g = e^{-\frac{1}{3}\alpha g^{\frac{2}{3}}/kT}, \qquad (7)$$

which is just Volmer's formula for the velocity of condensation of an oversaturated vapor resulting from the formation and further growth of droplets of the critical size determined by (6a). We thus see that our simple theory not only gives an accurate description of the condensation phenomenon, but also accounts for the phenomena connected with oversaturation.

The theory could be improved by taking into account the mutual action between the "molecules" of our "gas-mixture." This can be done in a formal way by multiplying the various $N_g$'s with the corresponding "activity coefficients." Practically this correction must result in a tendency of the larger "molecules" to coalesce into a single mass—liquid or crystalline, as the case may be.

The preceding theory can be applied with a few modifications to the phenomena of *polymerization* (i.e., the formation of large chain-like macromolecules), which can be considered as a kind of condensation (in the physical sense of the term) in one dimension, the van der Waals forces being replaced by valence forces. The residual van der Waals attraction between different macromolecules will be relatively ineffective in their coalescence to larger units. This case is also distinguished by the absence of oversaturation (or overcooling) phenomena, the free energy of the two ends of a macromolecule being independent of its size.

A full account of the theory will be published elsewhere.

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* They can easily be accounted for approximately if one limits himself to structures which are not very different from the normal ones, i.e., those corresponding to the minimum value of the energy for any given value of $g$. The complications of Mayer's theory are connected mainly with intermediate structures, corresponding to large deviations from the normal.

[1] J. E. Mayer, J. Chem. Phys. 5, 67 (1937). J. E. Mayer and S. F. Harrison, J. Chem. Phys. 6, 87, 101 (1938).
[2] G. E. Uhlenbeck and B. Kahn, Physica 5, 399 (1938).
[3] M. Born and R. Fuchs, Proc. Roy Soc. 166, 391 (1938).

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## Inhibition of Crystallization of Rubber by High Pressure

Bekkedahl[1] has shown that crude rubber at atmospheric pressure freezes in the temperature range from $-40°$ to $+10°C$ and melts in the temperature range from $6°$ to $16°C$. The transition is from amorphous I to crystalline I which is the stable modification between $-72°$ and $6°C$. His measurements of the freezing at $0°C$ showed that about 280 hours were necessary for completion of the transition, the volume decreasing by 2.2 percent in such a manner that the volume-time curve was S-shaped.

This communication reports the inhibition of crystallization at high pressure. Crude smoked sheets were packed tightly in a pressure chamber and isopropyl alcohol was used to transmit the pressure. The chamber was kept at $0°C$ in a well-circulated ice bath. A pressure of 8000 kg/cm² was applied and its constancy observed over a period of 14 days. The sensitivity of the manganin gauge used for pressure measurement was such that changes of 5 kg/cm² were detectable. Outside of slight erratic pressure changes caused by change of temperature around part of

the press that was not kept at $0°$, "no change of pressure due to crystallization was detected during the 14 days." Examination of the rubber immediately after pressure was released showed that it was still in the amorphous state.

Since the specific volume of amorphous I is greater than that of crystalline I, pressure raises the transition point and it can be said that the inhibition is due to supercooling. Using the data of Bekkedahl,[1] and Bekkedahl and Matheson[2] for melting temperature, change of specific volume on melting, and heat of fusion, computation by Clapeyron's equation shows that the melting point of crystalline I is of the order of $400°C$ at 8000 kg/cm². The inhibition of crystallization appears to be an effect of high viscosity of amorphous I at high pressure. Extremely high viscosities have been observed[3] in complicated organic compounds under pressure and when it is considered that the molecular aggregates in crude rubber may number several hundred chemical molecules, it is to be expected that the viscosity of amorphous rubber at 8000 kg/cm² may be increased enormously. Staudinger has computed an average molecular weight of a raw rubber in the hundred thousands, a value indicating that the pressure coefficient of viscosity must be very high since it is known that this coefficient increases with molecular weight.

The transition from crystalline I to amorphous I at high pressure appears to be an equilibrium phenomenon, however. Samples of smoked sheet crystallized at atmospheric pressure were observed to melt at $77.5°C$ at a pressure of 1270 kg/cm². $dT_m/dp$ is then 0.0484 as compared with a calculated value of $0.0518°C/kg/cm²$ by Clapeyron's equation at atmospheric pressure on the assumption that the normal transition point is $16°C$. Melting took place slowly, approximately five minutes being required for completion. If the normal melting point of the rubber is taken at $11°$ rather than $16°C$, the above value for melting under pressure will be increased accordingly.

Because of high viscosity it would appear that amorphous I can be kept in the metastable state over a long period of time at 8000 kg/cm². Bekkedahl concluded that the rate of crystallization of rubber below $-50°C$ at atmospheric pressure was too small to be measured during several weeks of observation. Examples of delayed equilibrium are well known. Deville observed a transition in sulphur over a period of 2 years, and it has been observed that the transition from white to gray tin at $18°C$ may require several centuries for completion under ordinary conditions. Many polymorphic changes at high pressures have been found by Tammann, Bridgman, and Cohen to take place very slowly, although the transitions are quite different in nature from the one discussed here.

The writer is indebted to Dr. Lawrence Wood of the National Bureau of Standards for suggesting these experiments and contributing much helpful adivce.

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The Pennsylvania State College,
State College, Pennsylvania,
February 1, 1939.

[1] Norman Bekkedahl, Nat. Bur. Stand. J. Research 13, 411 (1934).
[2] Norman Bekkedahl and Harry Matheson, Nat. Bur. Stand. J. Research 15, 512 (1935).
[3] R. B. Dow, H. E. Morgan and M. R. Fenske, Ind. Eng. Chem. 29, 1078 (1937).