

CONDENSATION OF SUPERSATURATED VAPOURS OF α - AND β -NAPHTHOLES IN THE DIFFUSION CLOUD CHAMBER

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Critical supersaturation of vapours of solid α - and β -naphtholes was measured in the diffusion cloud chamber in the temperature interval 250 to 310 K. The homogeneous nucleation of crystal nuclei is considered to be the most probable mechanism of condensation. By use of the equation for the rate of homogeneous nucleation the surface free energies of crystal nuclei of α - and β -naphtholes were estimated from experimental data.

Vapours of compounds are usually condensed from the stream of inert gas either by cooling the vapour mixture by cold walls of the condenser or by their mixing with the cooler fluid. As the vapour pressure of saturated vapours depends on temperature approximately exponentially, it usually decreases at cooling considerably faster than the actual vapour pressure and the bulk of the vapour mixture can be supersaturated. At condensation of the supersaturated vapour the nuclei of the condensed phase form at first inside the vapour phase. The nuclei can originate either spontaneously due to fluctuation of density of the vapour phase or due to existence of the condensation centers which are usually dust particles or ions. The nucleation rate is a very sharp function of supersaturation. For little supersaturations it is practically negligible so that the supersaturated vapour is relatively stable. If supersaturation exceeds a certain critical value S_{crit} , the nucleation rate steeply increases and an undesirable formation of the fog of condensed compound takes place. It is therefore useful to know the dependence of critical supersaturation on temperature for designing the condensation processes.

For the known mechanism of nuclei formation of the condensed phase, we can estimate S_{crit} from the corresponding equations for the nucleation rate obtained on basis of theoretical considerations. Quite good estimates are obtained for homogeneous nucleation of liquids from the classical equation¹, better results are in some cases obtained by the Lothe-Pound equation². The choice of a suitable equation for homogeneous nucleation of crystals nuclei is determined by the roughness of the surface of nuclei. As far as the surface of nuclei is "molecularly rough" it is possible to use the classical equation³ with the approximation of spherical shape of nuclei⁴ for the estimate of the dependence S_{crit} on temperature. For "molecularly smooth" surfaces, it is necessary to consider the two-dimensional nucleation on the surface of nuclei and to intro-

duce the corresponding shape factors^{3,4}. The use of these equations is considerably limited as the information on the surface free energy of solid compounds necessary for the estimate are at present practically inaccessible. The equations describing the rate of heterogeneous nucleation on ions have no substantial significance for the estimate of S_{crit} with regard to quite specific effects of various gaseous ions⁵ and to their unknown concentrations. The equations either do not express the experimentally observed different effect of positive and negative ions^{6,7} or they are too complicated⁸ and require the knowledge of a number of physical constants of compounds which are hardly available. The catalytic effect of ions at heterogeneous nucleation will usually not be very profound⁹. The estimate of the effect of foreign particles at heterogeneous nucleation is practically impossible as usually compositions and surface properties of these particles are completely unknown. Several experimental methods were developed and are summarized in the studies⁹⁻¹² for experimental measurement of the dependence S_{crit} in dependence on temperature. One of the methods applied successfully for studies of homogeneous nucleation of vapours of liquids is supersaturation of the vapour mixture at nonisothermal diffusion flow in the diffusion cloud chamber. The diffusion cloud chamber is in principle formed by two metal plates connected by a glass cylinder. One of the plates with the studied compound is heated and the second one is cooled. Molecules of compounds evaporating from the heated plate are diffusing through the inert gas to the cooled plate where they condense. Profiles of temperatures and of partial pressures of the evaporated compound in the chamber are obtained by solution of unidimensional equations for heat and mass fluxes. As both these profiles are approximately linear, while the vapour pressure of saturated vapours varies with temperature approximately exponentially and thus it decreases in the chamber considerably faster, the vapour phase is supersaturated. By increasing the temperature gradient between the plates the supersaturation can be arbitrarily increased until the particles of the condensed phase appear. This method was used in measurements of dependences of critical supersaturation on temperature for water¹³ and some organic compounds¹⁴⁻¹⁶. The obtained results are in a very good agreement with the classical theory of homogeneous nucleation.

We have made an effort to arrange the diffusion cloud chamber for measurements of critical supersaturation of vapours of solid compounds with regard to the relative simplicity of the experimental apparatus of the diffusion cloud chamber type in comparison to other methods and to obtained results on critical supersaturation of liquid vapours. For this purpose was built a simple model of the diffusion cloud chamber and its function was verified in measurements of critical supersaturation of vapours of solid benzoic acid in dependence on temperature¹⁷. On basis of the obtained results the operation of the diffusion cloud chamber was altered and it was used for measurements of critical supersaturation of solid α and β -naphtholes in dependence on temperature.

EXPERIMENTAL

The experimental apparatus used was described recently¹⁷. The chamber was lit with a 150 W lamp with heat filter.

Substances used. α - and β -naphtholes (analytical grade reagents, Lachema, Brno) were purified by distillation with water vapour. Helium and nitrogen were taken from pressure flasks, water residues were removed by cooling in a freezer with a mixture of solid CO_2 and ethanol. Physical

properties of chemicals used were: α -naphthol: Molecular weight $M = 144.19$ (g mol^{-1}); melting point 366.5 K (ref.¹⁸); equilibrium vapour pressure of solid substance $\log P_s = 12.68 \pm 0.07 - (4763.2 \pm 22.8)/T$, $296.76 - 313.05 \text{ K}$ (Torr) (ref.¹⁹); equilibrium vapour pressure of the liquid $\log P_1 = 8.907 - 3322/T$, $372.0 - 476.0 \text{ K}$ (Torr) (ref.²⁰); surface tension $\sigma = 48.8 - 0.1(T - 273.15)$ (dyn cm^{-1})*; density of liquid substance $d_1 = 1.17 - 0.000698(T - 273.15)$. (g cm^{-3})*; solid density $d_s = 1.289$ (g cm^{-3}) (ref.²¹); diffusion coefficient $D_{\text{He-naphthol}} = 0.246$ ($\text{cm}^2 \text{ s}^{-1}$), $D_{\text{N}_2\text{-naphthol}} = 0.072$ ($\text{cm}^2 \text{ s}^{-1}$), 300 K , 1 atm^{22} . β -Naphthol: $M = 144.19$ (g mol^{-1}); $\log P_s = 12.68 \pm 0.09 - (4919.5 \pm 27.2)/T$, $305.32 - 323.70 \text{ K}$ (Torr) (ref.¹⁹); $\log P_1 = 8.807 - 3322/T$, $418.7 - 483.0 \text{ K}$ (Torr) (ref.²⁰); $\sigma = 48.1 - 0.09(T - 273.15)$ (dyn cm^{-1})*; $d_1 = 1.174 - 0.000738(T - 273.15)$ (g cm^{-3})*; $d_s = 1.25$ (g cm^{-3}) (ref.²¹). Helium: thermal conductivity $\lambda = 0.0001392 + 0.74028 \cdot 10^{-6}T$ ($\text{cal cm}^{-1} \text{ s}^{-1} \text{ grad}^{-1}$)**. Nitrogen: thermal conductivity $\lambda = 0.0000915 + 0.17512 \cdot 10^{-6}T$ ($\text{cal cm}^{-1} \text{ s}^{-1} \text{ grad}^{-1}$)**.

Experimental procedure. As direct determination of the surface temperatures of the evaporated and condensing layer was difficult, the temperature of the surface of plates was measured and a correction has been introduced for the layer of deposited material. To decrease the resulting correction to minimum it is desirable that the condensing layer be grown very slowly. For this reason, the diffusion flow has been decreased by a high partial pressure of inert gas. The molecular diffusivity of the vapour mixture is in such case considerably smaller than the thermal diffusivity as the molecular weight of the evaporating matter is considerably higher than that of the inert gas. The concentration of the evaporated substance for the same temperature at higher heating rates will be smaller in any arbitrary horizontal layer of the chamber. So the deviations from the steady state at increasing temperature gradient between the plates are greater for the concentration profile than for the temperature profile. The appearance of the first visible particles in the chamber will thus correspond at higher heating rates to a larger resulting gradient. Such a dependence was observed in measurements with the benzoic acid¹⁷. The steady state was approximated by extrapolation of temperature gradients obtained for various heating rates of the heated plate to the zero rate. The supersaturation profile in the chamber could have been obtained by performing several experiments. Therefore we have tried to simplify the experimental procedure. From the testing experiments the temperature gradient was estimated under which the particles should originate in the chamber. In the actual measurement, the temperature difference was at first fixed by about 1 to 4 K smaller and was kept constant for about 10 to 15 min. At the given chamber height and molecular diffusivity of the vapour mixture the steady state²⁴ is reliably reached after elapse of this time. During this time no condensation has been observed in the bulk of the chamber. In the next phase the temperature of the heated plate was increased at the rate of about 0.002 to 0.05 K s^{-1} till the first particles appeared in the chamber. The resulting gradient corresponding to appearance of the first visible particles was always the same at heating *i.e.* it was independent of the heating rate. Thus the deviations from the steady state can be anticipated to be smaller in this phase of heating than the over-all experimental error. Because of that, the measurements in the whole temperature interval were performed by the described procedure with the subsequent heating rate of 0.005 K s^{-1} . The supersaturation profile was thus obtained from each measurement. The particles observed at condensation of α - and β -naphtholes originated obviously in one layer approx. in one tenth of the height from the bottom plate and were falling directly down to the bottom plate.

* Obtained by calculation from available data²¹.

** Obtained by calculation from available data²³.

RESULTS AND DISCUSSION

The measurements were performed in the chamber 43 or 21 mm high with helium or nitrogen as inert gases. The final pressure in the chamber was in the interval 760 to 770 Torr in all experiments. The thickness of the evaporated layer was 0.2 mm, correction for the surface temperature was within the range 0.3 to 0.7 K. The temperature interval of measurements was chosen so that the resulting thickness of the condensing layer would be smaller than 0.1 mm. Correction for temperature of the condensing surface was thus comparable to the accuracy with which the temperature was measured (0.1 K) and therefore was not taken into consideration. The results of measurements are presented in Table I where T_1 is the temperature of the condensing layer and T_2 the corrected temperature of the evaporated layer. The profiles of partial pressures and temperatures in the chamber were calculated from temperatures of both surfaces and the corresponding saturated vapour pressures. The analytical solution of heat and mass flux equations was used¹⁶ for calculation. With regard to small vapour concentrations in the inert gas and small diffusion flows the solution was simplified by additional approximations: 1. Thermal conductivity is independent of the concentration and equals to the thermal conductivity of the inert gas. 2. Heat flux related to the diffusion flux is negligible. By introduction

TABLE I
Experimental Results

Experiment	T_1 , K	T_2 , K	T_1 , K	T_2 , K
	α -naphthole		β -naphthole	
1	250.5	314.5	249.7	320.4
2	254.7 ^b	318.1	254.9	326.9
3	256.9	320.8	256.0	327.6
4	260.3 ^b	325.1	260.2	333.4
5	263.1 ^b	328.9	263.0	334.6
6	265.3 ^b	331.7	265.4	338.6
7	268.6 ^a	333.4	269.6	343.6
8	269.9 ^b	337.2	274.3	347.4
9	272.5 ^b	339.6	280.5	356.0
10	275.5 ^b	344.8	288.5	362.1
11	281.4	352.2	290.1	364.6
12	284.4 ^a	353.6	295.8	370.4

The inert gas was helium with the exception^a for nitrogen. The chamber height was 21 mm and^b 43 mm.

of these approximations the system of differential equations for the temperature and concentration profiles was obtained in the form

$$dP_v/dz = (P_v - P)L/TD_{vg}^0, \quad dT/dz = -q/(\lambda_0 + \lambda_1 T), \quad (1)$$

with boundary conditions: $z = 0$, $T(0) = T_1$, $P_v(0) = P_{v1}$; $z = 1$, $T(1) = T_2$, $P_v(1) = P_{v2}$, where z is the reduced chamber height, T temperature, P_v partial pressure of vapours, P total pressure, L diffusion flux, q heat flux, D_{vg}^0 constant of temperature and pressure dependence of the diffusion coefficient and λ_0 and λ_1 constants of the temperature dependence of thermal conductivity of inert gas. By elimination of dz and integration of the resulting differential equation, the relation was obtained

$$P_v = (P_{v1} - P)(T_1/T)^{\lambda_0 M} \exp(\lambda_1 M(T_1 - T)) + P, \quad (2)$$

where $M = L/(D_{vg}^0 q)$. Parameter M was obtained by substitution of the second boundary condition for P_v and T into (2). The relation (2) was used for calculation of supersaturation profiles in the chamber for the case of origin of crystalline (Fig. 1) or liquid nuclei. The supersaturation profiles, calculated according to the original equation¹⁶, *i.e.* without our approximations were identical. The height of the chamber

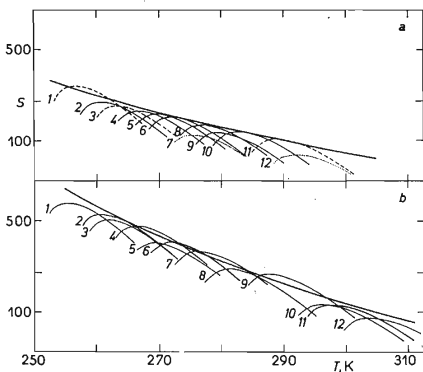


FIG. 1

Experimental Results of Critical Supersaturation of Vapours of α - and β -Naphtholes

The curves are denoted as those in Table I. *a* α -Naphthole, *b* β -naphthole.

did not have any measurable effect with helium as inert gas (Fig. 1). This means that the possible effect of convection is negligible and that the approximation of unidimensional diffusion and heat transfer is satisfactory. With nitrogen as inert gas the resulting profiles are smaller (Fig. 1). A small convective motion of particles upward along the chamber walls and at the distance about 20 mm from the wall of the chamber again back from the upper plane toward the lower one was observed in these experiments. A similar convective motion was observed with the use of argon and nitrogen when the effect of inert gas on supersaturation of vapours of *n*-butyl benzene was studied¹⁶. Due to the reversed heat and mass flows the resulting supersaturation profiles were in this case larger. The observed effect was due perhaps to larger sensitivity to the "macroscopic cell convection" which was the result of larger density and smaller thermal conductivity of inert gas¹⁶.

Particles observed by the side light were glittering and they were assumed to be crystalline. These particles were the result of growth of critical nuclei into the visible size. In spite of the fact that supersaturated vapour can also condense in the liquid form at temperatures considerably lower than the freezing point^{25,26} the observed particles can be also the result of growth of frozen drops. The critical nuclei themselves can be either liquid or crystalline and can be the result of homogeneous or heterogeneous nucleation on ions or foreign particles. The supersaturation profiles calculated for the case of origin of liquid nuclei were compared to the estimate of the dependence of critical supersaturation on temperature for homogeneous liquid nucleation according to the classical equation (3). For α - as well as for β -naphtholes the supersaturation profiles were in the vicinity of the maximum smaller by one order of magnitude than the estimate. As these estimates usually agree very well with the experiments¹³⁻¹⁶ the homogeneous liquid nucleation in our case is very improbable. As a rule, for a small catalytic activity of ions we can consider, for the same reason, heterogeneous nucleation of liquid on ions as improbable. At heterogeneous nucleation the condensation centres can be foreign particles contained or directly in the inert gas or produced by evaporation of the surface. The condensation on foreign particles contained in the inert gas was observed only in some cases when the chamber was freshly filled with inert gas. Condensation started by the appearance of dense fog practically in the whole volume of the chamber already at a considerably smaller difference of temperatures of both plates (about 40 K). By condensing onto these particles and by retaining the originated fog in the condensing layer at its preparation for next measurement the foreign particles were removed from the inert gas. The formation of this fog has not been observed in other experiments. Foreign particles produced by the evaporating surface can be of different nature. They can be either solid non-volatile particles contained in the original substance in the form of impurities or crystal particles evolved at evaporation from the microcrystalline surface. As the vapour mixture is supersaturated in the whole volume of the chamber, the crystal particles can have a subcritical or supercritical size with respect to super-

saturation in any arbitrary plane of the chamber. The crystal particles of subcritical size will evaporate while supercritical will grow. The presence of such particles would be identified by the appearance of visible particles diffusively spread in the whole volume of the chamber. We can expect that in the case of solid non-volatile particles these particles will differ by composition, size and surface properties and resultingly also by their catalytic effects²⁷. Differing catalytic effects would again correspond to the origin of diffusively spread particles in the whole volume. But the appearance of such particles has not been observed. For this reason, we have considered as the most probable the mechanism of origin of observed particles the homogeneous nucleation of crystal nuclei and their subsequent growth into the visible size. Due to the temperatures used it is possible to assume the "molecularly rough" surface and spherical shape of nuclei. For the dependence of critical supersaturation on temperature, equations for homogeneous nucleation can be in such case used in the form³

$$J = a(2N^3/\pi)^{1/2} (P_e/RT)^2 S^2(\sigma M/d^2)^{1/2} \exp \{(-16\pi N/3R^3)(M/d)^2 \cdot (\sigma/T)^3 (\ln S)^{-2}\} \quad (3)$$

where J is the nucleation rate ($\text{cm}^{-3} \text{s}^{-1}$), a a condensation coefficient, N Avogadro's number, R gas constant, M molecular weight, d density, σ surface free energy, P_e vapour pressure at temperature T and supersaturation S . Eq. (3) was solved iteratively for the nucleation rate J and the condensation coefficient a equal to one by use of corresponding physical constants. As the surface free energy of solid naphtholes is not known, it was chosen so that the calculated dependence of critical supersaturation on temperature would be in good agreement with the experimental results (Fig. 1). For the surface free energy of crystal nuclei of α - and β -naphtholes were obtained in such a way the relations

$$\begin{aligned} \sigma_{\alpha\text{-naphthol}} &= 54.0 + 0.09(T - 366.5) \quad (\text{erg/cm}^2), \\ \sigma_{\beta\text{-naphthol}} &= 49.0 \quad (\text{erg/cm}^2). \end{aligned} \quad (4)$$

The surface free energies of solid naphtholes, according to relations (4), are in vicinity of the melting point approximately by one third higher than of the corresponding liquid which is acceptable²⁸. The surface free energy of solid compounds decreases as a rule with increasing temperature. But, according to relation (4), the surface free energy of crystal nuclei of α -naphthole increases with increasing temperature and the surface free energy of nuclei of β -naphthole is about constant in the considered interval. This can result from the use of approximation of spherical shape of nuclei and of the isothropic surface free energy. Actually it is necessary to consider the polyhedral shape of nuclei with the surface free energy of individual crystal planes which is a function of the crystallographic orientation³. In the case of small

nuclei the effect of corners, edges, steeps and kinks should be appreciable. The relations (4) thus represent more or less the average surface free energy and include the eventual shape factor as well. This average surface free energy can also include the effect of changing sizes and shapes of nuclei and the structure of the surface²⁹ with temperature.

REFERENCES

1. Frenkel J.: *Kinetic Theory of Liquids*. Oxford University Press, Oxford 1946.
2. Lothe J., Pound G. M.: *J. Chem. Phys.* 36, 2080 (1962), 45, 630 (1966).
3. Dunning W. J.: *Nucleation* (A. C. Zettlemeyer, Ed.). Marcel Dekker, New York 1969.
4. Fletcher N. H.: *The Physics of Rainclouds*. Cambridge University Press, Cambridge 1962.
5. Castleman A. W. jr, Tang I. N.: *J. Chem. Phys.* 57, 3629 (1972).
6. Volmer M.: *Kinetik der Phasenbildung*. Theodor Steinkopf Verlag, Dresden 1939.
7. Russell K. C.: *J. Chem. Phys.* 50, 1809 (1969).
8. White D. R., Kassner J. L. jr: *Aerosol Sci.* 2, 201 (1971).
9. Pound G. M.: *J. Phys. Chem. Ref. Data* 1, 119 (1972).
10. Andres R. P.: *Nucleation* (A. C. Zettlemeyer, Ed.). Marcel Dekker, New York 1969.
11. Hirth J. P., Pound G. M.: *Condensation and Evaporation, Nucleation and Growth Kinetics*. Pergamon Press, Oxford 1963.
12. Amelin A. G.: *Theoretical Principles of Cloud Formation at Condensation of Vapours* (in Russian). Izd. Khimiya, Moscow 1972.
13. Heist R. H., Reiss H.: *J. Chem. Phys.* 59, 665 (1973).
14. Katz J. L., Ostermier B. J.: *J. Chem. Phys.* 47, 478 (1967).
15. Katz J. L.: *J. Chem. Phys.* 52, 4733 (1970).
16. Katz J. L., Scoppa II C. J., Canesh Kumar N., Mirabel P.: *J. Chem. Phys.* 62, 448 (1975).
17. Smolík J., Vitovec J.: *This Journal*, 41, 1471 (1976).
18. *Handbook of Chemistry and Physics*, 49th Ed., 1968—1969, C 418, The Chemical Tubber Co.
19. Colomina M., Roux M. V., Turrión C.: *J. Chem. Thermodyn.* 6, 571 (1974).
20. *Landolt-Börnstein, Zahlenwerten und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik*, 6th Ed. Vol. II-2, p. 123. Springer, Berlin 1956.
21. *Beilsteins Handbuch der Organischen Chemie*, 4th Ed. Springer, Berlin 1923, 1931, 1944, 1965.
22. Fuller E. N., Schettler P. D., Giddings J. C.: *Ind. Eng. Chem.* 58, 19 (1966).
23. Vargaftik N. B.: *Spravochnik po Teplofizicheskim Svoistvam Gazov i Zhidkostei*. Izd. Nauka, Moscow 1972.
24. Crank J.: *The Mathematics of Diffusion*, p. 47. Oxford University Press 1956.
25. Thomas D. G., Staveley L. K.: *J. Chem. Soc.* 4569 (1952).
26. De Nordwall H. J., Staveley L. K.: *J. Chem. Soc.* 224 (1954).
27. Fletcher N. H.: *J. Chem. Phys.* 29, 572 (1958).
28. Adamson A. W.: *Physical Chemistry of Surfaces*. Wiley, New York 1967.
29. Dunning W. J.: *The Solid-Gas Interface* (E. A. Flood, Ed.), Vol. 1. Marcel Dekker, New York 1967.

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