[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Vapor Pressure of Supercooled Liquid Sulfur

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Introduction

The condensation of sulfur vapor either above or below the melting point in the formation of aerosols produces liquid sulfur droplets, which remain in that state for at least a few hours at room temperature. This is in accord with Ostwald's law[1] of successive reactions. Becker and Döring's[2] theory of the rate of nucleation in supersaturated vapors in the formation of aerosols can be used to explain this instance of Ostwald's law.

Supercooled liquid sulfur aerosol particles produced in the generator[3] developed in This Laboratory for the production of monodispersed aerosols are suitable for vapor pressure measurements because of their high state of subdivision. Investigation shows that they are composed predominately of lambda sulfur; the variety which is soluble in carbon bisulfide and like solvents, and consists of molecular rings of S_8. Examination of supercooled liquid sulfur in bulk at room temperature shows that it is not a glass but is a relatively non-viscous liquid.

Experimental Details

Bacon and Fanelli[4] have emphasized the great importance of maintaining a high degree of purity of sulfur in any study of its properties. Our sulfur was purified and tested for the removal of organic matter by their methods.[5]

Sulfur aerosols were prepared by using a modified La Mer–Sinclair aerosol generator.[3] The modifications were minor and consisted of having the gases flow through coils of about 150 cm. of 8 mm. Pyrex tubing in the boiler compartment to bring the gases to the temperature of the boiler before entering the boiler. The gas mixture flowed through a similar coil in the reheater compartment before entering the reheater. Nuclei were made by spraying an aqueous 0.01 mg./ml. sodium chloride solution into a stream of prepurified nitrogen. This spray was passed over concentrated sulfuric acid and phosphorus pentoxide to remove the water. Sodium chloride particles estimated to be about 0.01 micron in radius resulted. The nitrogen containing the nuclei passed through a coil into the boiler at 90 to 130° where it was mixed with a stream of prepurified nitrogen entering the boiler through another coil. Sulfur evaporates into the gas stream, and the mixture of sulfur vapor, nitrogen and sodium chloride nuclei pass through a coil in the reheater compartment into the reheater at a higher temperature than the boiler (up to 155°). The gas mixture is mixed thoroughly in the reheater, a 2-liter flask, and then passes up a double-wall 20-mm., inside diameter, tube 60 cm. long, where slow cooling occurs. The sulfur condenses on the sodium chloride nuclei forming a monodispersed aerosol. Large particles condensed above the melting point were found to be liquid at room temperature by microscopic examination. Particles, too small for microscopic examination, condensed below the melting point were found to be liquid by comparing their vapor pressure with that of particles known to be liquid. Vapor pressures are the same within experimental error; measurements 2 and 3, Table I.

TABLE I

TEMPERATURES °C.

Boiler	Re-heater	V. p. 10^5 mm.	Time interval, min.	Flow rate, 1/min.	Radius,[a] μ
115	120	1.13	240	1.10	0.37
108	155	1.10	80	1.32	.20
99	145	1.14	130	1.78	.20
91	129	1.08	75	1.40	.10
125	146	2.64	70	1.42	
125	146	2.32	200	1.28	
128	137	4.52	115	1.26	
124	122	4.39	160	0.76	
119	120	4.62	330	1.32	
126	127	8.97	243	0.65	
126	127	23.7	108	0.29	
127	135	113	200	0.35	
127	135	90.5	260	0.35	

[a] Particle radius in microns before depositing on glass wool.

Aerosol particle size was controlled by changing the concentration of nuclei or the concentration of sulfur.

The generator makes an aerosol containing 10^5 to 10^6 particles per cu. cm. The aerosol particles for the vapor pressure measurements are passed through about 10 cu. cm. of glass wool in thin layers separated by glass spacers in a 3.5 × 50 cm. glass tube at 3 liters per minute for about twenty minutes, depositing an estimated 20% of the particles on the glass wool. This gives about 10^8 to 10^9 particles per cu. cm. of glass wool. The total thickness of glass wool is about 0.3 cm. With the highest flow rate, 1.8 liter/min. used in vapor pressure measurements, a volume of the gas spends about 0.3 sec. under conditions where there are 10^8 to 10^9 particles per cu. cm.

Vapor pressures were measured by a dynamic or flow method. Prepurified nitrogen was passed through a trap in a Dry Ice-bath, a coil in liquid nitrogen for the measurements at lower temperatures, the tube containing the sulfur particles on glass wool in a water-bath at the temperature of the vapor pressure measurement, through three coils each composed of 150 cm. of glass tubing, in a Dry Ice-bath, a trap in a Dry Ice-bath, a wash bottle with a fritted disk, and a gas meter. The tube connecting the vessel containing the sulfur to the first coil in the Dry Ice-bath was heated electrically to prevent the condensation of sulfur before the coil in the Dry Ice-bath. The total pressure at the sulfur on glass wool was measured with a manometer connected to the system through a trap in a Dry Ice-bath in order to correct for the pressure drop through the system. An all-glass system was used.

A mercury-in-glass thermometer with scale divided to 0.1° from −1 to 101° was used in the vapor pressure measurements. It checked to within 0.07° at 100° and 0.04° at 25° with standards in This Laboratory.

The entire apparatus for vapor pressure determination was cleaned with acid–dichromate solution, rinsed and steamed after every three or four vapor pressure measurements. The coils for collecting the sulfur were cleaned in this way for every determination.

A thermometer was inserted into the tube with the sulfur on glass wool to see if the nitrogen was reaching thermal

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(1) Findlay, "The Phase Rule and Its Applications," 8th ed., Dover Publications, New York, N. Y., 1945, p. 49.

(2) R. Becker and W. Döring, *Ann. Physik*, **24**, 719 (1935).

(3) La Mer–Sinclair, OSRD Report No. 119, Div. B, N. D. R. C., (1941) and later reports, *Chemical Reviews*, **44**, 245 (1949) (see p. 262).

(4) Bacon and Fanelli, THIS JOURNAL, **65**, 639 (1943).

(5) Bacon and Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

equilibrium with the water-bath. Thermal equilibrium was reached within limits of error (0.02°) of temperature comparison at 40° for a flow rate about twice that used in any of the measurements.

The amount of sulfur, usually about 50 micrograms, collected in the first coil in the Dry Ice-bath was determined by its ultraviolet absorption at 275 mμ in 95% redistilled ethanol in 10-cm. silica cells using a Beckman Model DU spectrophotometer. The spectrum from 225 to 320 mμ was measured and compared with that for sulfur by superimposing a plot of the logarithm of optical density against wave length on a similar plot for sulfur. If the two plots did not agree within about 5% in terms of optical density or at longer wave lengths within the error of measurement of optical density, the run was rejected. The spectrum of the contents of the second coil was measured in the same way to see if condensation was complete. Typical results are shown in Fig. 1. The low absorption around 225 mμ shows an absence of sulfur, while the higher absorption at longer wave lengths shows the presence of an appreciable amount of an unidentified contaminant. This contamination could not be avoided even when great care was taken in cleaning the apparatus. This foreign substance presumably was in variable amounts in the first trap or in the spectrophotometer blank and presumably is the cause for the deviations of vapor pressures from the average. The silica cells were cleaned with a potassium nitrate in concentrated sulfuric acid solution, rinsed and dried in a vacuum desiccator before use.

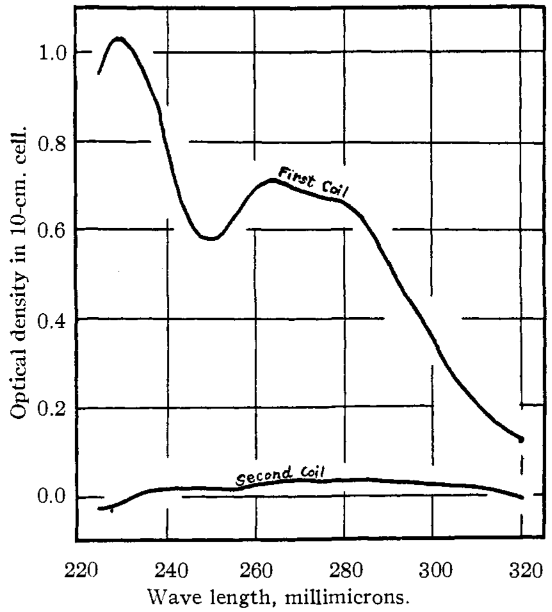

Fig. 1.—Typical absorption spectrum from first and second coils for collecting sulfur in the vapor pressure measurements.

Results

Vapor pressures of supercooled liquid droplets were measured between 25° and 74°. The results are collected in Table I. A line was fitted to values of log p against $1/T$ with an average deviation of 7% in vapor pressure units from the line (Fig. 2). The deviations were plotted against values of the variables which might affect the results. The variables are: time interval between preparation of the aerosol and the mid-time of vapor pressure measurement, boiler temperature, reheater temperature, and flow rate. No dependence on any of these variables was found in the examples reported as vapor pressures of supercooled liquid sulfur.

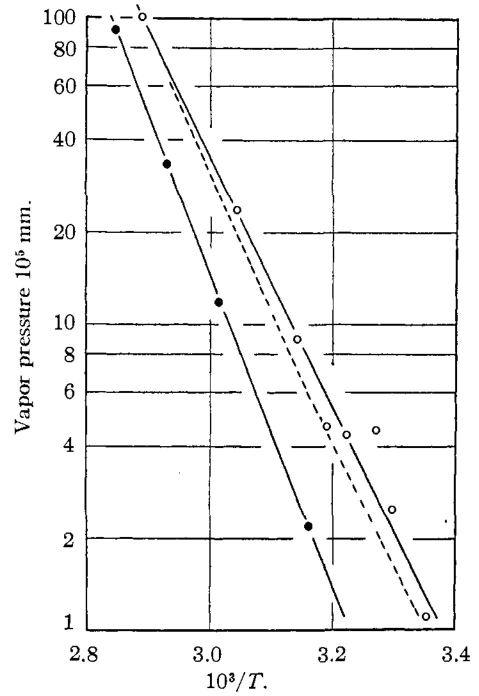

Fig. 2.—Logarithm of vapor pressure of sulfur as a function of reciprocal temperature: O, Ford and La Mer, supercooled liquid sulfur; ●, Fourtier, rhombic sulfur; ---- liquid Sλ, Lewis and Randall $\Delta G°$.

According to Kelvin the vapor pressure of small particles should increase exponentially with increase in the reciprocal of the radius. Four measurements of the vapor pressure as a function of particle radius at 25° show that this effect is within the present limits of experimental error for the size of particles used in this work. A plot of logarithm of vapor pressure against reciprocal of radius is given in Fig. 3.

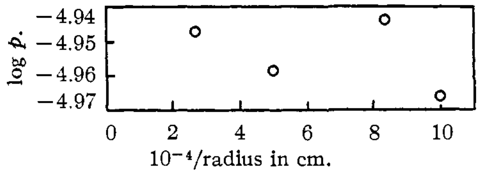

Fig. 3.—Dependence of logarithm of vapor pressure on reciprocal of particle radius at 25°.

At 25° the measured vapor pressure decreases with time as follows: one to three hours after preparation, 1.11×10^{-5} mm.; 1 day, 0.63×10^{-5} mm.; 6 days, 0.51×10^{-5} mm.; 20 days, 0.32×10^{-5} mm. After twenty days the measured vapor pressure does not change perceptibly for at least ten days. The vapor pressure twenty days after preparations is still about 60% larger than the vapor pressure of rhombic sulfur. This behavior indicates some allotropic modification of sulfur intermediate in stability between the liquid and rhombic forms. All of the values reported as vapor pressures of supercooled liquid sulfur were obtained by measurements made on the same day that the supercooled liquid particles were prepared. The decrease in the measured vapor pressure of such particles over a period of several days requires that our reported values be examined for time dependence. This was done by plotting (Fig. 4) deviations in $\log p$ from the best line through $\log p$ *vs.* $1/T$ against the time interval between the preparation of the particles and the time half way between the beginning and end of the vapor pressure measurement. If the values depend on the time, the dependence is negligible compared to other errors, such as contamination of the sulfur collected and determined.

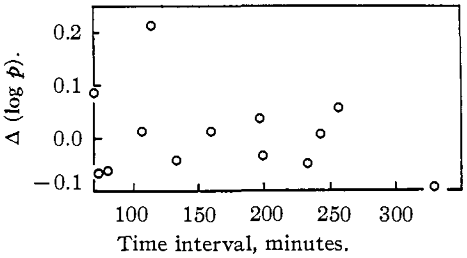

Fig. 4.—Dependence of deviations, from best line fitted to $\log p$ as a function of $1/T$, on time between preparation of particles and vapor pressure measurement.

Boiler temperature and reheater temperature might affect the measured vapor pressure by changing composition with respect to S_μ, the form which is insoluble in carbon bisulfide. If such an effect was present, it was too small to be detected. Deviations of $\log p$ from the best line of $\log p$ *vs.* $1/T$ are plotted against boiler temperature, Fig. 5, and reheater temperature, Fig. 6. The amount of S_μ at 120° is only 3.6% (8.5% at 150°)[6,7] and would be expected to decrease from this value at lower temperatures, since the liquid is a non-viscous mobile liquid. S_μ has a dark color, presumed to be due to sulfur chains. Large drops on a glass slide become lighter in color as they cool over a period of a few minutes and then do not change appreciably in color with time. If these large drops are cooled further to the temperature of Dry Ice their color becomes appreciably lighter but they regain the characteristic yellow color on warming to room temperature. Even though cooling to the temperature of Dry Ice freezes the drops, the fairly rapid attainment of equilibrium between S_μ and S_λ in the supercooled liquid is still indicated. These drops are soluble in carbon bisulfide.

As mentioned earlier, the gas spends at least 0.3 sec. under conditions where there are 10^8 to 10^9 particles per cu. cm. Under these conditions the gas will be saturated. This was confirmed by the lack of any dependence on flow rate of the deviation of $\log p$ from the best line fitted to $\log p$ *vs.* $1/T$ for flow rates between 0.29 and 1.8 liters per minute (see Fig. 7). Also a series of four measurements at 25° on particles that had changed state twenty days after preparation gave the same vapor pressure for flow rates between 0.98 and 2.3 liters per minute.

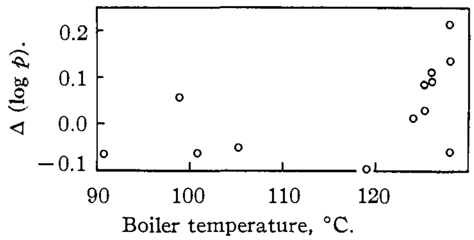

Fig. 5.—Dependence of deviations, from best to line fitted to $\log p$ as a function of $1/T$, on boiler temperature of aerosol generator.

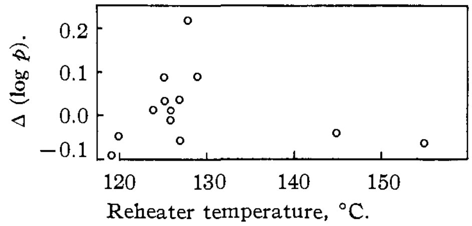

Fig. 6.—Dependence of deviations, from best line fitted to $\log p$ as a function of $1/T$, on reheater temperature of aerosol generator.

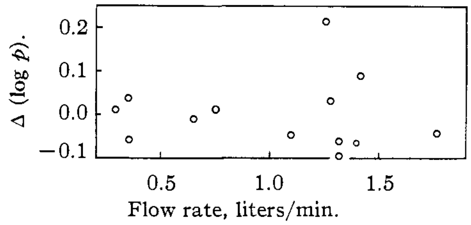

Fig. 7.—Dependence of deviations, from best line fitted to $\log p$ as a function of $1/T$, upon gas flow rate in the vapor pressure measurements.

The result of the vapor pressure measurements can be expressed by

$$\log p \text{ (mm.)} = -4055/T + 8.70$$

with an average deviation of 7% in vapor pressures, or

$$G = 5080 - 13.6\ T \text{ cal./mole}$$

for the Gibbs free energy of the liquid with respect to rhombic sulfur, based on Fourtier's[8] vapor pressure data for rhombic sulfur.

Lewis and Randall[9] (L. & R.) measured the heat evolved by cooling liquid sulfur to 23° in a calorimeter. Samples cooled from four different temperatures yielded three differences in en-

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[6] Smith and Holmes, THIS JOURNAL, **27**, 979 (1905).

[7] Hammick, Cousins and Langford, *J. Chem. Soc.*, 797 (1928).

[8] Fourtier, *Compt. rend.*, **218**, 194 (1944).

[9] Lewis and Randall, THIS JOURNAL, **33**, 476 (1911).

thalpy for liquid sulfur. They assumed a linear function of temperature for the specific heat of liquid S and calculated the constants in the equation

$$c = a + bt + q(\mathrm{d}x/\mathrm{d}t)$$

from the enthalpy differences. c is the specific heat of liquid sulfur at any temperature in cal. per g., a and b are the constants in the expression for the specific heat of liquid S_λ, x is the fraction of S_μ and q is the enthalpy increase of the reaction $S_\lambda \rightarrow S_\mu$, assumed to be constant on a weight basis, t is the temperature in °C. x was taken from the work of Alex. Smith and Holmes.[7] There are three constants in the equation and just sufficient data to determine them. L. and R. gave

$$c[S_\lambda(1)] = 0.21 + 0.0016t \text{ cal./g. °C.}$$

They then combine[10] this expression with the specific heat of S_{rh}, the transition temperature for $S_{rh} \rightleftarrows S_\lambda$, and the enthalpy increase of the reaction $S_\lambda \rightarrow S_{rh}$ at 100° to calculate an expression for the Gibbs free energy difference between liquid S_λ and S_{rh} at the same temperature. Their values for the free energy difference are compared in Table II with our values for the free energy difference between S_{rh} and supercooled liquid sulfur, which we consider to be essentially liquid S_λ. Vapor pressures of liquid S_λ calculated from L. & R.'s free energy difference expression and Fourtier's expression for the vapor pressure of S_{rh} are compared with our measurements in Table II. The agreement is better at higher temperatures as is expected since L. & R.'s free energy expression is based on an extrapolation of specific heat from above 100°.

TABLE II

T, °K.	Vapor pressure, 10^5 mm. Obs.	Vapor pressure, 10^5 mm. Calcd. L. & R. ΔG^0	ΔG^0, cal./g., atom S Ford, calcd. from v. p.	ΔG^0, cal./g., atom S L. & R. Obs.	ΔG^0, cal./g., atom S L. & R. Cor. for S_μ	ΔG^0, cal./g., atom S L. & R. ΔH P. & E. theory
298.2	1.11	0.97	128	93	94	88
319.4	8.97	7.15	94	74	73	71
347.1	102	104	45	45	43	45

Hammick, Cousins and Langford[7] (H. C. & L.), in a process similar to that of Alex. Smith, measured the percentage S in sulfur cooled from the liquid but more rapidly and in smaller drops than studied by Smith. They obtained higher values for per cent. S_μ than Smith when the sulfur was cooled from above 170° (Smith believed that some of the S_μ in the liquid was converted to S_λ in the cooling and hardening process.)

We have recalculated the free energy difference between liquid S_λ and S_{rh} using L. & R.'s assumptions and data except for per cent. S_μ. For per cent. S_μ we used values indicated by H., C. & L. The agreement with our results is little better than L. & R.'s calculation based on Smith's per cent. S_μ.

Powell and Eyring[11] (P. & E.) have developed a theory concerning the equilibrium between S_μ and S_λ. For the reaction

$$\frac{x}{8}\, S_8 \rightleftarrows S_x$$

P. & E. consider the enthalpy increase Δh to be a constant, independent of x, equal to 27.5 kcal. for N(= Avogodro's number) such reactions because the net effect of the reaction is to break one S–S bond no matter how many molecules of S_8 rings are involved. This is in contrast with L. & R.'s assumption, ΔH = const. for unit weight. P. & E. give a table of Z/Z_0 and φ as a function of temperature. Z is the number average chain length and Z_0 is the low temperature limit of Z. They choose $Z_0 = 27{,}000$ to account for the viscosity of liquid sulfur. φ is the weight fraction of S_μ in the liquid calculated from their theory. φ agrees well with the results of A. Smith and H., C. & L. up to the temperature where Smith and H., C. & L. disagree. Above this temperature φ is larger than either, as is expected.

P. & E.'s theory accounts for the viscosity data of Bacon and Fanelli[5] for pure liquid sulfur as well as sulfur containing small amounts of iodine.

From L. & R.'s enthalpy data combined with P. & E.'s fraction of S_μ, number average chain length, and enthalpy increase for the reaction $(x/8)\, S_8 \rightleftarrows S_x$ we calculate the free energy difference between S_{rh} and liquid S_λ, assuming as L. & R. did, that the specific heat of liquid S_λ is a linear function of temperature. Thus

$$\Delta H = \int_{T_1}^{T_2} (a + bT)\mathrm{d}T + y\Delta h$$

Here ΔH is the enthalpy change per gram of sulfur between absolute temperatures T_1 and T_2, a and b are constants. y is the number of moles of S_x obtained by dividing P. & E.'s φ by $32.06Z$. This procedure does not give an entirely correct value for y because all the molecules of S_x are not the same length. To get a correct value for y requires solving an integral equation.

Because of the high value of the number average chain length of S_x molecules $y\Delta h$ is negligible except at the highest temperature (390°) used by L. & R.

P. & E.'s theory and L. & R.'s enthalpy data lead to $c[S_\lambda(1)] = 0.233 + 4.29 \times 10^{-6}T$ cal./g. S °C. This specific heat of S_λ with Eastman and McGavock's specific heat of S_{rh} produce an expression for the free energy difference between liquid S_λ and S_{rh} (see Table II).

P. & E.'s theory permits one to test L. & R.'s enthalpy data for internal consistency, since there are now two constants to be determined and three given enthalpy differences. The integrated equation

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + y\Delta h$$

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[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 532.

[11] Powell and Eyring, THIS JOURNAL, **65**, 648 (1943).

fitted to L. & R.'s data in the form

$$\frac{\Delta H - y\Delta h}{T_2 - T_1} = a + \frac{b}{2}(T_2 + T_1)$$

yields the following results

$T_1 + T_2$	$\frac{\Delta H - y\Delta h}{T_2 - T_1}$ measured	$\frac{\Delta H - y\Delta h}{T_2 - T_1}$ calcd.	Deviation
786.4	0.250	0.238	−0.012
830.4	.251	.266	+ .015
1036.4	.255	.253	− .003

These deviations correspond to as much as 5% in the enthalpy differences which L. & R. considered to be reliable to within 0.5%. This situation may warrant further investigation.

The ΔH of evaporation for the supercooled liquid based upon our vapor pressure data is 18.1 kcal. per mole of S_8. For rhombic sulfur[12] the data of various observers yield the values: Fourtier[8] 23.6 kcal., Taillade[13] 24.0 kcal., Neuman[14] 24.0 kcal. Neuman's data indicate 23.2 kcal. for monoclinic sulfur.

The entropy of rhombic sulfur as determined by Eastman and McGavock,[15] Fourtier's vapor pressures of rhombic sulfur and our vapor pressures of the liquid gives for the entropy of the liquid $S^0_{298.1} = 76.0$ cal./deg. per mole of S_8.

Formation of Supercooled Liquid Sulfur.—Becker and Döring[2] have developed a theory which predicts the rate of nucleation in a supersaturated vapor to form a condensed phase. Their theory is in excellent agreement with the experimental results of Volmer and Flood.[16]

Volmer[17] has used Becker and Döring's theory to explain Ostwald's law of successive reactions for an hypothetical case. A lack of data on a suitable substance forced him to attribute the lower nucleation rate of the solid as compared with rate of the liquid to a non-spherical shape of the solid nucleus. It seems preferable to base sufficient conditions for the prediction of the formation of a supercooled liquid upon other information since we cannot be sure that a solid nucleus would not be approximately spherical.

Interfacial tension data by Gorskii[18] for liquid and solid sulfur, our vapor pressure measurements and Fanelli's[19] surface tension value for liquid sulfur, 64 dynes/cm. at 90°, are sufficient to predict that condensation of sulfur below the melting point produces liquid sulfur. Becker and Döring give as an approximate expression for the rate of nucleation J in nuclei per cubic centimeter per second

$$J = Z \exp(-A/kT) \qquad (1)$$

where Z is the number of collisions between molecules of the vapor per second per cubic centimeter. A is the work, primarily of surface formation, required to form the nucleus isothermally and reversibly in the interior of the vapor; k is Boltzman's constant and T is the absolute temperature. Volmer[18] (p. 97), following Gibbs, gives $A = 1/3\ \gamma\sigma$ where γ is the surface tension of the condensed phase and σ is its surface area. The nucleus is defined as a mass of the condensed phase just large enough that surface effects are not sufficient to make its chemical potential (or vapor pressure) larger than the chemical potential in the vapor phase. The radius of curvature, r, of a nucleus is then given by Kelvin's equation

$$p = p_\infty \exp(-2\gamma M/rdRT) \qquad (2)$$

where p is the partial pressure of the vapor; p_∞ is the vapor pressure of the bulk liquid at absolute temperature T; M is the molecular weight; R is the gas constant and d is the density.

The situation in the aerosol generator is not quite the same as that for which Becker and Döring developed their theory for self-nucleation since foreign nuclei are introduced. The effect of foreign nuclei is to lower the value of A. This lowering of the work required to form a stable nucleus could come about by either of two mechanisms: (1) the foreign nucleus provides something on which the sulfur can condense in such a way that a smaller mass of sulfur is required to attain a radius large enough for the nucleus to be stable. With less sulfur required to form a stable nucleus less work is required. (2) In the region of supersaturation too low for appreciable spontaneous nucleation abortive nuclei too small to be stable are being continually produced and re-evaporated.[20] Some of these otherwise abortive nuclei could collide with foreign nuclei, thereby increasing their radius of curvature. With a smaller mass of sulfur required to attain a radius of curvature large enough for stability less work is required. For qualitative purposes, it is immaterial which of these two possibilities actually occurs.

We wish to compare the rate, J_1, of formation of liquid nuclei, to the rate, J_s, of formation of solid nuclei in the condensation of the vapor. From equation (1)

$$\frac{J_1}{J_s} = \exp\frac{(-A_1 + A_s)}{kT} \qquad (3)$$

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[12] The most recent measurements of the vapor pressure of rhombic sulfur are those of Fourtier[8] and Taillade.[13] The former measured the pressure of the vapor directly with a torsion balance; the latter used a flow method. Their expressions, namely $\log p = 11.669 - 5166$ (Fouretier) and $\log p = 11.984 - 5267/T$ (Taillade) agree within 6% in terms of vapor pressure between 25 and 74°. Neuman[14] measured the vapor pressure of rhombic sulfur by a recoil torsion balance method. His expression, $\log p = 11.866 - 5267/T$ gives vapor pressures uniformly 31% lower than Taillade's expression and from 24% (at 74°) to 38% (at 25°) lower than Fourtier's expression. Earlier measurements by Gruener (THIS JOURNAL, **29**, 1396 (1907)) and by Ruff and Graff (*Ber.*, **40**, 4199 (1907), and *Z. anorg. Chem.*, **58**, 209 (1908)) do not agree with either Fourtier and Taillade or Neuman.

(13) Taillade, *Compt. rend.*, **218**, 836 (1944).

(14) Neuman, *Z. physik. chem.*, **A171**, 416 (1934).

(15) Eastman and McGavock. THIS JOURNAL, **59**, 145 (1937).

(16) Volmer and Flood, *Z. physik Chem.*, **A170**, 273 (1934).

(17) Volmer, "Kinetic der Phasenbildung," Steinkopf, Dresden, 1938, and Edwards Bros., Ann Arbor, Mich., 1945, p. 200.

(18) Gorskii, *Journal of Experimental and Theoretical Physics, USSR*, **18**, 45 (1948); also *C. A.*, **42**, 8564 (1948).

(19) Private communication from R. Fanelli.

(20) Frenkel, "Kinetic Theory of Liquids," Oxford Press, New York, N. Y., 1946, p. 385.

where A_l and A_s are the works required to form a stable nucleus when foreign nuclei are provided. Although the coefficient of the exponential in equation (1) may be different for foreign nuclei, it is sufficient for our purpose for the coefficient for the formation of solid nuclei to be not larger than the coefficient for the formation of liquid nuclei. Since the crystal structure of the foreign nuclei (NaCl) is not similar to the crystal structure of sulfur, there is no reason for the coefficient for solid nuclei to be larger than for liquid. For convenience we have taken the coefficients to be equal

$$A = \frac{1}{3}\gamma_l\sigma_l - B_l \qquad (4)$$

$$A_s = \frac{1}{3}\gamma_s\sigma_s - B_s \qquad (5)$$

B_s and B_l are the amounts by which the required works are reduced by the presence of foreign nuclei. For mechanism 2, $B_s = 0$ since a solid cannot arrange itself around the foreign nucleus, while $B_l > 0$. For mechanism 1 it is difficult to see why B_s should be greater than B_l since the only way in which this could happen is for a greater attraction to exist between the foreign nucleus and sulfur molecules in solid sulfur than for sulfur molecules in liquid sulfur. Since the molecules are the same it seems likely that such is not the case. For either mechanism then

$$A_s - A_l \geqslant 1/3\ (\gamma_s\sigma_s - \gamma_l\sigma_l) \qquad (6)$$

Reiss and Wilson[21] have shown that Young's equation

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \qquad (7)$$

holds for a liquid and its melt even though $\theta = 0$. Gorskii[20] reports 3.84 ergs/sq. cm. for the interfacial tension of solid and liquid sulfur obtained by means of studies of nucleation in the supercooled liquid. Under these conditions $\theta = 0$. Therefore

$$\gamma_{sv} - \gamma_{lv} = \gamma_s - \gamma_l = 3.84 \text{ ergs/sq. cm.} \qquad (8)$$

For the solid nucleus to be in equilibrium with the vapor at the same pressure as the liquid nucleus the chemical potential must be the same in both nuclei. Let μ_l and $\mu_{l\infty}$ be the chemical potentials in the liquid nucleus and the bulk liquid, respectively, and μ_s and $\mu_{s\infty}$, the chemical potentials in the solid nucleus and the bulk solid, respectively. We wish to show that the solid nucleus must be larger than the liquid nucleus. For this purpose we will apply Kelvin's equation and assume that the solid nucleus is spherical. If it is not spherical its surface area will be even larger and make the ratio of nucleation rates even more favorable for the production of liquid sulfur.

From Becker and Döring's[2] theory we have calculated the metastable limit for the condensation of sulfur vapor to liquid sulfur at 90°. The calculation gives $p/p_\infty = 293$ and a radius of 9.6×10^{-8} cm. A nucleus of this size consists of about 16 molecules of S_8 if the density is the same as the bulk liquid. However, it is under a pressure of 1300 atm. by Kelvin's equation and, therefore, may have more molecules in it. From Kelvin's equation

$$\mu_l - \mu_{l\infty} = \frac{2\gamma_l M}{r_l d} \qquad (9)$$

$$\mu_s - \mu_{s\infty} = \frac{2\gamma_s M}{r_s d} \qquad (10)$$

Since $\mu_l = \mu_s$

$$\frac{2\gamma_l M}{r_l d} + \mu_{l\infty} - \mu_{s\infty} = \frac{2\gamma_s M}{r_s d} \qquad (11)$$

From our measurements of the vapor pressure of supercooled liquid sulfur and Fourtier's[8] vapor pressure data for rhombic sulfur

$$\mu_{l\infty} - \mu_{s\infty} = 5.86 \times 10^9 \text{ ergs/mole } S_8$$

Substituting this in equation (11) we obtain

$$r_s = 9.81 \times 10^{-8} \text{ cm.}$$

From equations (3) and (6) we have

$$\frac{J_l}{J_s} \geqslant \exp\left(\frac{1}{3kT}\left[\gamma_s\sigma_s - \gamma_l\sigma_l\right)\right]$$

$$J_l/J_s \geqslant 2.7 \times 10^2$$

Thus at least 200 liquid aerosol particles should be formed for every solid particle. No solid particles have been observed.

A calculation similar to the above indicates that at 80° $J_l/J_s \geqslant 10$.

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Conclusions

We have established that sulfur vapor condenses as a liquid aerosol even below its melting point in the La Mer–Sinclair aerosol generator.

The vapor pressure of supercooled liquid sulfur droplets was measured between 25 and 74°, permitting the calculation of the enthalpy of evaporation, Gibbs free energy with respect to rhombic sulfur, and the entropy of the liquid.

Supercooled liquid sulfur as made above is predominately S_λ, and is not a glass.

Ostwald's law of successive reactions for the condensation of sulfur vapor is explained in terms of Becker and Döring's theory of rate of nucleation in supersaturated vapors.

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[21] H. Reiss and I. Wilson, *Journal of Colloid Science*, **3**, 552 (1948).