On the Mechanism of Evaporation in Vacuum. II. Vapor Pressure and Evaporation Velocity.(1)

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It is suggested in the preceding paper(2) that the estimation of vapor pressure is valuable when discussig the evaporation of various substances. The phase diagram of one component system is composed, in the simplest case, of three curves, that is sublimation, evaporation and fusion curves. These curves are described by Clapeyron-Clausius' equation:

$$\mathrm{d}\ln p/\mathrm{d}T = L/RT^2 \qquad (1)$$

where p is pressure, T is absolute temperature, L is the latent heat of the phase transition, and R is the gas constant. This is integrated after expanding the latent heat L in power series, according to Nernst, and obtained,

$$\log p(\mathrm{mm.}) = 2.88 - L_0/4.59\,T + 1.75 \log T - \mathcal{E}T/4.59 + \kappa \qquad (2)$$

where p (mm.) is the pressure expressed in mm. Hg., $\mathcal{E}$ is a parameter determined from some experimental data, and κ is the conventional chemical constant. The latter is calculated for monoatomic gases by the following equation:

$$\kappa = -1.587 + 1.5 \log M \qquad (3)$$

where M is the molecular weight. All three curves in the phase diagram cross at one point, named a triple point. At this point, in general, the heat of sublimation and the heat of evaporation are not equal, while the relationship:

$$L_{sub.} = L_{fus.} + L_{evap.} \qquad (4)$$

is obtained thermodynamically(3). As for many metals, it is seen that,

$$L_{fus.}/L_{sub.} \simeq 0.015 \sim 0.058 \qquad (5)$$

The following approximation is, therefore, used:

$$L_{sub.} \simeq L_{evap.} \qquad (6)$$

Under this approximation sublimation and evaporation curves are described by one curve. Moreover, the melting point curve is often approximated by a straight line parallel to the pressure axis. Then, a simplified phase diagram is drawn for every metal, using the data tabulated in Table 1. For various metals, atomic weight M, and boiling point T_b inserted in the "Rika-Nenpyo"(4), and the heat of sublimation at absolute zero temperature L_0 by Slater(5) are cited in the Table. Among the data of L_0, those marked with $*$ are values at room temperature by Seitz(6). The difference of the latent heat at absolute zero and room temperature is, in general, negligible, since it is less than 1 kcal./mole for these metals. The value of conventional chemical constant obtained from equation (3) is cited in the fifth column. The parameter $\mathcal{E}$ is calculated by equation (2), using the fact that the temperature corresponding to the pressure $p=760$ mm. Hg is the boiling point T_b; and cited on the sixth column. Then, the vapor pressure curve is drawn, using Eq. (2) and values L_0, $\mathcal{E}$, and κ, cited above. By the assumption that the temperature for the triple point is nearly equal to the melting point T_m, given in "Rika-Nenpyo"(4) and Slater's book(5), the pressure for the triple point p_t, is obtained. These are cited in the seventh and eighth column. Phase diagrams are depicted in Fig. 1 for various metals. They approximately coincide with curves by Law(7), excepting Be, Al, Cr and Fe. The disagreements will be studied later.

Yarwood(8) recorded the temperature of vacuum evaporation T_e. These values are cited in the tenth column of Table 1. The pressure in the vessel was 10^{-5} mm. Hg. The plots of these temperature data on the vapor

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(1) These results were presented befor the Meeting of Colloid Chemistry held by the Chemical Society of Japan at Osaka, November, 1950.

(2) M. Nakagaki, This Bulletin, **24**, 206 (1951).

(3) J. C. Slater, "Introduction to Chemical Physics", New York, 1939, p. 172.

(4) Edited by the Tokyo Astronomical Observatory, "Rika-Nenpyo", 1950, Tokyo.

(5) J. C. Slater, *loc. cit*, pp. 259 and 454.

(6) F. Seitz, "The Modern Theory of Soild", New York, 1940, p. 3 and 61.

(7) R. R. Law, *Rev. Sci. Instr.*, **19**, 920 (1948).

(8) J. Yarwood, "High Vacuum Technique," London, 1948, pp. 84~90.

Table 1

Substances	Atomic or molecular wt. M	Boiling point T_b, °C.	Latent heat L_0 (kcal./mole)	Parameters in Eq. (2)		Triple point		Vacuum evaporation temp. T_e, °C.	
				κ	ε, cal./deg.^{2}	T_m, °C.	$\log p_t$, mm. Hg	Calcd.	Obsd.
Cs	132.91	670	18.7	1.599	0.0121	28.5	−7.26	200	433
Rb	85.48	700	20.6	1.311	0.0091	38.	−8.06	250	450
Cd	112.41	764	27.0	1.487	0.00487	320.9	−1.78	400	541
Zn	65.38	907	31.4	1.136	0.00288	419.5	−1.69	500	623
Mg	24.32	1110	36.6	0.491	0.00070	651.	−0.48	650	712
Li	6.94	1340	36.0	−0.325	0.00120	186.	−10.70	700	821
Sr	87.63	1150	47.0*	1.327	−0.00113	800.	0.02	700	811
Ca	40.08	1170	47.8*	0.818	−0.00280	810.	−0.15	750	878
Bi	209.00	1450	47.8	1.893	0.00405	271.	−11.00	750	913
Pb	207.21	1620	46.7	1.887	0.00547	327.3	−8.50	800	1000
Sb	121.76	1380	54.4	1.543	0.00000	630.5	−3.79	850	973
Be	9.02	(1500)	75.0*	−0.154	−0.0095	1350.	1.6	1150	—
Al	39.94	1800	67.6	0.815	−0.0011	659.	−6.7	1150	1461
Ag	107.88	1950	69.4	1.463	0.00107	960.5	−2.98	1200	1319
Sn	118.70	2260	68.0	1.526	0.00296	231.9	−21.09	1250	1148
Cu	63.54	2360	81.7	1.117	0.00061	1083.	−3.99	1450	1542
Cr	52.01	2200	89.4	0.987	−0.0018	1580.	−0.2	1500	1190
Si	28.06	2600	85.0*	0.585	0.00028	1420.	−1.94	1550	—
Au	197.2	2680	90.7	1.855	0.0016	1063.	−5.0	1600	1445
Ni	58.69	2900	98.1	1.066	0.00067	1454.	−3.12	1800	1717
Fe	55.85	3200	96.5	1.034	0.00155	1530.	−2.77	1850	1694
Pt	195.23	4300	125.	1.848	0.00231	1765.	−3.98	2400	2332
Mo	95.95	3700	156.	1.386	−0.00100	2620.	−0.87	2600	2755
C	12.01	(4000)	170.*	0.032	−0.0025	3600.	1.7	2900	—
Wo	183.92	5900	210.*	1.810	0.00076	3400.	−2.2	3800	3505
SiO_2(A)	60.06	2590	190.8	1.319	−0.01145	1710.	−6.0	2200	—
SiO_2(B)	60.06	—	95.4	1.319	−0.01145	—	—	1200	—
SiO_2(C)	60.06	—	127.2	1.319	−0.01145	—	—	1550	—

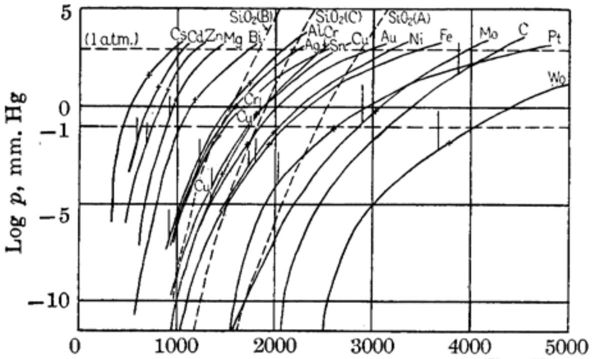

Fig. 1.—Phase diagrams of metals.

pressure curves in Fig. 1 (marked with +) show, however, that these temperatures correspond roughly to 10^{-1} mm. Hg of pressure, though the pressure is somewhat higher than 10^{-1} mm. Hg for volatile metals owing to the "over-heating". According to this fact, it is concluded that the vapor pressure near the specimen (10^{-1} mm. Hg) is usually not equal to the pressure in the vessel distant from the specimen (10^{-5} mm. Hg). This circumstance will be discussed later in detail. Temperature corresponding to the vapor pressure 10^{-1} mm. Hg is obtained from vapor pressure curve in Fig. 1, and cited on the ninth column as calculated values of vacuum evaporation temperature T_e. These agree well with values by Yarwood, excepting Al, Cr and Wo. It is commonly accepted that aluminum evaporates more easily than silver or chromium. This fact coincides with the calculated evaporation temperature, while Yarwood's values show that aluminum evaporates at higher temperature than silver or chromium. Some questions remained concerning this point. Data on silica, discussed in the preceding paper⁽²⁾, are also cited in Table 1 and Fig. 1. From the Table and Fig., it is seen that quartz, SiO_2(A), evaporates at 2200°C. or with as great difficulty as platinum, while idealized silica gel, SiO_2(B), evaporates at 1200°C., or as easily as silver. The vacuum evaporation temperature of actual silica gel, $SiO_2(C)$, is estimated to be 1550°C., which is nearly equal to that of chromium or gold, and also coincides with experience.

Although the technique of vacuum evaporation is frequently used in electron microscopy, little has been discussed from the physicochemical point of view, so that even an approximate estimation will bring forth some contributions. To evaluate the rate of evaporation, the following assumptions are made. The molecules of an evaporating specimen fly away straightly in every direction with the mean square velocity:

$$\bar{v}=\sqrt{3RT/M}=15800\sqrt{T/M} \quad \text{(cm./sec.)}. \qquad (7)$$

At a point, apart enough from the specimen, collisions between specimen molecules are, therefore, negligible, as long as collisions between specimen molecules and air molecules are negligeile. This latter is easily verified as follows. Let the number of collisions with air molecules done by one specimen molecule in unit time be Z, then,

$$Z=\pi\left(\frac{\sigma+\sigma_a}{2}\right)^2\cdot\sqrt{\bar{v}^2+\bar{v}_a{}^2}\cdot n_a, \qquad (8)$$

where σ and σ_a are collision diameters of specimen and air molecule, respectively, and both are considered to be nearly equal to 3 Å. $\bar{v}$ and $\bar{v}_a$ are mean square velocities of specimen and air molecules, the values of which are obtained by the insertion of each value of temperatures and molecular weights into Eq. (7). n_a is the number of air molecules in unit volume and is expressed with the pressure p_a (mm. Hg) in the vessel by the equation:

$$n_a=p_a/k\,T_a. \qquad (9)$$

The mean free path of specimen molecule in this air, λ, is given by

$$\lambda=\bar{v}/Z. \qquad (10)$$

Since silica gel, as an example, evaporates at $T_e=1830$°K., and its molecular weight is $M_0=60$, the mean free path in air, where $T_a=293$°K. and $M_a=28.8$ are calculated by

$$\lambda=0.96\times10^{-2}/p_a \qquad (11)$$

If $p_a=10^{-4}$ or 10^{-5} mm. Hg, then $\lambda=96$ or 960 cm., respectively. Under the usual experimental conditions, therefore, the probability of collision between specimen molecule and the air is safely omitted.

The number of specimen molecules in unit volume, n, placed at a distance r from the specimen is to be calculated as follows. Imagine a spherical shell of radius r, thickness $\mathrm{d}r$, and volume $4\pi r^2\mathrm{d}r$. Then the time required to pass through this shell by a molecule of velocity $\bar{v}$ is $(\mathrm{d}r/\bar{v})$. The number of molecules evaporated in unit time is $-(N_A/M)\times(\mathrm{d}w/\mathrm{d}t)$, where w is the weight of specimen (g.), and N_A is Avogadro's number, so the number of specimen molecules in the shell is $-(N_A/M)(\mathrm{d}w/\mathrm{d}t)\times(\mathrm{d}r/\bar{v})$. Therefore,

$$n=-(N_A/M)\times(\mathrm{d}w/\mathrm{d}t)/(4\pi r^2\bar{v}). \qquad (12)$$

Let the temperature of a specimen be T_0 and the vapor pressure corresponding to it be p_0. The density of this vapor, n_0, is

$$n_0=p_0/k\,T_0. \qquad (13)$$

The specimen is surrounded by the layer of such vapor, but the thickness of the atmosphere is assumed to be very slight. Then, in Eq. (12), $n=n_0$ if $r=r_0$ = the radius of the specimen itself. The rate of evaporation becomes, therefore,

$$-\mathrm{d}w/\mathrm{d}t=4\pi r_0{}^2\bar{v}n_0(M/N_A). \qquad (14)$$

From Eqs. (12) and (14),

$$n=n_0(r_0/r)^2. \qquad (15)$$

That is to say, the vapor density n at a place distant as r from the specimen is greater when n_0 is greater, r is less, or r_0 is greater. n_0 becomes great when the temperature of specimen is high, since, in Eq. (13), p_0 increases exponentially when T_0 increases. If r_0 is great, the area of evaporation and the vapor density n are great.

When a shadow is cast using some metal as a specimen for electron microscopy, it is generally accepted that the shadow becomes diffuse if the pressure of air in the vessel is not low enough. Let us consider a unit area, of the distance l from the evaporating specimen, and of the angle of inclination θ to the direction of flying of a specimen molecule. Since the mean kinetic energy of a gas molecule is $(3/2)kT$, the sum of kinetic energy of a specimen molecule hitting this unit area per unit time, K_0, is

$$K_0=(3/2)kT_0n\bar{v}\sin\theta \qquad (16)$$

where Eq. (15) is used for n, with $r=l$. While the sum of kinetic energy of air molecule hitting this area, K_a, is

$$K_a=(3/2)k\,T_a\,n_a(RT_a/2\pi M_a)^{1/2}. \qquad (17)$$

It may be assumed that a shadow is clearly cast if $K_0 > K_a$, while the shadow becomes diffuse by the disturbance of air if $K_0 < K_a$. The value of l corresponding to $K_0 \simeq K_a$ is written as l_e:

$$l_e \simeq \left(6\pi \frac{T_0 M_a}{M_0 T_a}\right)^{1/4} (\sin\theta)^{1/2} r_0 (p_0/p_a)^{1/2}. \qquad (18)$$

If the distance between the evaporating specimen and the area, where the shadow is to be cast, l is smaller than l_e, then a clear shadow will be obtained, and if l is greater than l_e, a diffuse shadow will be obtained. Let us assume, following ordinary experimental conditions, that $T_a = 293°\text{K.}$, $M_a = 28.8$, $\sin\theta = 1/5$, $r_0 \simeq 10^{-1}$ cm., and $p_0 \simeq 10^{-1}$ mm. Hg. The calculated value of l_e is cited in Table 2 for some metals. It is seen that the value of l_e is about 1 cm. when the pressure of air in the vessel p_a equals 10^{-3} mm. Hg, and l_e is about 10 or 14 cm. for $p_a = 10^{-5}$ mm. Hg. In ordinary conditions, that is l is 6 cm. or so, a clear shadow will be obtained if the vacuum in the vessel is more than 10^{-4} mm. Hg, while the shadow will be disturbed if the vacuum is less than 10^{-4} mm. Hg. According to Eq. (18), it is understood that a clear shadow is easily obtained, if p_a is small by a sufficient preliminary evacuation, if p_0 is great by the high temperature of evaporating specimen, and if angle θ is not too small. These conclusions coincide with common experiences.

The rate of evaporation of a specimen has been given by Eq. (14). This is integrated with the equation:

$$(4/3)\pi r_0^3 \rho = w \qquad (19)$$

and the time τ (sec.) required to evaporate w_0(g.) of the specimen completely is obtained as

$$\tau = \left(\frac{3\rho^2}{4\pi}\right)^{1/3} \left(\frac{RT_0}{M\bar{v}p_0}\right) w_0^{1/3} \qquad (20)$$

where ρ is the density of the specimen. In the case of silica gel, it is assumed that $\rho = 2.2$, $M = 60$, $T_0 = 1830°\text{K.}$, $\bar{v} = 8.73 \times 10^4$ cm./sec. and $p_0 = 10^{-1}$ mm. Hg, and

$$\text{for} \quad w_0 = 5 \text{ mg.}, \qquad \tau = 39 \text{ sec.} \qquad (21)$$

is obtained. This agrees well with the experimental data cited in the preceding paper(2), that is 4∼8 mg. of silica gel requires 20∼40 sec. for evaporation.

Table 2

Metals	M_0	T_0, °K.	l_e, cm. $p_a = 10^{-3}$ mm. Hg.	 10^{-4} mm. Hg.	 10^{-5} mm. Hg.
Al	27	1410	1.4	4.4	14
Ag	108	1440	1.0	3.2	10
Cr	52	1740	1.3	4.1	13
Au	197	1860	0.9	2.7	9
Ni	59	2040	1.3	4.4	13

Concerning the Eq. (20), two facts should be emphasized. The one is that the temperature of evaporation in a vacuum is defined as the temperature corresponding to the vapor pressure $p_0 = 10^{-1}$ mm. Hg. This is only a conventional definition and has no theoretical meaning. The time required to evaporate 5 mg. of silica gel is calculated for various temperatures and depicted on Fig. 2. As easily seen from this Figure, time τ increases enormously if the temperature is somewhat lowered from the evaporation temperature $T_e = 1830°$K. It is, therefore, concluded that the definition of T_e is significant practically. The second is that the rate of evaporation is mainly affected by the temperature of the evaporating specimen T_0, since the pressure p_0 is only dependent on T_0 for a given substance. The pressure of air in the vessel p_a, as far as $p_a < p_0$, is of least importance for evaporation velocity, although the distinctness of the shadow cast is largely affected by p_a.

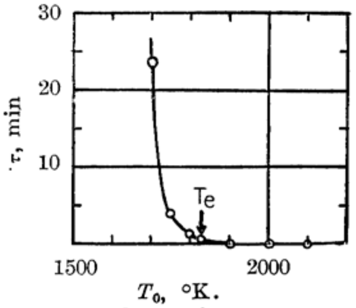

Fig. 2.—Dependence of τ on temperature.

The temperatures of tungsten filament and silica gel are directly measured by an optical pyrometer under the ordinary experimental condition of evaporation. The temperature obtained by the optical pyrometer is "brightness temperature" or "black body temperature". The emissivity of the substance should be known to recalculate the black body temperature to actual temperature(9). As for tungsten, the data necessary to this correction are given for 0.665 μ of wave length of light(10). As for silica gel, no data are given on its

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(9) Edited by American Institute of Physics, "Temperature; Its Measurement and Control in Science and Industry," 1941, p. 1129.

(10) International Critical Tables, Volume V, pp. 243 and 245.

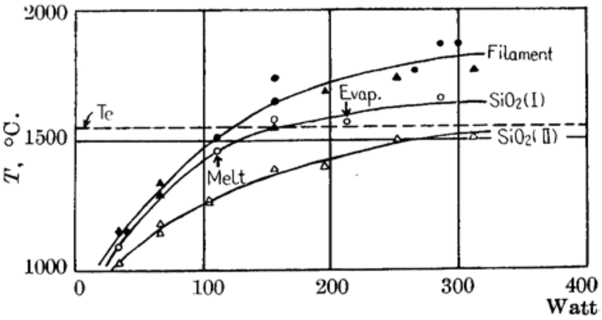

Fig. 3.—Temperature of filament and specimen.

emissivity. For a convention, the calibration curve for tungsten is also used for silica gel. The relation between electric power (watt) used and temperature observed are depicted in Fig. 3. The apparatus for evaporation and tungsten filament used are the same as reported in the preceding paper(2). The relation between the temperature of tungsten filament and electric power used varies with the length of tungsten wire and the manner of its coiling. The data cited are examples. Five mg. of silica gel are used. When a piece of silica gel is placed in the bottom of a tungsten basket, it melts at about 1450°C. and evaporates at 1600°C., as shown in the Fig. 3 as SiO_2(I). This agrees with the estimated evaporation temperature cited in Table 1. While the piece is placed on the upper part of the basket, it cannot be made to evaporate by less than 300 watts heating as shown as SiO_2(II). This fact should be remembered when an evaporation experiment is done.

Whether the substance evaporates after fusion or sublimates without fusion may have some significance in the rate of evaporation, since the melted substance adheres to the filament, and high temperature will readily be obtained. For example, the evaporation of silver is far easier than that of chromium. The main reason for this will be that the evaporation temperature shown in Table 1 of silver is even 300°C. lower than that of chromium. However, there may also be another reason that silver evaporates after fusion while chromium sublimates without fusion.

Summary

Phase diagrams are drawn for many metals under some approximations, and "vacuum evaporation temperature" is estimated as the temperature corresponding to 10^{-1} mm.Hg of vapor pressure. This temperature agrees well with that given by Yarwood. The rate of evaporation is calculated, and the result agrees well with experience, at least, for silica gel. As for shadow casting, it is concluded that high temperature of specimen and low pressure of air in the vessel are the necessary conditions to obtain clear shadow. The temperature of evaporating silica gel is measured with optical pyrometer, and a satisfactory result is obtained.

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