the quantitative determination of organic cyanides. Benzyl cyanide was converted very largely into sodium cyanide, but in the experiments with methyl cyanide this reaction was greatly decreased. In the latter case the chief product of the reaction seemed to be ethyl amine, resulting from the reduction of the methyl cyanide presumably, according to the following equation,

$$CH_3CN + 4NH_3 + 4Na = C_2H_5NH_2 + 4NaNH_2.$$

The behavior of alkyl halides and other substances with liquid ammonia alone and also in the presence of sodium, is being studied and further results will be published later.

Summary.

1. It has been shown that the reaction between liquid ammonia, sodium and organic compounds, leads to the formation of cyanides only in a few special cases whose nature has been discussed.

2. A list of quantitative determinations of halogen in various classes of organic compounds has been given which will supplement those formerly published by us and by Chablay.

3. Application of this method to the quantitative determination of cyanides in organic compounds met with no success.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM THE PHYSICS LABORATORY, STATE UNIVERSITY OF IOWA.]

THE VAPOR PRESSURE CURVES OF SOLID AND LIQUID SELENIUM NEAR THE MELTING POINT.

BY L. E. DODD.

Object and Scope.

The object of this investigation has been to determine by the method of molecular flow the saturated vapor pressure of selenium in the vicinity of the melting point. This required the determination of both the sublimation curve of the crystalline solid and the vaporization curve of the liquid. Further, the aim has been to find from these data values for some of the physical constants of selenium near its melting point.

Molecular Flow of Gases and Knudsen's Equations.

Knudsen's[1] equations for resistance to molecular flow of gases are, for an aperture in a thin partition,

$$W_1 = \sqrt{2\pi}/A_1 \qquad (1)$$

and for a tube

$$W_2 = {}^3/_8\sqrt{\pi/2}\int^L O/A_2^2\, dl \qquad (2)$$

where l is length of tube, O is circumference, and A_2 cross-sectional area, which may be variable.

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[1] Knudsen, *Ann. Physik.*, 28, 75, 999 (1909).

For a combination of a thin partition with an aperture placed across a tube, and the tube, the total resistance is $W = W_1 + W_2$. If there is a steady flow of gas through this combination, such that the pressure where the gas enters the tube is p_2 and the pressure where it issues is p_1, the quantity flowing through in time t is given by

$$G = 1/W \,.\, (p_2 - p_1) \sqrt{\rho_1}\, t, \tag{3}$$

where G is weight of gas in grams, and ρ_1 the density at unit pressure and at the temperature of the apparatus. All quantities are in absolute units. ρ_1 can be obtained from the known density of the gas at unit pressure and 0°,

$$\rho_1 = (\rho_1)_0/(1 + at), \tag{4}$$

where a is the expansion coefficient and t the temperature. Knudsen verified (1), (2) and (3) experimentally with the gases hydrogen, oxygen and carbon dioxide.

Application of the Method of Molecular Flow to the Measurement of Saturated Vapor Pressures.

Knudsen[1] used the method of molecular flow to measure the vapor pressure of mercury at lower temperatures than are possible by other methods. For calculation of ρ_1 in this case he employed (4), which is applicable to any substance in the vapor state if the number of atoms per vapor molecule is known, since

$$(\rho_1)_0 = (1409.2 \times 10^{-12})/(2 \times 16)nA, \tag{4a}$$

where the number in the enumerator is the density of oxygen at unit pressure and 0°, n an integer expressing the number of atoms per molecule, and A the atomic weight. He made 2 standard determinations of mercury vapor pressure at 0° and 7°, respectively The vapor was condensed at the temperature of solid carbon dioxide, so that p_1 was negligible. For the other temperatures the vapor was condensed at 0°, and the standard value already found was used in this case for p_1.

Following up this application of the method Egerton,[2] at the suggestion of Nernst, applied it to determine the vapor pressure of metallic zinc and cadmium. To save time in these pressure measurements, Egerton decreased W in (1) by using, instead of one, several circular apertures in parallel in the same thin partition. He showed that the total resistance of a partition varies inversely as the number of apertures. Egerton used as many as 17 apertures in parallel with good results.

The present work was a continuation of some preliminary experiments by F. C. Brown, applying this method to selenium. As far as known to the present writer, this is the first application of the method to a substance with other than a monatomic vapor at the temperatures of the ex-

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[1] Knudsen, *Ann. Physik*, **29**, 179 (1909).

[2] Egerton, *Phil. Mag.*, 33, 33 (1917).

periment. The preliminary results were spoiled by the lack of a high enough vacuum and by an important temperature difference inside and outside the vapor tube. In the present investigation selenium crystals of large size, as first produced by Brown[1] and furnished by him for this work, were used for the element in the solid state.

Apparatus.

The Egerton type of apparatus, which with some changes was used here, was a modification of that of Knudsen. Fig. 1 is a longitudinal section of the type of vapor tube employed for selenium. It consists of a glass tube set into a larger one by a ground joint. The whole apparatus may be called simply the "tube," made up of an "inside tube" and an "outside tube." The latter has near the top an arm through which the air is pumped out. A lower chamber is separated from the remaining space in this tube by a thin perforated partition of platinum. The substance being studied is placed below the partition and kept at a constant temperature in a suitable oven. The inner, or "condensation," tube is fitted with a stopper through which pass 2 narrower glass tubes, one acting as a nozzle for the inflow of a cooling fluid, such as water, the other for its outflow. The vapor molecules pass up through the partition to the inside tube, where they are condensed as a solid deposit.

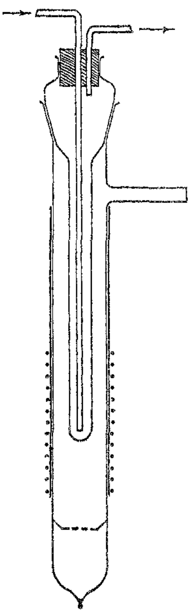

Fig. 1.

The vapor tube was inserted into a Freas oven through a hole drilled in the top, so that the tube projected into the oven space and was supported in place by its arm. The drilled hole was lined by a brass tube fitting it closely and providing a thermally conducting envelope. The platinum partition in the vapor tube extended one cm. or more below the roof of the oven chamber. Around the brass tube over this distance, the wire of an auxiliary heater was wound, to prevent condensation on the outside tube by maintaining a fairly uniform temperature up to the zone of deposit. Through the brass tube next to the ceiling of the oven chamber holes were drilled for a chimney effect, to give ready access of oven air to the vapor tube near the place of condensation.

A platinum resistance thermometer was hung in the oven chamber through a tube from above, so that the exposed helix of resistance wire was within about one cm. of the lower or vaporization chamber of the vapor tube when the latter was in place. A mercury thermometer also was passed through the wall of the oven chamber near the top, and its entire thread was always inside the oven. The bulb was within 2 cm.

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[1] Brown, *Phys. Rev.*, 5, 236 (1915). See also Brown and Sieg, *ibid.*, **28**, 497 (1914).

of the glass wall of the vaporization chamber. This thermometer was read through the glass door of the oven, and an allowance of 0.5° was made for parallax at each reading. The 2 thermometers thus occupied very nearly the same relative positions. In the earlier work the mercury thermometer was used as a check on the resistance thermometer, which it was at first proposed to use for the temperature readings at one-minute intervals, but it was unexpectedly found that the mercury thermometer was more suited to the purpose, with the other as a check. Temperature readings were taken in this manner for the present data.

A small electric motor outside the oven operated a rotary fan, placed with shaft vertical near the floor of the oven chamber, and with a diameter about $^2/_3$ the width of the oven. Motor and fan were at first connected by a spiral spring belt, but later by a shaft with friction drive. Thorough stirring of the air insured freedom from serious temperature gradient.

Preliminary Standardization of Tubes.

A vapor tension tube such as described can be standardized with some substance whose vapor pressure is known, by applying Equation 3, or by calculation from measurements of the tube dimensions according to Equations 1 and 2.

Effect of Poor Vacuum on Tube Resistance.[1]—Comparison of Equations 1 and 2 with results by the first method showed, as expected, that a poor vacuum introduces serious error. The effect of an air pressure large enough to render inapplicable the Knudsen expressions is shown in Table I(*a*). The resistance with roughly constant air pressure in the tube increases rapidly with the temperature, due to the collisions of the mercury molecules with those of the air.

Validity of the Knudsen Equations with Good Vacuum Conditions.—Of the two methods for determining tube resistance the second is more accurate, as Egerton points out, unless with the first method the mean of quite a number of determinations should be taken. It is comparatively easy to make accurate measurements of the dimensions for calculation of W in the second method.

The first method, however, was used in a preliminary checking of Equations 1 and 2, with mercury as the standardizing material. Two tubes used earlier in the work were standardized in this wy. For Tube A the values of W given in Table I(*b*) were obtained with theL angmuir pump. The mean value for this tube was 40.4 absolute units. The diameter of the circular apertures in the platinum partition was very nearly 2 mm. This value of the area gives 40.0 units for W, leaving but 0.4 unit for W_2, for which 2 units would have been more nearly correct. This would require 38.4 units for W_1, or a diameter of 2.04 mm. for the apertures.

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[1] Dodd, *Phys. Rev.*, 11, 242 (1918).

Comparison of the diameter values for Tubes D, E, F, indicates that the diameters in Tubes A and B were likewise above 2 mm.

TABLE I.—VERIFICATION OF KNUDSEN'S EQUATIONS.

(*a*) Tube B, 6 apertures. Poor vacuum.

Temp. ° C.	*W*. abs. units.	Remarks. Determinations averaged.
87	227	12
97	294	3
106	329	3
120	629	2
129	771	3

(Approximate calculated value of W = 15 units.)

(*b*) Tube A, 2 apertures. Good vacuum.

Run No.	Temp. ° C.	*W* abs. units.
1	80	41.3
2	80	44.4
3	80	37.7
4	80	37.4
5	90	42.0
6	90	41.1
7	90	40.5
8	96	45.7
9	94	37.1
10	96	44.8
11	70.5	42.0
12	70	37.0
13	70	41.6
14	70	36.2
15	70	38.8
16	76	38.5
		Mean, 40.4

(Approximate calculated value of W = 40 units.)

That with good vacuum the effect of temperature on tube resistance is negligible was thus confirmed, and further, the value agreed with the Knudsen equations.

Calculation of Tube Resistances by Knudsen's Equations.

Calculation of W_1.—For the aperture measurements an enlarged photograph was made of the platinum partitions, with the glass broken away sufficiently to expose them. A millimeter scale was included in the photograph, for determining magnification. Measurements of diameters were made with Vernier calipers. The total aperture area for each tube was equal to A in Equation 1. Careful measurements of the individual apertures should have been carried out before the platinum partitions were sealed into the glass tubes. This was not done, as the holes were designed to be exactly 2 mm. diameter. Unfortunately, the method used in cutting them permitted slight departures from this specification.

Calculation of W_2.—The value of W_2 in (2) was determined for each tube from interior measurements of the dimensions. For the integrations a tube was regarded as divided conveniently into 4 parts, each part contributing its share of W_2. Thus, $W_2 = W_a + W_b + W_c + W_d$. In calculating W_2 it was necessary to decided what point should be taken as the upper limit, since the selenium condensed not only on the hemispherical end of the condensation tube, but to some degree spread up the sides. This upper limit of the part of the tube regarded as offering resistance to molecular flow was then taken as "the place of the deposit." The upper limit was in all cases put at one cm. from apex of condensation tube. This was done after a careful observation of the distribution of the condensed material, especially after the tube had been in continuous operation for an unusual length of time so that the thickness of the deposit was easily measured at various points with micrometer microscope, subsequent to breaking the deposit shell partially away from the glass.

Experimental Procedure.

The procedure in taking a measurement of vapor pressure was first to place the tube in the oven, at the same time starting the flow of tap water through the condensation tube. The pump system was not connected with the vapor tube until it had reached equilibrium temperature. At least 15 minutes, and usually more, was allowed for this, undoubtedly more than was necessary. The oil pump was then started and the pressure went down in 2 or 3 minutes to where the Gaede pump could be started. When this pump ceased to throw air up through the mercury at the revolving drum the time count by ordinary watch was begun. The apparatus was then allowed to run for 30 minutes, usually longer. Temperatures were read, as stated, at one-minute interval, and to 0.5°, and time was again read when air was let into the tube by disconnecting the short length of thick-walled rubber tubing between vapor tube and glass tubing connecting with Langmuir pump. The vapor tube was then removed from the oven, the inside tube removed from its place, and the selenium deposit scraped off on a previously weighed filter paper and weighed.

Data and Curves.

Data have been obtained for the vaporization curve of liquid selenium and the sublimation curve for the hexagonal crystals. Equation 3 was applied in the form

$$p = W.1/\sqrt{\rho_1}.G/t, \qquad (5)$$

where p_1 in Equation 3 has been neglected, since the vapor pressure of selenium at the condensation temperature must have been negligible compared with that near the melting point, some 200° higher. The condensation temperature was fairly constant at about 17°, and was that of the tap water used for cooling. For the temperature corresponding to a given pressure measurement, and determining the value of p_2, the mean of the one-minute readings was taken. This average temperature was regarded as equal to a constant temperature that would have given the same amount of condensed material. The mean value was subjected to 2 corrections, one for thermometer calibration, the other for difference in temperature inside and outside the vaporization chamber of the tube. Both the mercury and the resistance thermometers had been standardized at the boiling point of C. P. naphthalene (Bureau of Standards sample) and the freezing point of water. Calibration was carried out under the same conditions as prevailed when the thermometers were in use in the oven. Both corrections of the mean temperature for a pressure measurement were conveniently made from a total correction curve. Since each of the 2 corrections is represented by a linear relation the total correction is similarly represented.

The factor ρ_1 in Equation 5 was evaluated graphically. The constant in Equation 4, $(\rho_1)_0$, was found for selenium by putting $n = 2$, and the vapor pressure curves as here presented were plotted on this basis (see later discussion).

The data as thus treated are assembled in Table II, for the "F series" of the selenium crystals and the "E series" of the liquid, together with data for some check measurements. The 2 letters, E and F, indicate the vapor tube concerned in each case. The F series consisted of 11 successive measurements, or "runs," under best conditions, and the E series, with the exception of 2 runs omitted due to experimental conditions going wrong, of 30 successive measurements.

A plotting of the p and T values as thus computed is inadequate for locating the melting point with any precision, even if it indicated the presence of a change in slope in the general curve, for this change, as is well known, is slight. But there is found from the present data a decided difference in the characteristics of the 2 curves when log p is plotted with $1/T$. This form is suggested for short temperature ranges by the first latent heat equation, as shown later, if L is regarded as constant.

Egerton treated his data in this manner. His temperature range for zinc was 106° and for cadmium 134°. The lowest temperature in the first instance was 162° below the melting point, while in the second it was 182° below. His plotted results showed some departure from a straight line, as might be expected. Assuming Kirchhoff's equation, after a preliminary assumption of a value for C in Equation 11, he could find the constants A and B by applying the relation at 2 experimental temperatures. In Egerton's work there was a gap of 56° between the highest temperature and the melting point for zinc, and of 48° for cadmium, and the relation for p and T had to be assumed over this gap to solve

TABLE II.—VAPOR PRESSURE DATA.

(*a*) F series, hexagonal crystals of selenium.

Tube F, W = 12.41; thermometer J.

Run No.	Aver. temp., ° C.	Corr. temp., ° C.	T, ° abs.	Total time, secs.	G, g.	G/t, $\times 10^4$.	$1/\sqrt{p_1}$ $\times 10^{-4}$.	p bars.	$1/T$ $\times 10^3$.	log. p.
1...	205.3	193.6	466.6	3000	0.0300	0.1000	1.566	1.94	2.143	0.2378
2...	209.8	197.6	470.6	2760	0.0422	0.1525	1.573	2.98	2.124	0.4742
3...	212.6	200.3	473.3	2205	0.0396	0.1795	1.577	3.51	2.112	0.5453
4...	215.9	203.2	476.2	2370	0.0506	0.2130	1.582	4.18	2.099	0.6212
5...	217.1	204.4	477.4	2610	0.0666	0.2550	1.584	5.01	2.094	0.6998
6...	219.4	206.5	479.5	2445	0.0690	0.2825	1.588	5.57	2.085	0.7458
7...	222.0	208.9	481.9	2130	0.0690	0.3240	1.592	6.40	2.075	0.8062
8...	223.9	210.6	483.6	2025	0.0800	0.3950	1.594	7.81	2.067	0.8926
9...	225.9	212.5	485.5	2010	0.0956	0.4650	1.598	9.22	2.059	0.9647
10...	227.5	214.0	487.0	1830	0.0914	0.5000	1.600	9.92	2.053	0.9965
11...	229.1	215.5	488.5	2070	0.1140	0.5500	1.620	11.05	2.047	1.0433

(*b*) E series, liquid selenium.

Tube E, 6 apertures, W = 11.46, thermometer J.

No. Run.	Aver. of temp ° C.	Corr. temp. ° C.	T ° abs.	Total time, secs.	G. g.	G/t $\times 10^4$.	$1/\sqrt{p_1}$ $\times 10^{-4}$.	p bars.	$1/T$ $\times 10^3$.	log. p.
1...	231.7	221.0	494.0	2055	0.1360	0.6618	1.611	12.22	2.024	1.0870
2...	229.8	219.0	492.0	2950	0.2086	0.7071	1.680	13.61	2.032	1.1338
3...	238.6	228.0	501.0	2520	0.2184	0.8666	1.623	16.12	1.996	1.2074
4...	237.4	226.8	499.8	2400	0.2430	1.0125	1.621	18.80	2.001	1.2741
5...	244.1	233.7	506.7	2430	0.3408	1.4024	1.632	26.22	1.973	1.4186
6...	248.3	238.0	511.0	2355	0.3984	1.6917	1.639	31.77	1.957	1.5020
7...	242.1	231.7	504.7	2210	0.2826	1.2787	1.629	23.87	1.981	1.3778
8...	241.7	231.2	504.2	2520	0.3000	1.1904	1.628	22.20	1.983	1.3463
9...	242.5	232.0	505.0	2400	0.3034	1.2640	1.630	23.61	1.980	1.3731
10...	240.1	229.6	502.6	2400	0.3000	1.2500	1.626	23.29	1.989	1.3672
11...	233.3	222.7	495.7	2355	0.2046	0.8687	1.614	16.06	2.017	1.2057
12...	232.9	222.2	495.2	2470	0.2130	0.8623	1.613	15.935	2.019	1.2022
13...	235.4	224.8	497.8	2400	0.2430	1.0125	1.618	18.68	2.009	1.2714
14...	234.7	224.0	497.0	2460	0.2360	0.9593	1.616	17.77	2.012	1.2497
15...	234.0	223.4	496.4	2400	0.2240	0.9333	1.615	17.27	2.014	1.2373
16...	238.3	227.7	500.7	2400	0.2536	1.0566	1.622	19.64	1.997	1.2931
17...	238.0	227.5	500.5	2370	0.2556	1.0784	1.622	20.05	1.998	1.3021
18...	236.0	225.5	498.5	2400	0.2424	1.0100	1.619	18.73	2.006	1.2725
19...	236.4	225.8	498.8	1930	0.1926	0.9979	1.619	18.51	2.005	1.2674
20...	235.4	224.8	497.8	2910	0.2936	1.0089	1.618	18.70	2.009	1.2718
21...	234.5	223.8	496.8	2430	0.2534	1.0427	1.616	19.31	2.013	1.2858
22...	237.2	226.6	499.6	2460	0.2866	1.1650	1.621	21.63	2.001	1.3350
23...	234.8	224.1	497.1	1830	0.1642	0.8972	1.617	16.62	2.012	1.2206
24...	233.9	223.2	496.2	2385	0.2116	0.8872	1.615	16.42	2.015	1.2154
25...	232.0	221.3	494.3	2400	0.2078	0.8658	1.612	15.99	2.023	1.2038
26...	232.6	222.0	495.0	2400	0.1952	0.8133	1.613	15.03	2.020	1.1769
27...	235.1	224.5	497.5	2430	0.2286	0.9407	1.617	17.43	2.010	1.2413
28...	234.5	223.9	496.9	2400	0.2160	0.9000	1.616	16.67	2.012	1.2219
29...	236.7	226.2	499.2	2430	0.2418	1.0197	1.620	18.92	2.003	1.2769
30...	238.7	228.2	501.1	2400	0.2964	1.2350	1.623	22.97	1.995	1.3611

(*c*) Check Measurements.

Tube	No. of apertures.	W	Run No.	Aver. temp. ° C.	Corr. temp. ° C.	Total time, secs.	G g.	G/t × 10^4.	$1/\sqrt{p_1}$ × 10^{-4}.	p bars.
E	7	11.46	Ea1	219.7	208.6	3600	0.1050	0.2916	1.591	5.31
D	7	10.87	Da1	228.1	214.0	2415	0.0966	0.4000	1.600	6.95
D	7	10.87	Da2	218.6	204.6	2190	0.0360	0.1643	1.585	2.83
C	2	36.74	C1	243.2	228.7	2600	0.0988	0.380	1.624	22.67
C	2	36.74	C2	243.0	228.5	2460	0.0820	0.333	1.624	19.87

for the pressure at the melting point. In the present work the range for the solid was roughly 25°, and for the liquid 15°, while the pressure measurements were carried to within 2 or 3° of the melting point in both parts of the experiment, so that dependence need not be placed to any appreciable extent on an extrapolated curve for computations at the melting point.

The log p and $1/T$ relations from the present data for selenium and for a diatomic vapor are at least approximately linear, and there is a decided difference in slope between the two curves. To the extent that the relations can be regarded as linear and constants found on this basis, the melting point can be located with precision. But since the data have been obtained so near the melting point, considerable precision in locating it is to be expected anyway, as the extrapolation is not extensive. Even if the results thus plotted are segments of curves that are not linear, their slopes, readily found graphically, cannot differ appreciably from the slopes of the true curves over the experimental temperature ranges, that is, in a limited region including the melting point.

TABLE III.

n.	f.	$(p)_n$ m. p. bars.	L_1.	L_2.	L_3.	$(dp/dT)_1$	$(dp/dT)_3$
			calories per gram.			bars per degree.	
2	...	12.68	135.5	83.9	219.4	0.57	1.05
4	0.707	8.95	67.7	42.0	109.7	0.40	0.74
6	0.577	7.31	45.1	28.0	73.1	0.33	0.60
8	0.500	6.34	33.9	20.9	54.8	0.28	0.52
10	0.447	5.66	27.1	16.8	43.9	0.25	0.46
12	0.408	5.17	22.6	14.0	36.6	0.23	0.42

Data for the log p and $1/T$ relations are given in Table III. For the F series the location of the mean straight line was quite easy. Even for the E series for the liquid, where the plotted points are more erratic than in the F series, there can be little doubt in locating the mean straight line when this is based on the points with lower values of mean temperature deviation during a run, or those where the deviation was less than 0.3%. These points were 16 in number, *viz.*, 5, 6, 8, 11, 13, 15–19, 22, 24–28. While temperature variation was not the only source of error more confidence was placed in those runs where this variation was not large. At any rate the points for the remaining runs group themselves well about the mean straight line as thus drawn, particularly points 4, 7, 9, 14. The points lying farthest removed from the line above it, with the single exception of 22, had larger temperature variation, *viz.*, 10, 13, 20, 29, 30. The points corresponding to the first 3 runs of the series may be neglected, as the required vacuum was slowly reached in all 3, due probably to gases coming off from the molten selenium. In the 4th run, however, the vacuum was not readable on the McLeod gage after 7 minutes. Vacuum conditions for the 6 runs of larger temperature variation were good, with the possible exception of 20, but even in this case they were obviously not poor enough to interfere with molecular flow. The mean straight line as determined from the 16 points of lower temperature deviation was, therefore, accepted.

The equations for the 2 lines are,

$$\text{F series: } \log p = -7644 \times 1/T + 16.692 \qquad (6)$$

$$\text{E series: } \log p = -4722 \times 1/T + 10.733 \qquad (7)$$

The values for y and x for the point of intersection give, respectively, $p_{\text{m. p.}}$ in abs. units, and the melting point itself on the absolute scale. As thus found, $p_{\text{m. p.}} = 12.7$ bars (0.00957 mm.), and melting point = 217.4°.

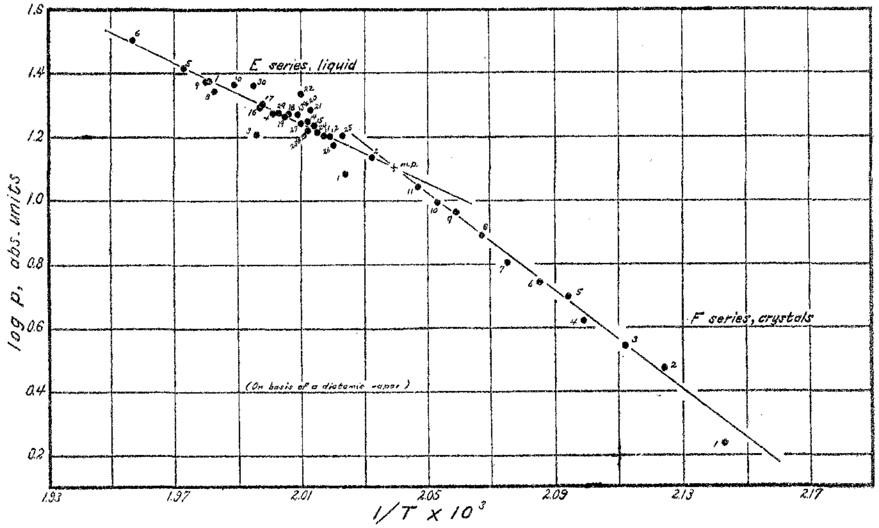

Fig. 2.

The exponential relations corresponding to Equations 6 and 7 are of the form

$$p = 10^{(b+m/T)} = c_1\, 10^{c_2/T} \qquad (8)$$

where m is the slope and b the y-intercept of the $\log p$ and $1/T$ line whose equation is

$$\log p = m.1/T + b \qquad (9)$$

Equations 8 and 9, with the numerical values above, are empirical expressions for the temperatures of the present experiments, and on the basis of a diatomic vapor.

From the slopes of these 2 lines, Fig. 2, the slopes of the p and T curves may be found by

$$dp/dT = -2.3\, m/T^2 \times 10^{(b+m/T)} \text{ bars/degree} \qquad (10)$$

The values at the melting point were,

$$\text{for the solid, } dp/dT = 1.050 \text{ bars/degree}$$

$$\text{for the liquid, } dp/dT = 0.573 \text{ bar/degree}$$

The two p and T curves assembled in Fig. 3 were plotted from Equation 8. The triangles indicate points computed from the empirical expressions.

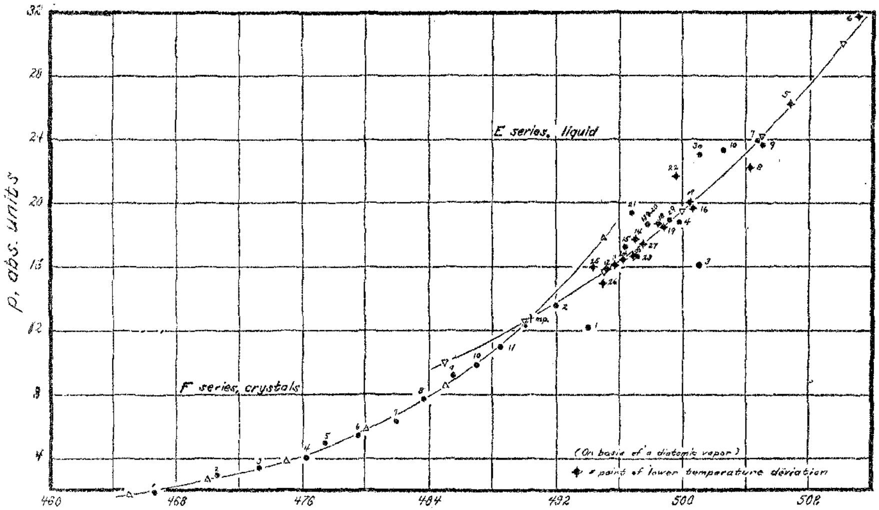

Fig. 3.

Five check values of pressure, with different tubes, are given with data in Table II(c). The 3 check values for the solid curve are all low for reasons known. Check measurements C_1 and C_2 were of most value, for they were obtained with a tube having but 2 apertures as contrasted with Tube E with 7 apertures. It was desired to make more check measurements with this tube at different temperatures, but unfortunately an accident during a third run destroyed the platinum partition. But the 2 measurements C_1 and C_2 are regarded as satisfactory. In addition there was the check on the method in the preliminary work with mercury already described.

Sources of Error.

There are various sources of error in the molecular flow method as here used, some of them of sufficient importance to be particularly guarded against.

To prevent serious temperature gradient in the oven a fan was operated as described. The temperature during a run was as constant as the thermostat of the oven gave. The average deviation from the mean for all 41 measurements of both series was 0.357%. The pressure value is affected by temperature variations in 2 ways, directly through ρ_1, and indirectly by giving an experimental value of G that does not correspond to the mean tube temperature and is likely to be too large, for the pressure of a saturated vapor rises more rapidly than the temperature. Error through ρ_1 can be neglected, since this factor is but slowly variable with temperature. As to the error through G, the indications are that it is small.

The important temperature correction for difference inside and outside the tube at the vaporization chamber was made for Tubes D, E, F, with C. P. tin and silver nitrate crystals as standardizing materials. These were used inside evacuated thin-walled glass Tubes as usual for melting point determinations. They were suspended one at a time in the central part of the vaporization chamber with the vapor tube in the oven as for a pressure measurement. The melting points of these substances were taken at 232 and 209°. In future work a thermocouple sealed into the vapor tube might be found useful and preferable.

The method of molecular flow requires a good vacuum, otherwise the tube resistance cannot be regarded as constant, as already shown. In the present work the vacuum soon reached a desirable degree, 0.00005 mm. or better, as indicated by the McLeod gage, which became useless for precise reading of the lower pressures obtained.

Another difficulty in this method is the uncertainty regarding when to begin the time count. Ideally the vacuum would reach the desired degree at the time zero, and the error will be least when this time is a minimum. Experience has shown that the Langmuir pump reduces the pressure in the vapor tube to a value permitting molecular flow in a brief interval, varying somewhat, possibly because of various amounts of adsorbed gases coming from the apparatus itself and so depending to some degree on the time of standing of the tube between runs. But, as a general rule, after 6 minutes, when the McLeod gage was usually read for the first time in a run, the pressure was less than 0.0002 mm., much below that necessary for molecular flow. In several cases noted, particularly E4, the vacuum was not readable after 7 minutes. But a study of the results shows no consistent variation with time of run.

For most precise measurement of aperture areas they should be perfectly circular, which was not completely realized. Since W_2 was in no case greater than 16% of W_1 any departure of the tube from the cylindrical has been neglected. Integration, however, was carried out for change in shape of cross-section. The distance the deposit spreads up the sides of the tube increases somewhat with temperature, but this slight increase was neglected, as was likewise any error in W_2 due to error in dimensional measurements. There may be some error in the resistance values due to locating the place of condensation in the manner already described, but no attempt has been made to correct for it. A test of the chemical balances showed an error of 0.3%, also neglected.

Adsorbed moisture gathered on the deposit between time of removal from condensation tube and time of weighing. Evidence of this was obtained on a humid day. For E3 the weight of the deposit had increased 0.91% in 1 hour, and 2.1% in 2 hours following the first weighing; E4 had increased 1.56% in 2 hours; E5, 0.41% in 2 hours; while E6, permitted to stand all night for a test weighing, showed no change in 11 hours. Evidently the humidity fell as the day advanced. E10, a run made 2 days afterward, showed an increase of 0.47% in over 2 hours following the first weighing, and E13, made later in the same day, showed a 0.41% increase in 11 hours. Usually the time elapsing from removal of tube from oven until the weighing, amounted to from 10 to 40 minutes. Measurements were not taken to determine this disturbance in all cases. It was noticeable that even with E3, where the adsorption rate appeared to be a maximum, the plotted point on the p and T diagram was low, due to other causes which more than offset error due to adsorption.

It was assumed that the outside tube was kept at the same temperature, at least up to a point opposite the place of deposit on the condensation tube. The precautions taken have been described.

The Kirchhoff Equation.

The Kirchhoff equation has the form

$$\log p = A - C \log T - B/T. \qquad (11)$$

It may be derived from the Clapeyron-Clausius equation by integration after assuming a linear relation. By assuming certain constants for this relation there is obtained

$$\log p = k/2.3 - L_0/2.3R_1 . 1/T - (c - c_p)/R_1 . \log T \qquad (12)$$

proposed by Hertz for mercury.

Knudsen found that this form applied to empirical results at higher temperatures, when extrapolated gave pressure values in good agreement with those obtained by him at lower temperatures by the molecular flow method. He used for mercury the value 0.847 for C in Equation 11, from experimental values of the specific heats. Egerton assumed for both zinc and cadmium the simpler value of 0.5 for this constant, based on theories of Boltzmann,[1] where both solid and vapor are monatomic.

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[1] Partington, "Thermodynamics," 1914, p. 17.

While admitting that this value cannot be true Egerton[1] justified it on the ground that it would make possible the simplest approximation for a comparison of results with different elements. But the specific heats of selenium have not been determined. Moreover, the vapor is probably not monatomic.

It is not necessary to regard the variability of L for short temperature ranges as in the present work. These ranges are not sufficient here to determine how strictly the Kirchhoff type applies to selenium. The present data do not conflict with that type.

It seems desirable to let the results stand for the present expressed by the simple exponential relation, which will suffice for a limited temperature range near the melting point, and to regard it as empirical, with the understanding that it is based on a diatomic vapor, although to the extent that it is exponential the number of atoms assumed per vapor molecule does not change the shape of the curves. That this simple relation may be taken to hold quite generally for temperatures considerably below the critical has been stated recently by Richards.[2]

The Three Latent Heats at the Melting Point.

From the empirical relation of Equation 10, $1/p.\mathrm{d}p/\mathrm{d}T.T^2 = -2.3m$, and from the latent heat equation (in the form $L = R/m.T^2/p.\mathrm{d}p/\mathrm{d}T$ the same quantity is equal to L/R_1 (see also Richards[3]). Equating

$$L = -2.3R_1m. \qquad (13)$$

Thus the latent heat is simply obtained from the slope of the log p and $1/T$ curve, by combining the theoretical latent heat equation with empirical results. The latent heat equation can then be used to find the latent heat at any temperature, provided the slope of the true log p and $1/T$ curve is known at that temperature. The actual relation between log p and $1/T$ can be regarded as linear over a limited segment of the true curve to the extent that the latent heat can be regarded as constant over the same limited temperature range. Obviously then, when Equation 13 is applied near the melting point the value of L is the value of L_0 in Equation 12. Now if the Kirchhoff equation (11) holds, the log p and $1/T$ curve can vary from a straight line only through the log T term. It follows from Equation 13 that the physical meaning of the variability of this term would be the variability with temperature not only of the difference in the specific heats but also of the latent heat. Otherwise m in Equations 10 and 13 and B in 11 would be identical. As it is, $m = -L/2.3R_1$, while $B = -L_0/2.3R_1$.

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[1] *Loc. cit.*, p. 43.

[2] Richards, *J. Franklin Inst.*, 187, 584–5 (1919).

[3] *Loc. cit.*

Treatment of Data on Basis of Different Numbers of Atoms Per Molecule of Vapor.

At 700° or 800° selenium vapor is apparently diatomic,[1] but that of itself probably tells little of conditions near the melting point. In the absence of direct density measurement of the vapor at the experimental temperatures, the 3 latent heats, the pressures, and the slopes have been computed at the melting point for 6 cases, depending on the number of atoms per molecule. See Table III.

Let n be number of atoms per vapor molecule. This enters the factor ρ_1 which by Equation 5 affects the pressure, while W is a constant of the apparatus and G and t are both experimental. Although ρ_1 depends also on temperature that is likewise experimental. Let $(\rho_1)_2$ be density at unit pressure for the data as already computed for a diatomic vapor. From Equation 4 by Avogadro's law, $1/\sqrt{(\rho_1)_n} = \sqrt{2/n} \, . \, 1/\sqrt{(\rho_1)_2}$, and from Equation 3, $p_n = \sqrt{2/n} . p = f_p$, where p is pressure for a diatomic vapor and f is the conversion factor. For the melting point and $p_{\text{m. p.}}$, in Equation 8 $c_1 = 10^b$ and $c_2 = m$. The log p and $1/T$ relation remains linear if the initial relation with $n = 2$ is taken as linear, and the slope c_2 in Equation 8 is unchanged in the conversion, while the y-intercept is varied by an increment, log f. On this basis then the melting point does not depend on n; but $p_{\text{m. p.}}$, and the latent heats as computed from the vapor pressure data, do depend upon it. L changes only through R_1, and from the values of L already computed, $L_1 = 271/n$, and $L_3 = 438.8/n$. Also, $\mathrm{d}p/\mathrm{d}T = K'p$, so that $[(\mathrm{d}p/\mathrm{d}T)_1]_{\text{m. p.}} = 0.9451\ p$, and $[(\mathrm{d}p/\mathrm{d}T)_3]_{\text{m. p.}} = 0.0828\ p$. Pending a determination of the vapor density this treatment will serve for a simple approximation. The computed pressure values in Table III may be regarded as depending upon experiment rather than theory, since the Knudsen equations have been experimentally confirmed.

Summary.

1. By the method of molecular flow data for the sublimation curve for selenium crystals of the hexagonal system have been obtained over the approximate temperature range from 190° to 215°.

2. By the same method data for the vaporization curve for the liquid of vitreous, amorphous selenium have been obtained over the approximate temperature range from 220° to 235°.

3. The relation between vapor pressure and temperature for Se over the temperature ranges studied and on the basis of a diatomic vapor may be expressed by a simple exponential relation, $p = c_1 e^{c_2/T}$, where T is absolute temperature.

4. On the basis of a diatomic vapor the results appear to locate the

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[1] See Roscoe and Schorlemmer, "Chemistry," 1, 469 (1911).

melting point at 217.4°, and give a pressure value at the melting point of 12.68 bars (0.00954 mm.), and slope values for the p and T curves at the melting point of 1.050 bars/degree (0.000767 mm./degree) for the crystals, and 0.573 bar/degree (0.000431 mm./degree) for the liquid.

5. The slope at the melting point was thus found to be greater for the solid than for the liquid, as required by thermodynamics, and as found for other substances. The difference between the 2 slopes is seen to be 0.477 bar/degree (0.000358 mm./degree) on the basis of a diatomic vapor.

6. From the first latent heat equation (Clapeyron) of thermodynamics, the 3 latent heats at the melting point were computed on the basis of a diatomic vapor as follows, for vaporization, 135.5; for sublimation, 219.4; and for fusion, 83.9 cals./g. Since the density of the vapor at the present experimental temperatures has not been determined, the 3 latent heats, the pressure at the melting point, and the slopes of the p and T curves at the melting point, have been computed on the basis of 4, 6, 8, 10, and 12 atoms per vapor molecule. The computed latent heat values vary inversely as these numbers.

7. The results are not out of harmony with the requirements of the Kirchhoff equation, based on thermodynamics, relating vapor pressure and temperature, but they do not give positive evidence that this equation is applicable to selenium, as would be expected from the limited temperature ranges even if that relation should apply.

8. As a preliminary to the present work the Knudsen equations for resistance to molecular flow have been further verified, with mercury as the standardizing material.

In conclusion, the writer wishes to express his thanks to the members of the Physics Department of the State University of Iowa for their interest. Particularly is he indebted to Dr. F. C. Brown, who suggested the problem, and under whose direction the research has been carried out, and also Dr. G. W. Stewart, who has contributed materially to its completion. His gratitude is also due the instrument makers, M. H. Teeuwen, and his successor, at the University, J. B. Dempster.

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