Proceedings of the Iowa Academy of Science

Volume 26 | Annual Issue

Article 50

1919

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Recommended Citation

THE SUBLIMATION CURVE FOR SELENIUM CRYSTALS OF THE HEXAGONAL SYSTEM

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The type of apparatus used in the present work on the vapor tension of selenium, as well as the method, is due originally to Knudsen.[1] The apparatus in the form in which Knudsen used it was modified somewhat by Egerton.[2] Egerton's experimental scheme has been followed essentially in the present work.

The selenium was placed in the lower chamber of a glass tube, which in turn was set in place in a Freas electric oven, after the temperature had been adjusted. Tap water was run through the condensation tube for cooling. The apparatus was exhausted by oil pump, Gaede mercury pump, and Langmuir condensation pump, all in series, so that a good vacuum was obtained, as shown on the McLeod gauge. The saturated selenium vapor passed up through apertures in a platinum partition. This partition, as well as the tube itself, offered resistance to the vapor flow, which was of the molecular type described by Knudsen. The resistance is a constant of the tube, which includes partition with apertures. Its value was determined by measurements of the dimensions and calculation therefrom by the use of Knudsen's equations for molecular flow, and the calculated value was then checked by experimental values obtained with mercury as the standardizing material.

The vapor tension was computed from the Knudsen equation,
$$p—p^1 = W/\sqrt{P^1}.G/T,$$
where p is the vapor tension whose value is sought, p^1 the vapor tension at the temperature of the condensation tube, regarded here as negligible, W is the tube resistance, G the amount in grams of selenium passing over in time T, and P^1 the vapor density at unit pressure and at temperature of the tube.

A considerable amount of data was taken on the vapor tension of selenium during the past year. One of the latest and best of the sublimination curves for selenium crystals of the hexagonal system is presented. The measurements, which will be found in Table I,

[1] Annalen der Physik, 29, p. 179, 1909.
[2] Egerton, Philosophical Magazine, V. 33, 193, p. 33.

TABLE I

W = 12.4; Tube, "F".

No.of Mes't a	t (°C.)	T (secs.)	G/T ×10⁴	1/ √p₁ ×10⁻⁴	p (diat. vapor)	1/T ×10³	log p
1	193.6	3000	0.1000	1.566	1.94	2.143	0.2378
2	197.6	2760	.1525	1.573	2.98	2.124	.4742
3	200.3	2205	.1795	1.577	3.51	2.112	.5453
4	203.2	2370	.2130	1.582	4.18	2.099	.6212
5	204.4	2610	.2550	1.584	5.01	2.094	.6998
6	206.5	2445	.2825	1.588	5.57	2.085	.7458
7	208.9	2130	.3240	1.592	6.40	2.075	8062
8	210.6	2025	.3950	1.594	7.81	2.067	.8926
9	212.5	2010	.4650	1.598	9.22	2.059	.9647
10	214.0	1830	.5000	1.600	9.92	2.053	.9965
11	215.5	2070	.5500	1.620	11.05	2.047	1.0433

Slope = −7644
y-intercept = 16.692
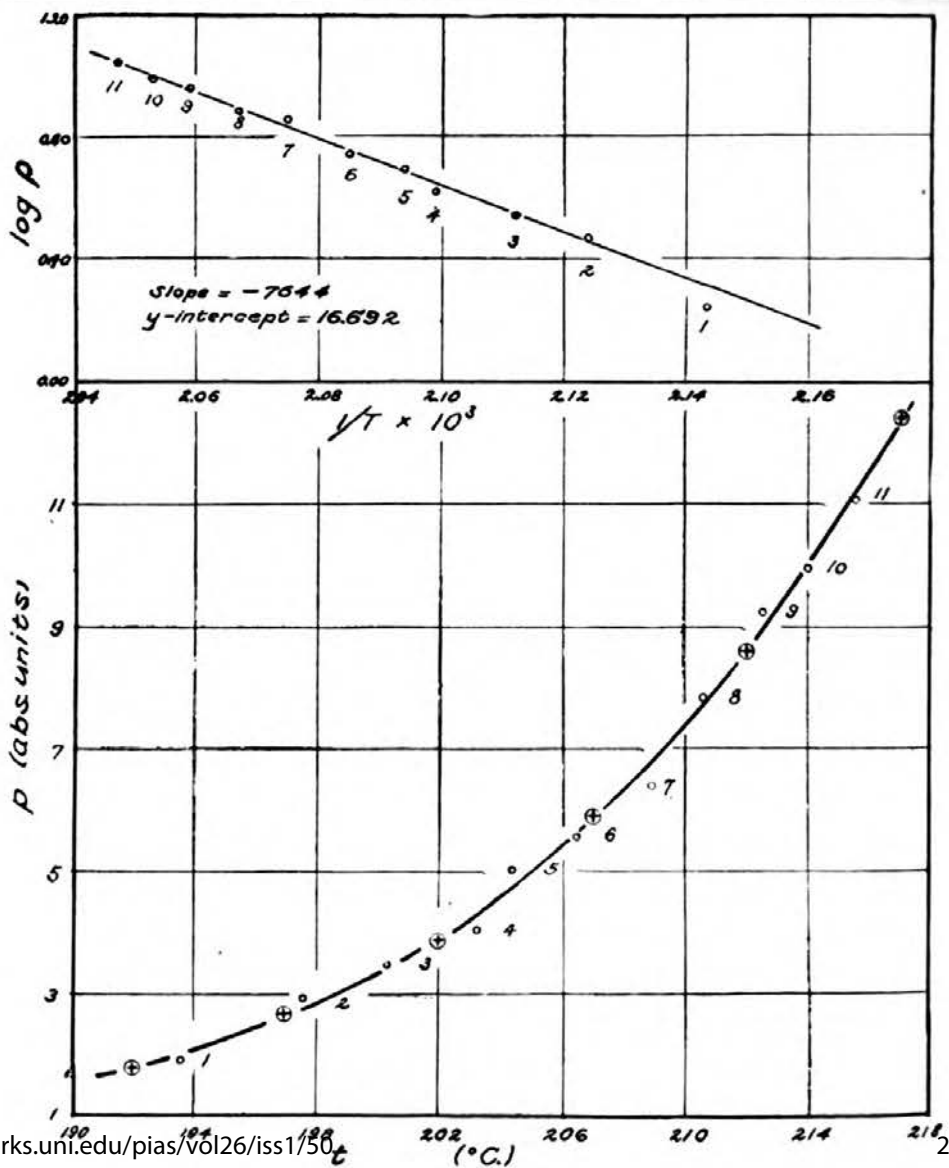
FIGURE 127

are treated on the basis of a diatomic vapor, in absence of knowledge as to the real state of aggregation of atoms in the molecule of selenium vapor at the temperatures of the experiment. Such treatment of the data gives a vapor pressure curve, figure 127, that, empirically at least, and for the present range of temperatures, can be expressed by a simple exponential relation, $p = C_1 e [C_2/T]$. For selenium vapor treated as diatomic this becomes, on the basis of the present measurements, $p = 4.92 \times 10^{16} \cdot 10[-7644/T]$.

TABLE II

T	p
465	1.8
470	2.7
475	3.9
480	5.9
485	8.6
490	12.4
495	17.8

The pressures for six temperatures as computed from this empirical equation are given in Table II, and the corresponding points on the curve are indicated by the large circles, enclosing crosses.

If the relation is either exactly exponential or very nearly so, the only effect of regarding the vapor molecule as other than diatomic will be to change the magnitude of the constant C_1, which change will not destroy the characteristic exponential shape but only affect the computed pressure values, by decreasing them as the number of atoms taken per molecule is increased. Thus, the lower, p_1, and the upper, p_2, limiting pressure values for six different values of the number of atoms, m, assumed per molecule, are given in the following Table III, in absolute units.

TABLE III

m	Factor	p_1	p_2
2	1.000	1.94	11.05
4	0.707	1.37	7.81
6	.577	1.12	6.38
8	.500	0.97	4.96
10	.447	.86	4.43
12	.408	.79	4.05