Physical Chemistry

An. N. NESMEYANOV and DE DYK MAN

1960

SovietRxiv

Abstract

Full Text

Physical Chemistry

An. N. NESMEYANOV and DE DYK MAN

MEASUREMENT OF THE VAPOR PRESSURE OF SOLID CHROMIUM BY THE METHOD OF RADIOACTIVE TRACERS

(Presented by Academician V. I. Spitsyn, January 3, 1960)

The vapor pressure of liquid chromium was measured by the boiling-point method (1,2). Owing to the unreliability of the method of conducting the measurements and the low purity of the metal, these data are incorrect. Measurements of the vapor pressure of solid chromium were carried out by the method of evaporation from an open surface (3–5).

The data of (3) and (4) agree satisfactorily with one another. The somewhat lower values in (4) can be explained by condensation of the metal during evaporation on the suspension filaments. The results of (5) lie considerably higher. Their difference from (3,4) is difficult to comment on. It may be the result both of a systematic error in the measurements and of the greater purity of the metal in (5). The data on the vapor pressure of chromium require verification.

We measured the vapor pressure of solid chromium by the integral variant of the Knudsen effusion method, using the radioactive isotope of chromium, Cr^{51}, to determine the amount of condensate. For the work, 99.99% chromium was taken, which had first been melted in vacuum. The chromium was irradiated with neutrons in sealed ampoules in a nuclear reactor. Its radiochemical purity was demonstrated by the decay curve, which showed the absence of both long- and short-lived radioactive impurities.

The apparatus on which the measurements were made and the procedure for carrying out the experiment were analogous to those described previously (6).

Radioactive chromium in the form of turnings was loaded into a molybdenum effusion chamber with a molybdenum diaphragm, the openings in which were changed from experiment to experiment from $9.847 \cdot 10^{-3}$ to $7.740 \cdot 10^{-4}$ cm^2. The chamber had an internal diameter of 0.9 cm. Heating of the chamber in the apparatus was carried out by means of the high-frequency field of the external inductor of an MVP-3M furnace. The temperature was measured with a Pt—PtRh thermocouple by the compensation method, with a PPTN-1 potentiometer and an M21/4 galvanometer as the zero indicator. The thermocouple was calibrated under the experimental conditions directly in the effusion chamber by the melting points of high-purity copper, gold, and nickel.

Fig. 1

Figure 1: Fig. 1

Fig. 1. Dependence of the vapor pressure of solid chromium on temperature: 1 –according to data of (^{3}); 2 –according to data of (^{4}); 3 –according to data of (^{5}) (chromium condensed from vapor); 4 –according to data of (^{5}) (chromium melted in vacuum); 5 –experimental data with an opening in the diaphragm of $9.847 \cdot 10^{-3}$ cm^2; 6 –experimental data with an opening in the diaphragm of $1.384 \cdot 10^{-3}$ cm^2 (a), with an opening of $7.74 \cdot 10^{-4}$ cm^2 (b).

Chromium was washed from the vapor receiver with three portions of hot sulfuric acid. The acid was removed by evaporation to dryness. The residue was dissolved in dilute acid. From the solution, samples for measurement were prepared in two ways. In the first, chromium hydroxide was precipitated from the solution and separated on a Büchner funnel. The filter with the dried precipitate served as the sample for measurement. In the second method, the solution was evaporated from miniature glass cups to dryness, after which the activity of the dry residue was measured. The activity was measured on setup B with a γ-counter AMM-4. Both methods gave identical results.

The specific activity of the metal was determined from an aliquot portion of the solution of the chromium charge in the same way as the activity from the condensate solution.

The vapor pressure was calculated from the formula:

$$P = \frac{I}{I_0 a t K} \sqrt{\frac{T}{M}} \text{ mm},$$

where I is the activity of the condensate, I_0 is the specific activity, a is the area of the effusion orifice, t is the exposure time, T is the absolute temperature, M is the molecular weight of the vapor, and K is the Clausing coefficient.

Fig. 2. Dependence of chromium vapor pressure on the ratio of the area of the effusion orifice to the cross section of the chamber

The results obtained are given in Table 1 and in Fig. 1. From Table 1 and Fig. 1 it follows that the effusion rate increases when the area of the effusion orifice decreases. However, at orifice areas of $1.384 \cdot 10^{-3}$

Table 1

Vapor pressure and heat of sublimation of chromium

Temp., °C	t, sec	Weight of condensate $1 \cdot 10^6$, g	$a \cdot 10^3$, cm^2	K	Evaporation rate $1 \cdot 10^6$, g/cm^2	$P \cdot 10^4$, mm	$\Delta\Phi^*$, cal/deg· g-at.	ΔH_0°, cal/g-at.
1114	3082	8.15	9.847	0.965	0.269	0.246	–	–
1198	691	11.8	9.847	0.965	1.74	1.63	–	–
1262	302	18.4	9.847	0.965	6.20	5.98	–	–
1044	14401	2.52	1.384	0.924	0.0928	0.100	34.54	92962
1078	10825	3.69	1.384	0.924	0.246	0.227	34.50	93123
1110	3612	2.33	1.384	0.924	0.466	0.445	34.47	93436
1120	5412	5.82	1.384	0.924	0.778	0.723	34.46	92758
1149	3602	6.21	1.384	0.924	1.25	1.21	34.43	93193
1161	1504	5.82	1.384	0.924	2.80	2.74	34.40	92880
1201	911	5.05	1.384	0.924	4.03	3.92	34.38	93078
1236	596	7.38	1.384	0.924	8.94	8.83	34.34	92797
1285	305	10.5	1.384	0.924	24.8	25.2	34.29	92489
1092	7262	1.94	0.774	0.923	0.345	0.328	34.49	93078
1213	1237	5.24	0.774	0.923	5.47	5.44	34.37	92855
1254	897	8.74	0.774	0.923	12.6	12.6	34.37	92784

and $7.74 \cdot 10^{-4}$ cm^2 the evaporation rates practically coincide, i.e., at these values of the orifice areas saturation is reached in the chamber, and the results obtained correspond to the saturated vapor pressure. This is clearly seen from Fig. 2. Using the values of the evaporation rates at different areas of the orifices of the effusion chamber, we calculated the Langmuir coefficient for solid chromium ($\alpha = 0.5$) by the method described earlier (7). The saturated vapor pressures obtained from the data of (3), and the values of α, differ by only 15% from the vapor-pressure values measured by us at the smallest effusion orifices. An even smaller difference is obtained when the data of (4) are used.

Thus, the inequality of the Langmuir coefficient to unity for solid chromium under the conditions of evapora-

It also follows from this that the vapor pressures calculated from evaporation rates from an open surface are incorrect.

On the basis of the foregoing, we took as equilibrium vapor pressures those at effusion-orifice areas of $1.384 \cdot 10^{-3}$ and $7.74 \cdot 10^{-4}$ cm^2 and, using them, found by the method of least squares the equation:

$$\log P_{\mathrm{mm}} = 10.807 - \frac{20907}{T}.$$

Further, from the equilibrium vapor pressures obtained by us and from the values of the thermodynamic potentials for the solid and gaseous phases, calculated from the data of (^{8}), we found the heat of sublimation of chromium at 0°K (ΔH_0°) from the formula:

$$\Delta H_0^\circ = T(\Delta\Phi^* - R\ln P_{\text{atm}}), \quad \text{where } \Delta\Phi^* = \Phi^*_{\text{gas}} - \Phi^*_{\text{cond}}$$

Φ^*_{gas} and Φ^*_{cond} are the reduced thermodynamic potentials of the vapor and of the solid metal.

The data obtained are presented in Table 1. The mean value of the heat of sublimation is 92952 ± 184 cal/g-atom.

Moscow State University
named after M. V. Lomonosov

Received
23 XII 1959

CITED LITERATURE

1. H. C. Greenwood, M. S. B. Pellow, Proc. Roy. Soc., A **82**, 396 (1909); A **83**, 483 (1910).
2. E. Baur, K. Brunner, Helv. Chim. Acta, **17**, 958 (1934).
3. R. Speiser, H. L. Johnston, P. B. Blackburn, J. Am. Chem. Soc., **72**, 4142 (1950).
4. E. A. Gulbransen, K. F. Andrew, J. Electrochem. Soc., **99**, 402 (1952).
5. V. D. Burlakov, *Physics of Metals and Metallography*, **5**, 90 (1957).
6. An. N. Nesmeyanov, L. A. Smakhtin, V. I. Lebedev, DAN, **112**, 700 (1957).
7. An. N. Nesmeyanov, De Dyuk Man, DAN, **123**, No. 6 (1958).
8. D. K. Stull, G. C. Sinke, *Thermodynamic Properties of the Elements*, Washington, 1956.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.