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An. N. Nesmeyanov and De Dyk Man

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Abstract

Full Text

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PHYSICAL CHEMISTRY

An. N. Nesmeyanov and De Dyk Man

MEASUREMENT OF THE VAPOR PRESSURE OF COBALT AND NICKEL

(Presented by Academician V. I. Spitsyn, 21 VII 1958)

The vapor pressure of cobalt had previously been measured by the Langmuir evaporation-rate method ⁽¹⁾ and by the effusion method ⁽²⁾. The data obtained by the Langmuir method lie considerably below those found by the effusion method. This indicates that, for cobalt, the Langmuir coefficient in the formula

$$P = \frac{G}{a} \sqrt{\frac{T}{M}}.$$

may possibly be not equal to unity.

Consequently, the literature data on the vapor pressure of cobalt are incorrect.

The vapor pressure of nickel has been measured only by the Langmuir method ⁽³⁻⁶⁾. The results obtained differ greatly from one another. Data on the Langmuir coefficient for nickel are absent from the literature.

We measured the vapor pressure and the Langmuir coefficient for cobalt and nickel by the integral variant of the effusion method. The apparatus on which the measurements were made, and the experimental procedure, were analogous to those described in work ⁽⁷⁾. The effusion chamber was made of molybdenum. The size of the aperture in the molybdenum diaphragm of the effusion chamber was varied from experiment to experiment. In the work we used cobalt, melted in vacuum, which according to spectral analysis contained 0.2% Ni, 0.09% O, 0.025% Si, 0.01% C, 0.01% Cu, and 0.08% Fe, irradiated with neutrons in a uranium nuclear reactor. The radiochemical purity of the preparation was demonstrated by the constancy of the activity of the cobalt preparation over the course of a month. According to spectral analysis, the nickel contained 0.026% Co, 0.029% Fe, 0.007% Si, 0.052% Cu, 0.04% C, 0.007% S, 0.0036% N, and 0.041% P.

The measurement experiments were carried out in the usual way (7). The condensate was washed from the receiver with 25% HNO₃. The acid was evaporated from the solution to dryness. The residue was dissolved in 1% HNO₃. Cobalt in the solution was determined radiometrically, and nickel colorimetrically. For this purpose, cobalt chloride was added to the cobalt solution as a carrier, and cobalt hydroxide was precipitated from the solution; it was filtered off on a Büchner funnel. The activity of the precipitate obtained was measured on a B-2 apparatus with an AMM-4 gamma counter and compared with the specific activity of the metal measured under the same conditions. Colorimetric determination of nickel was carried out with dimethylglyoxime. The sensitivity of the determination was 0.2γ in 1 ml. The accuracy of determination was of the order of 2%. The data obtained are given in Table 1.

From these data, using the relation derived on the basis of the formula of Rossman and Yarwood (8),

$$p = \frac{p'p''(k''a'' - k'a')}{k''a''p'' - k'a'p'}, \quad \alpha = \frac{p''k''a'' - p'k'a'}{A(p' - p'')},$$

Table 1

Vapor pressure of cobalt and nickel

Temp., °C	Condensate weight $g \cdot 10^6, g$	Exposure time, s	Area of effusion opening $s \cdot 10^3, \text{cm}^2$	k	Pressure, mm
Cobalt	Cobalt	Cobalt	Cobalt	Cobalt	Cobalt
1118	0.866	3600	9.847	0.9655	$2.103 \cdot 10^{-6}$
1218	3.520	1500	9.847	0.9655	$2.124 \cdot 10^{-5}$
1267	7.584	900	9.847	0.9655	$7.763 \cdot 10^{-5}$
1118	0.7542	4200	1.834	0.8236	$9.883 \cdot 10^{-6}$
1218	3.324	1620	1.834	0.8236	$1.169 \cdot 10^{-4}$
1267	6.188	900	1.834	0.8236	$3.985 \cdot 10^{-4}$
1116	1.481	5700	0.7740	0.9228	$3.023 \cdot 10^{-5}$
1215	4.986	1800	0.7740	0.9228	$3.336 \cdot 10^{-4}$
1233	5.950	1270	0.7740	0.9228	$5.649 \cdot 10^{-4}$
1266	10.36	1200	0.7740	0.9228	$1.059 \cdot 10^{-3}$
1118	1.522	5700	0.1673	0.8786	$1.495 \cdot 10^{-4}$
1218	5.15	1800	0.1673	0.8786	$1.679 \cdot 10^{-3}$
1274	13.27	1200	0.1673	0.8786	$6.575 \cdot 10^{-3}$
Nickel	Nickel	Nickel	Nickel	Nickel	Nickel
1130	2.60	3600	9.847	0.9655	$6.353 \cdot 10^{-5}$
1210	1.93	660	9.847	0.9655	$2.640 \cdot 10^{-4}$
1264	3.85	420	9.847	0.9655	$8.445 \cdot 10^{-4}$

Temp., °C	Condensate weight $g \cdot 10^6, g$	Exposure time, s	Area of effusion opening $s \cdot 10^3, \text{cm}^2$	k	Pressure, mm
1139	1.75	3600	1.520	0.9174	$2.928 \cdot 10^{-4}$
1205	1.50	1020	1.520	0.9174	$9.058 \cdot 10^{-4}$
1266	3.90	600	1.520	0.9174	$4.091 \cdot 10^{-3}$
1123	1.90	4260	0.774	0.9228	$5.213 \cdot 10^{-4}$
1202	3.40	1800	0.774	0.9228	$2.271 \cdot 10^{-3}$
1251	3.65	1201	0.774	0.9228	$3.712 \cdot 10^{-3}$
1120	2.20	4801	0.1673	0.8786	$2.602 \cdot 10^{-3}$
1204	4.15	2100	0.1673	0.8786	$1.154 \cdot 10^{-2}$
1252	4.60	1200	0.1673	0.8786	$2.275 \cdot 10^{-2}$

where p is the vapor pressure measured by the Knudsen method; a is the area of the effusion opening; A is the cross section of the chamber; k is the Clausing coefficient (the primes ' and '' refer to results obtained when the size of the opening of the effusion chamber was varied). We determined the equilibrium vapor pressure of both metals for three temperatures and the Langmuir coefficients (see Table 2).

Table 2

Equilibrium vapor pressures and condensation coefficients of cobalt and nickel

Temp., °C	Pressure, mm	α
Cobalt	Cobalt	Cobalt
1118	$3.642 \cdot 10^{-3}$	$3 \cdot 10^{-4}$
1218	$2.683 \cdot 10^{-2}$	$3 \cdot 10^{-4}$
1267	$5.823 \cdot 10^{-2}$	$3 \cdot 10^{-4}$
Nickel	Nickel	Nickel
1126	$7.027 \cdot 10^{-3}$	$6 \cdot 10^{-4}$
1198	$2.675 \cdot 10^{-2}$	$6 \cdot 10^{-4}$
1254	$8.220 \cdot 10^{-3}$	$6 \cdot 10^{-4}$

If the condensation coefficient of nickel is taken to be $6 \cdot 10^{-4}$, and that of cobalt $3 \cdot 10^{-4}$, and the equilibrium vapor pressure is taken, then, according to the Rossman and Yarwood formula, the size of the effusion opening at which the equilibrium vapor pressure is obtained should be less than $8 \cdot 10^{-5} \text{ cm}^2$ for nickel and $6 \cdot 10^{-5} \text{ cm}^2$ for cobalt. We made openings in the diaphragm of the effusion chamber equal to $7.85 \cdot 10^{-5} \text{ cm}^2$ and $5.79 \cdot 10^{-5} \text{ cm}^2$, respectively, and measured the vapor pressures of nickel and cobalt. In this case, data close to the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

equilibrium values were obtained, calculated from the results of measurements with other opening sizes.

Figures 1 and 2 show the experimental and calculated data on the vapor pressure of cobalt and nickel.

Although our data require refinement because of the insufficient number of points on the vapor-pressure curves and the large deviations of the values of α and p , calculated from individual pairs of determinations, from the mean value,

Fig. 1. Change in the vapor pressure of nickel with change in temperature. 1 –according to data of ⁽³⁾; 2 –according to ⁽⁴⁾; 3 –according to ⁽⁵⁾; 4 –according to ⁽⁶⁾; 5-9 –according to our data: 5 –at $a = 9.847 \cdot 10^{-3} \text{ cm}^2$, 6 –at $a = 1.52 \cdot 10^{-3} \text{ cm}^2$, 7 –at $a = 7.74 \cdot 10^{-4} \text{ cm}^2$, 8 –at $a = 1.673 \cdot 10^{-4} \text{ cm}^2$, 9 –calculated value of P ; 10 –according to ⁽³⁾, calculated value of P ; 11 –according to the data of the present work at $a = 7.85 \cdot 10^{-5}$.

nevertheless, at present they are the most reliable for both nickel and cobalt. It should be noted that at an orifice area of

Fig. 2. Change in the vapor pressure of cobalt with change in temperature. 1 –according to data of ⁽¹⁾; 2 –according to ⁽²⁾; 3-7 –according to our data: 3 –at $a = 9.847 \cdot 10^{-3}$, 4 –at $a = 1.884 \cdot 10^{-3}$, 5 –at $a = 9.847 \cdot 10^{-4}$, 6 –at $a = 7.74 \cdot 10^{-4}$, 7 –calculated value of P ; 8 –according to ⁽¹⁾, calculated value of P .

$7.74 \cdot 10^{-4} \text{ cm}^2$ our data on the evaporation rate of cobalt coincide with Kornev's data ⁽²⁾, obtained with an orifice of $1 \cdot 10^{-3} \text{ cm}^2$, but with a different chamber cross section. Thus, the data of Edwards and Johnston ⁽¹⁾ are erroneous.

For nickel it follows that, if the Langmuir coefficient is equal to $6 \cdot 10^{-4}$, then from the data of Johnston and Marshall ⁽³⁾ one can calculate an equilibrium vapor pressure that differs by only 20% from that calculated from our data. Thus, the data on the vapor pressure of nickel obtained by the Langmuir method are incorrect. They should be corrected using the Langmuir coefficient. The rate of evaporation of nickel, from this point of view, was determined correctly in our work and in the work of Johnston and Marshall ⁽³⁾.

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