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Physical Chemistry

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Abstract

Full Text

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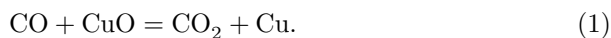
TEMPERATURE DEPENDENCE OF THE SEPARATION COEFFICIENT FOR THE SYSTEM $C^{13}O-C^{12}O$

The most widely used and accurate methods for determining the separation coefficients of isotopic compounds at liquid–vapor equilibrium are Rayleigh distillation and the differential method. The essence of the latter consists in the direct measurement of the difference in the vapor pressures of two samples differing in their isotopic composition. This method, however, requires the availability of a product highly enriched in the rare isotope, and also samples of very high purity, since the presence of more volatile impurities can significantly distort the values of the separation coefficients.

As the object of study we chose the system $C^{13}O-C^{12}O$, for which the determination of the quantities had previously been carried out by a number of authors (¹⁻⁴) in the interval between the melting and boiling temperatures. We carried out measurements over a broader temperature range, when the pressure of carbon monoxide is above atmospheric.

The difference in vapor pressures was measured between samples of carbon monoxide with the natural content of the isotopes C^{13} and O^{18} and samples containing 23 and 32% C^{13} .

Carbon monoxide with the natural isotopic content was obtained by the reaction between chemically pure sulfuric and formic acids at 100°C. The carbon monoxide obtained was passed through a trap placed in liquid oxygen, in which traces of moisture were frozen out, and entered a tube furnace filled with copper oxide and heated to 300°C, in which it was converted into CO_2 according to the reaction



The carbon dioxide was collected in a trap placed in liquid oxygen, while the accompanying noncondensable gases (N_2 , O_2 , Ar, etc.) were pumped off to a pressure of $5 \cdot 10^{-5}$ mm. The pure CO_2 was then fed into a tube furnace filled with asbestos pellets bearing deposited zinc dust. The furnace was first pumped

Fig. 1. Diagram of the apparatus used for measuring the difference in vapor pressures of two isotopic forms

Figure 1: Fig. 1. Diagram of the apparatus used for measuring the difference in vapor pressures of two isotopic forms

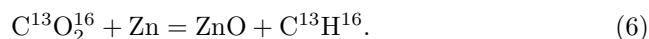
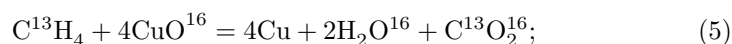
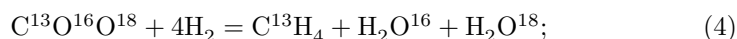
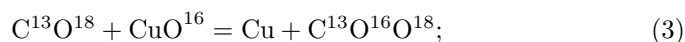
for a long time at 300–320°C to a pressure of $5 \cdot 10^{-5}$ mm. In this furnace the reaction proceeded between CO_2 and zinc heated to 300°C:



The purity of the carbon monoxide samples obtained was checked on a mass spectrometer (MS-4) and by the freezing temperature.

At our disposal were CO samples containing an excess amount of C^{13} and O^{18} (the enriched samples were obtained from the Laboratory of Adsorption Processes of the Karpov Physico-Chemical Institute). It was necessary to separate these isotopes and obtain samples containing an excess amount of C^{13} and natural O^{18} . Se-

separation was carried out by means of the following reactions:



The CO samples obtained were then subjected to the same purification and purity control as the standard samples.

Fig. 1. Diagram of the apparatus used for measuring the difference in vapor pressures of two isotopic forms

Measurement of the difference in vapor pressures (ΔP) was carried out on an apparatus (Fig. 1), the main part of which is a vessel (1), divided into cells. One cell was filled with the standard sample, the other with the sample enriched in C^{13} . Each of the cells was connected to one side of a differential manometer (4). A mercury vacuum gauge (9) was connected to the cell that was filled with the standard, for measuring the absolute value of the CO pressure in the cells.

Fig. 2. Temperature dependence of the separation coefficient for the system C13O and C12O

Figure 2: Fig. 2. Temperature dependence of the separation coefficient for the system C13O and C12O

Fig. 2. Temperature dependence of the separation coefficient for the system C¹³O and C¹²O

The vessel was placed in a cryostat consisting of a Dewar vessel (2), placed in a metal hermetic jacket (3) with windows for observing the liquid levels.

Liquid nitrogen or liquid oxygen was poured into the Dewar vessel, and in the cryostat, by means of a pumping system and a dosing valve (10), the required pressure, and consequently the temperature, was established. The pressure in the cryostat was measured with a vacuum gauge (8) or a manometer (13). The temperature was varied in the range from -170 to 205°C , which corresponded to a change in the CO pressure in the cells from 100 mm Hg to 5 atm. The differential manometer was filled with mercury and placed in a thermostat at 25°C , which was maintained with an accuracy of $\pm 0.1^{\circ}\text{C}$. The pressure difference across the differential manometer was measured by means of a cathetometer with an accuracy up to ± 0.02 mm.

The apparatus had previously been calibrated. Both cells were filled with standard CO samples, and over the entire temperature interval there was carried out—

measurements of the readings of the differential manometer were made. This operation was carried out several times with different standard samples, and the calibration curves agreed well with one another.

Next, one cell was filled with the standard CO sample, and the other with a CO sample containing 23 or 32% C¹³, and measurements of the differential-manometer readings (ΔP) were likewise made. From equation (1) the values of the separation coefficients were calculated:

$$(\alpha - 1) = \frac{\Delta P}{P(N_1 - N_2)}, \quad (1)$$

where ΔP is the measured pressure difference, P is the pressure in the cells, and N_1 and N_2 are the C¹³ content in the two cells, in mole fractions.

Table 1

Results of measurements of the temperature dependence of α for the system C¹³O—C¹²O

Fig. 3

Figure 3: Fig. 3

Temp., °K	$\frac{1}{T} \cdot 10^3$	P_{CO} , mm Hg	P_{CO} with 23% C^{13} , mm	P_{CO} with 32% C^{13} , mm	P_{CO} with 100% C^{13}	α	Error	$\log \alpha \cdot$ 10^3
69.0	14.492	132.0	0.38	—	1.73	1.0131	± 0.0004	5.65
69.4	14.409	144.0	—	0.57	1.84	1.0128	± 0.0004	5.52
70.1	14.265	155.0	—	0.59	1.90	1.01226	± 0.0004	5.29
71.0	14.084	174.0	0.48	—	2.18	1.0125	± 0.0003	5.39
79.8	12.531	553.7	—	1.88	6.06	1.0102	± 0.0003	4.41
80.7	12.391	656.0	1.43	—	6.50	1.00991	± 0.0002	4.28
81.6	12.254	760.0	—	2.2	7.10	1.00934	± 0.0002	4.04
81.9	12.210	800.0	1.65	—	7.50	1.00938	± 0.0002	4.05
85.0	11.764	1026	—	2.8	9.03	1.00903	± 0.0002	3.90
85.2	11.737	1064	2.03	—	9.23	1.00867	± 0.0002	3.75
90.2	11.086	1634	—	3.91	12.61	1.00772	± 0.0001	3.34
91.7	10.905	1824	3.00	—	13.64	1.00748	± 0.0001	3.23
99.2	10.080	3116	4.43	—	20.14	1.00646	± 0.0001	2.79
101.2	9.881	3752	—	7.21	23.26	1.00620	± 0.0001	2.68

The results of the measurements are presented in Table 1 and in Fig. 2. As is seen from Table 1, the value of α decreases with increasing temperature. The temperature

Fig. 3: Comparison of values of the separation coefficients obtained by different studies: **1** —according to (4), **2** —according to (2), **3** —according to (3), **4** —experimental data with a sample containing: a —23% $C^{13}O$, —32% $C^{13}O$

dependence of the separation coefficient can be represented by the equation:

$$\alpha = Ae^{B/T}. \quad (2)$$

In coordinates $\log \alpha - 1/T$ it is a straight line. The values of the constants A and B can be determined with the aid of Fig. 2.

$$A = 0.9954 \quad \text{and} \quad B = 1.477.$$

The coefficient B in the equation is the ratio of the difference in heats of vaporization for the two isotopic forms of carbon monoxide to the gas constant

$$B = \frac{\lambda_{\text{C}^{13}\text{O}} - \lambda_{\text{C}^{12}\text{O}}}{R} = \frac{\Delta\lambda}{R}. \quad (3)$$

$$R = 1.987 \text{ cal/deg}, \quad \Delta\lambda = 2.93 \text{ cal/mole}.$$

As a result of measuring the values of the separation coefficients for the C^{13}O — C^{12}O system over a broad temperature interval from -250 to -170°C , it was established that our data agree well with the data of Devyatykh et al. ⁽³⁾ and differ somewhat from the data of Groth et al. ⁽²⁾, Kronberger ⁽¹⁾, and Johns ⁽⁴⁾.

Figure 3 presents the temperature dependences of α obtained by various investigators.

Physico-Chemical Institute
named after L. Ya. Karpov

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