PHYSICAL CHEMISTRY

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1958

SovietRxiv

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Fig. 2. Dependence of lg Kp on 1/T

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Abstract

Full Text

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ON QUESTIONS OF THE THERMODYNAMICS OF CHLORINATION OF RARE-EARTH METAL OXIDES BY GASEOUS CHLORINE

(Presented by Academician I. I. Chernyaev, 16 XI 1957)

The present work is a continuation of our investigations of the thermodynamics and chemistry of the interaction of rare-metal oxides with gaseous chlorine (1,2). Equilibria were studied for reactions of the type $4\mathrm{MeCl_3(s)} + 3\mathrm{O_2(g)} leftarrows 2\mathrm{Me_2O_3(s)} + 6\mathrm{Cl_2(g)}$, where Me denotes Sc, La, Nd, and Sm. The investigations were carried out under conditions of a two-sided equilibrium state, i.e., from the chloride—oxygen side and from the oxide—chlorine side. The metal chlorides were prepared from compounds supplied to us by I. N. Zaozerskii, according to the procedure described in the handbook (3). The equilibrium composition of the gases was determined by a static method; namely, after equilibrium had been established in the system, a gas sample was withdrawn through a capillary from the reaction space above the mixture of oxide and chloride.

Fig. 1. Dependence of the Cl_2 content in the equilibrium gas mixture on temperature

Fig. 2. Dependence of $\lg K_p$ on $1/T$

The analysis was carried out in a gas thermostated burette; the confining liquid was concentrated sulfuric acid saturated with chlorine. Chlorine was absorbed from the gas mixture with a 20% solution of caustic soda; oxygen was determined as the difference between the volume of gas taken for analysis and that absorbed.

The "flow" method used in the above-mentioned works is not applicable in the case of the oxides under consideration because of the extremely low rates—

Table 1

Results of the study of equilibrium in the systems
$4MeCl_3$ (s) $+3O_2$ (g) $leftharpoons 2Me_2O_3$ (s) $+6Cl_2$ (g)

Temp., °C	Cl_2, vol.%	O_2, vol.%	K_p	ΔZ, cal	ΔH, cal
Reaction $4ScCl_3$ **(s)** $+3O_2$ **(g)** $leftharpoons 2Sc_2O_3$ **(s)** $+6Cl_2$ **(g)**					
250	23.5	76.5	$3.762 \cdot 10^{-4}$	8190	+24580
295	27.2	72.8	$1.051 \cdot 10^{-3}$	7740	+24580
340	34.2	65.8	$8.747 \cdot 10^{-3}$	6310	+24580
364	40.6	59.4	$2.136 \cdot 10^{-2}$	4860	+24580
Reaction $4LaCl_3$ **(s)** $+3O_2$ **(g)** $leftharpoons 2La_2O_3$ **(s)** $+6Cl_2$ **(g)**					
274	20.5	79.5	$1.478 \cdot 10^{-4}$	8450	+25230
330	26.7	73.3	$9.198 \cdot 10^{-4}$	8380	+25230
415	38.0	62.0	$1.264 \cdot 10^{-2}$	5980	+25230
425	40.2	59.8	$1.972 \cdot 10^{-2}$	5440	+25230
505	50.6	49.4	$1.393 \cdot 10^{-1}$	3050	+25230
533	54.4	45.6	$2.733 \cdot 10^{-1}$	2070	+25230
Reaction $4NdCl_3$ **(s)** $+3O_2$ **(g)** $leftharpoons 2Nd_2O_3$ **(s)** $+6Cl_2$ **(g)**					
270	19.0	81.0	$8.857 \cdot 10^{-5}$	10070	+25700
368	28.6	71.4	$1.504 \cdot 10^{-3}$	8270	+25700
440	38.3	61.7	$1.344 \cdot 10^{-2}$	6100	+25700
575	55.7	44.3	$3.438 \cdot 10^{-1}$	1800	+25700
600	60.5	39.5	$7.962 \cdot 10^{-1}$	395	+25700
615	61.4	38.6	$9.319 \cdot 10^{-1}$	120	+25700

Temp., °C	Cl_2, vol.%	O_2, vol.%	K_p	ΔZ, cal	ΔH, cal
Reaction $4SmCl_3$ **(s)** $+3O_2$ **(g)** $leftharpoons 2Sm_2O_3$ **(s)** $+6Cl_2$ **(g)**					
290	18.5	81.5	$7.406 \cdot 10^{-5}$	10630	+25520
340	23.5	76.5	$3.762 \cdot 10^{-4}$	9600	+25520
372	24.3	75.7	$4.597 \cdot 10^{-4}$	9750	+25520
480	37.2	62.8	$1.069 \cdot 10^{-2}$	6785	+25520
585	50.6	49.4	$1.393 \cdot 10^{-1}$	3360	+25520

for establishing equilibrium in the reactions, especially at low temperatures. We have found that the equilibrium state in the oxide–chlorine system is not established even after 10 days (at 350°). Therefore, the data concerning the composition of the gas phase over the systems Nd_2O_3—Cl_2 and La_2O_3—Cl_2 in work (^{2}) evidently do not correspond to the equilibrium state, in contrast to the data for the chloride–oxygen system, in which equilibrium is established much more rapidly.

Taking this circumstance into account, in studying equilibrium from the oxide –chlorine side, in order to create an excess of the latter in the gas phase (as compared with the equilibrium composition), the method described in work (^{4}) was used. The chloride placed in the furnace in an oxygen atmosphere was superheated by 50-80° above the experimental temperature, and after a constant pressure had been established in the system, the temperature was rapidly lowered to the required value. Equilibrium in the chloride–oxygen system was reached after 3-5 days, depending on the experimental temperature.

Chlorination of oxides and oxidation of metal chlorides proceed without the formation of intermediate products. Thus, as a result of analysis of Sc, La, Nd, and Sm oxides chlorinated at 400°, chlorides of the compositions $ScCl_3$, $LaCl_3$, $NdCl_3$, and $SmCl_3$ were found in the products (the ratio Me : 3Cl, respectively, 0.421; 1.30; 1.32; 1.40; theoretical: 0.424; 1.30; 1.36; 1.42).

According to the equation of the law of mass action, the equilibrium constants of the reactions

$$4MeCl_3(s) + 3O_2(g) leftharpoons 2Me_2O_3(s) + 6Cl_2(g)$$

were calculated as follows:

$$K_p = P^6_{Cl2} / P^3_{O2},$$

where P_{Cl2} and P_{O2} are the equilibrium partial pressures of chlorine and oxygen; in this case

$$P_{\mathrm{Cl2}} = \frac{P_{\mathrm{syst}}}{760}\frac{A}{100}, \qquad P_{\mathrm{O2}} = \frac{P_{\mathrm{syst}}}{760}\frac{100-A}{100},$$

where A is the percentage content of chlorine in the gas phase, and P_{syst} is the pressure in the system corresponding to equilibrium (see Table 1).

Calculated in accordance with the known expression

$$\Delta Z = -RT\ln K$$

the changes in the free energy of the reaction are also given in Table 1.

The average values of the thermal effects of the reactions, according to the reaction isochore equation

$$\lg K_{T_2} - \lg K_{T_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

were, in the indicated temperature intervals, respectively +24580; +25230; +25700; +25520 cal. Figure 1 gives the equilibrium composition of the gas phase, and Figure 2 the dependence of $\lg K_p$ on $1/T$. As is seen from Fig. 2, the values of $\lg K_p = f(1/T)$ fall satisfactorily on straight lines.

The results obtained show that the similar physical and chemical properties of the elements considered determine the closeness of their thermodynamic properties.

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Received
11 XI 1957

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