THE STUDY OF SYSTEMS COBALT–IODINE AND NICKEL–IODINE AT HIGHER TEMPERATURES*

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The reaction of cobalt with iodine leading to the formation of cobalt diiodide and the reaction of nickel with iodine resulting in the formation of nickel diiodide were studied in the temperature interval 970—1 330 K and 952—1 233 K, respectively. The thermodynamic quantities of cobalt diiodide and nickel diiodide were determined from the measurements of equilibria of these reactions. For the reaction $Co(s) + 2 I(g) = CoI_2(g)$ at 1 200 K, $\Delta G° = -20.5$ kcal, $\Delta H° = -28.6$ kcal and $\Delta S° = -6.7$ cal deg^{-1}. For the reaction $Ni(s) + 2 I(g) = NiI_2(g)$ at 1 100 K, $\Delta G° = -14.0$ kcal, $\Delta H° = -20.5$ kcal and $\Delta S° = -6.0$ cal deg^{-1}. The mean bond energy of Co–I is 64.3 kcal and for Ni–I 60.3 kcal.

With the aim of determining the thermodynamic properties of cobalt diiodide and nickel diiodide, the equilibria were measured for the reactions

$$Co(s) + 2 I(g) = CoI_2(g) \qquad (A)$$

and

$$Ni(s) + 2 I(g) = NiI_2(g). \qquad (B)$$

There are no direct data on the reactions (A) and (B) in the literature but only estimations of some thermodynamic properties of both iodides[1-5] which, however, are not sufficient even for the prediction of the order of values of equilibrium constants of the given reactions.

EXPERIMENTAL

Chemicals. Cobalt (99·92%) and nickel (99·95%), obtained from Research Institute of Metals, Panenské Břežany, were cut to fine shavings which were washed with 56% hydroiodic acid (analytical reagent) and rinsed with distilled water and methanol (analytical reagent). Iodide was a resublimed analytical grade reagent dried above magnesium perchlorate. Argon (min 99·9%) from

pressure cylinders was used as a carrier gas. Pure metals, *viz.* zinc (99·95%), aluminium (99·99%) and silver (99·99%) were used for calibration the thermocouples designated for measuring temperature in equilibrium apparatus. The other chemicals were altogether of the analytical grade purity.

Method. A flow method was chosen for studying the equilibrium of reactions (*A*) and (*B*). The inert gas saturated with vapours of iodine at a certain temperature was led through a layer of metal (cobalt or nickel) in a heated reactor. In the gas mixture leaving the reactor, the content of iodine was determined; on the assumption that the equilibrium between the gaseous iodine and metal has been attained in the reactor, it is possible to evaluate the partial pressure of the iodide of corresponding metal from the difference of the partial pressures of iodine before the reactor and after the outlet from it. The equilibrium apparatus was described in foregoing paper[6]. To analyze the equilibrium gas mixture the photometry in the liquid phase[7] was used.

RESULTS AND DISCUSSION

In the cobalt–iodine system, altogether 26 experiments were carried out in the temperature interval of 970–1330 K; six of them were neglected in the final treatment owing to the evident experimental errors. In the nickel–iodine system, on the whole 36 experiments were carried out in the temperature interval of 952–1233 K; for the final treatment, however, only 23 experiments were considered because in case of the first ten experiments it was found that the equilibrium had not yet been established and in case of the last three ones, a considerable nickel transport into the cooler region already had taken place. In Tables I and II, the experimental equilibrium values of iodine partial pressures in the systems cobalt–iodine and nickel–iodide are presented.

The treatment of the experimental data was based on the assumption that the only stable compound in the system metal M (cobalt or nickel)–iodine is the iodine MI_2. According to the literature data none of higher iodides is stable[5,8]; on the other hand, the existence of monoiodides which are allegedly formed[9,10] during the decomposition of diiodides, was not clearly proved. It was therefore assumed that only the reaction (*A*) or (*B*) and

$$I_2(g) = 2 I(g) \qquad (C)$$

take place in the system.

The mass balance of entire process leads to the system of equations:

$$K_C = 4(P^0_{I_2})_R (y - x)^2/(1 - y), \qquad (1)$$

$$K_A, \text{ or } K_B = x/4(P^0_{I_2})_R (y - x)^2, \qquad (2)$$

$$(P_{I_2})_R = (P^0_{I_2})_R (1 - x), \qquad (3)$$

where x is the degree of conversion in the reaction (*C*), y analogously the degree

TABLE I

Equilibrium Vapour Pressures of Iodine in the Cobalt–Iodine System
$(P^0_{I_2})_R = 2.627 . 10^{-4}$ atm.

T, K	$P(J_2) . 10^4$, atm	T, K	$P(J_2) . 10^4$, atm
970·1	1·850	1 124·0	2·215
970·2	1·787	1 190·5	2·376
970·2	1·893	1 191·4	2·364
1 013·7	2·001	1 191·4	2·376
1 014·3	2·003	1 241·9	2·421
1 014·7	1·983	1 243·3	2·425
1 072·8	2·127	1 243·9	2·434
1 072·2	2·177	1 329·0	2·469
1 121·2	2·253	1 329·5	2·489
1 122·2	2·236	1 329·6	2·488

TABLE II

Equilibrium Vapour Pressures of Iodine in the Nickel–Iodine System
$(P^0_{I_2})_R = 2.627 . 10^{-4}$ atm.

T, K	$P(J_2) . 10^4$, atm	T, K	$P(J_2) . 10^4$, atm
953·3	2·382	1 105·3	2·452
952·4	2·392	1 105·0	2·481
952·5	2·369	1 104·2	2·476
952·3	2·365	1 161·1[a]	2·099
1 008·3	2·355	1 160·5[a]	2·071
1 007·7	2·411	1 160·5[a]	2·101
1 007·6	2·395	1 160·1[a]	2·065
1 005·7	2·393	1 160·0[a]	2·064
1 047·9	2·444	1 232·8	2·526
1 048·1	2·404	1 232·3	2·516
1 048·1	2·424	1 231·9	2·521
1 047·2	2·413		

[a] Vapour pressure of iodine in the initial gas mixture argon–iodide $(P^0_{I_2})_R = 2.175 . 10^{-4}$ atm.

of conversion in the reaction (A) or (B), $(P_{I_2})_R$ are measured values of the iodine partial pressure in equilibrium mixture and $(P^0_{I_2})_R$ the values of the iodine partial pressure in the initial gas mixture argon–iodine (Table I and II). For the temperature dependence of equilibrium constant of reaction (C), the following relation was taken from literature[11]

$$\log K_C = 5.531 - 7911/T. \qquad (4)$$

The simultaneous solution of equations (1) to (4) yields the degrees of conversion x and y. The equilibrium constants K_A or K_B, resp. then follow directly from the equation (2). Applying the method of least squares, one obtains for the temperature dependence of equilibrium constants K_A or K_B, resp. the following relations:

$$\log K_A = -(1.469 \pm 0.090) + (4250 \pm 100)/T \qquad (5)$$

which holds in the temperature range of 970–1330 K and

$$\log K_B = -(0.885 \pm 0.140) + (3060 \pm 150)/T \qquad (6)$$

which holds in the temperature range of 952–1233 K. The standard deviation between the experimental and calculated values of $\log K$ is 1.34% for the reaction (A) and 2.36% for the reaction (B).

All thermodynamic quantities calculated from the measured data for the reactions (A) and (B), the energy of metal–iodine bond in MI_2 iodide and the absolute entropies of gaseous iodide, all for approximate middle of the respective temperature interval
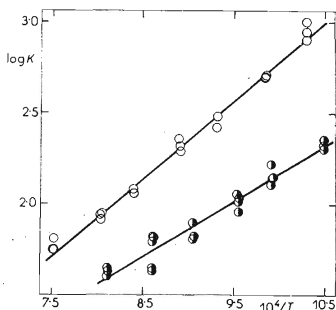

Fig. 1

Temperature Dependence of Equilibrium Constant of Reaction (A) ($\circ$) and Reaction (B) ($\circleddash$)

Table III

Calculated and Literature Values

Quantity	Reaction	CoI_2	NiI_2
	For a temperature of 1 200 K (CoI_2), or 1 100 K (NiI_2)		
$\Delta H°$, kcal	M(s) + 2 J(g) = MJ$_2$(g)	-28.6 ± 0.5^a	-20.5 ± 0.7^a
$\Delta S°$, cal deg^{-1}	M(s) + 2 J(g) = MJ$_2$(g)	-6.7 ± 0.4^a	-6.0 ± 0.6^a
$\Delta G°$, kcal		-20.5 ± 1.0^b	-14.0 ± 1.4^b
Bond energy M — I, kcal	—	64.3 ± 0.3^c	60.3 ± 0.3^d
$S°[MJ_2(g)]$, cal deg^{-1} mol^{-1}	—	110.0 ± 0.6^e 104.7^g	110.2 ± 0.8^f 102.6^g
	For a temperature of 298 K		
$S°[MJ_2(s)]$ cal deg^{-1} mol^{-1}	—	— 37.8^i	39.8^h 37.7^i
$\Delta H°$, kcal	M(s) + J$_2$(g) = MJ$_2$(s)	-39.5 ± 2.7^j -36.0 ± 1^m -34.8^n -36.2^p	-39.0^k -38.0 ± 1^m -36.8^o -35.9^g
$\Delta H°$, kcal	M(s) + J$_2$(s) = MJ$_2$(s)	-24.6 ± 2.7^q -24.2^r -24.4^s -25.8 ± 3^u	-24.1^q -22.4^r -23.0^t -23.5 ± 3^u

^{a} The values resulting from Eqs (5) and (6). ^{b} Calculated from the experimental values of $\Delta H°$ and $\Delta S°$; the error indicated is the maximum one. ^{c} Calculated from $\Delta H°$ for the reaction (A) and the heat of sublimation of cobalt[12]. ^{d} Calculated from $\Delta H°$ for the reaction (B) and the heat of sublimation of nickel[12]. ^{e} Calculated from the experimental value of $\Delta S°$ for the reaction (A), the value of absolute entropy of monatomic gaseous iodine[13], the value of absolute entropy of cobalt at 298 K (ref.[14]) and the molar heat capacity of cobalt[15,16]. ^{f} Calculated from the experimental value of $\Delta S°$ for the reaction (B), the values of absolute entropy of nickel at 298 K (ref.[17]) and the molar heat capacity of nickel[16,18,19]; the error indicated is the maximum one. ^{g} Calculated by means of the method proposed by Brewer and coworkers[20] on the basis of electronic contributions[21] and molecular constants estimated by Brewer; the magnitude of error of the calculated value cannot be estimated. ^{h} Calculated from the value of absolute entropy of gaseous nickel diiodide at 1 100 K (see^e), the entropy of vaporization of nickel diiodide estimated by Schäfer and coworkers[4] and the relative entropy of nickel diiodide[1]; the magnitude of error cannot be estimated. ^{i} The values estimated by Latimer[3]; the magnitude of error is not given. ^{j} Calculated from the value of $\Delta H°$ for the reaction (A), the relative enthalpy of gaseous cobalt diiodide calculated by the Brewer method, the relative enthalpy of gaseous monoatomic iodine[13], the relative enthalpy of cobalt calculated from molar heat capacities[15,16], the heat of vaporization of cobalt diiodid[28] and the heat of dissociation of gaseous diatomic iodine[13]; the error indicated is the maximum one. ^{k} Calculated from

the value of ΔH° for the reaction (B), the relative enthalpy of gaseous nickel diiodide calculated by the Brewer method, the relative enthalpy of gaseous monoatomic iodine[13], the relative enthalpy of nickel calculated from molar heat capacities[16,18,19], the heat of dissociation of gaseous diatomic iodine[13] and the heat of sublimation of nickel diiodide estimated by Brewer and coworkers[20]. [m] The values estimated by Brewer[1]. [n] The approximate calculation on the basis of experimental data[22] on the equilibrium of reduction of liquid cobalt diiodide with hydrogen. [o] The approximate calculation on the basis of experimental data[23]. [p] Calculated from heats of solution[24]. [q] Calculated from ΔH^0_{298} for the reaction $M(s) + I_2(g) = MI_2(s)$ (see[j], or[k]) and the value of heat of sublimation of iodine at 298 K (ref.[13]), [r] Tabulated values[25]. [s] Tabulated value[26,14]. [t] Tabulated values [26,27]. [u] The values estimated on the basis of the theory of crystal field.[2]

and further the values converted to 298 K are presented in Table III. The available literature data are summarized, as well, for comparison in this table. As it is seen from the data given in Table III, there exist relatively considerable differences between the values of absolute entropies of gaseous diiodides calculated on the one hand from the experimental data and on the other hand by means of the procedure proposed by Brewer and coworkers[20]. These differences can be caused either by some assumptions included in the Brewer method which are not quite adequate or by the fact that it was not possible to take into account some further reactions (the dimerization of iodides, formation of triiodides, of monoiodides, and the like), which cannot be excluded with certainty in the given systems. The latter, together with the fact that for converting to the temperature 298·15 K it was necessary to use a great number of approximations, may also be the reason for the discrepancies between the values of heats of formation at 298·15 K determined by us and by other authors.

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