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MASS SPECTROMETRIC INVESTIGATIONS OF $NiTe_2O_5$ AND $Ni_2Te_3O_8$ AT HIGH TEMPERATURES

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Summary

The dissociation of $NiTe_2O_5$ and $Ni_2Te_3O_8$ was investigated between 900 and 1000 K using the mass spectrometric Knudsen effusion method. It was found that both substances evaporate incongruently according to the following reactions.

$$2NiTe_2O_5(s) \rightleftarrows Ni_2Te_3O_8(s) + TeO_2(g)$$

$$Ni_2Te_3O_8(s) \rightleftarrows 2NiO(s) + 3TeO_2(g)$$

From the measured equilibrium vapour pressure of TeO_2 for both reactions in the given temperature interval and from the values of C_p for $TeO_2(s)$ and $TeO_2(g)$, the entropy $S_{298\,K}$ and C_p for $Ni_2Te_3O_8$ and $NiTe_2O_5$ were estimated, allowing the calculation of some thermodynamical data according to the second and third law methods. The second law heats of reactions at 298 K were found to be 283.3 ± 12.6 and 880.7 ± 25.1 kJ mol^{-1} and for the third law heats of reaction 269.9 ± 4.1 and 851.0 ± 8.1 kJ mol^{-1} for the first and second reaction respectively. The standard enthalpies of formation of $Ni_2Te_3O_8$ and $NiTe_2O_5$ were found as 1549.8 ± 25.0 and 948.0 ± 37.1 kJ mol^{-1} respectively.

1. Introduction

The behaviour of several metal–tellurium compounds became of interest because of their electrical properties [1]. In particular, the solid state reactions of TeO_2 with MnO, NiO and other oxides have been systematically investigated. A variety of compounds were identified using X-ray diffraction and differential thermal analysis (DTA) methods [2, 3]. However, no data

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on the composition of the vapour phase under reaction conditions and their thermodynamic properties are known. For $NiTe_2O_5$ under nitrogen, two endothermic peaks have been observed at temperatures of 910 K and 1163 K [3] and NiO, TeO_2 and $Ni_2Te_3O_8$ were identified in the solid phase by X-ray diffraction [2, 3]. In connection with these observations, a systematic investigation of the behaviour of $Ni_2Te_3O_8$ at higher temperatures was undertaken by the mass spectrometric Knudsen effusion method. It was the aim of this work to obtain an insight into the dissociation reactions of $Ni_2Te_3O_8$ and $NiTe_2O_5$ by measuring the equilibrium partial pressures of the species present in the gas phase in a Knudsen cell connected to a mass spectrometer. From this some thermochemical properties of these compounds become accessible using the second law method. By making use of the estimated entropy, third law calculations could be compared with the results obtained from the second law method.

2. Experimental details

The measurements were performed using a single focusing mass spectrometer equipped with a Knudsen effusion cell. The ions of the molecules escaping from the Knudsen cell were produced by electron impact and detected with 12-stage Cu–Be electron multiplier. The ionization efficiency curves were recorded and evaluated by the method of Winters *et al.* [4].

Owing to the reactivity of the compounds under question at higher temperatures, pure gold was used as the material for the Knudsen cell in order to avoid chemical reactions between the substances and the inner wall of the cell. The Knudsen cell was 10 mm long with a diameter of 6 mm and orifice of 0.3 mm. Temperatures were measured with a chromel–alumel thermocouple and the estimated accuracy of the sample temperature was ±3 K.

The compounds for investigation were prepared by heating a stoichiometric mixture of NiO and TeO_2 in a nitrogen atmosphere by a method described elsewhere [2, 3]. It was proved by X-ray diffraction that $Ni_2Te_3O_8$ was the only phase present in the sample, whereas for $NiTe_2O_5$, $Ni_2Te_3O_8$ was also found in the solid phase.

3. Results and discussion

3.1. Gaseous phase

During investigation of $Ni_2Te_3O_8$ in a Knudsen cell made from sintered Al_2O_3 at temperatures above 1000 K, TeO_2^+, TeO^+, $(TeO_2)_2^+$, Te_2^+, Te^+, O_2^+ and O^+ were identified in the gaseous phase, NiO, TeO_2 and $Ni_2Te_3O_8$ were found in the solid phase. Measured ionization energy (IE) and appearance energy (AE) showed that ions were formed mainly by the ionization and fragmentation of TeO_2 and only to a small extent by the dissociation of

$TeO_2(g)$ prior to ionization. These observations are in good agreement with the results obtained by Muenow *et al.* [5] indicating the equilibrium reaction in the gas phase.

$$6TeO_2 \rightleftharpoons Te_2 + 2TeO + (TeO_2)_2 + 3O_2 \qquad (1)$$

which is shifted strongly to the left at temperatures about 1000 K. Therefore, we can assume that only TeO_2 is present in the gaseous phase. However, it was proved that the solid phase contains $Ni_2Te_3O_8$, NiO and TeO_2 (deposited on the colder parts of the Knudsen cell).

According to the Gibbs phase rule for such a system, consisting of four phases and two components, the equilibrium pressure could be obtained only at a defined temperature. This was also confirmed by the low reproducibility of the vapour pressure measurements of TeO_2 at various temperatures.

By using gold as the material for the Knudsen cell, only NiO and $Ni_2Te_3O_8$ could be found in the solid phase.

As proved by IE and AE measurements, only ions governed by the ionization and fragmentation of TeO_2 molecules were detected in the gaseous phase.

On the basis of these observations, the dissociation reaction

$$2NiTe_2O_5(s) \rightleftharpoons Ni_2Te_3O_8(s) + TeO_2(g) \qquad (2)$$

could be postulated with certainty.

The observed endothermic peaks in DTA in vacuum at temperatures of 1100 K and 1163 K are related to reactions (3) and (2) respectively. It is appropriate to point out that the ratio of these two peaks corresponds to the heats of reaction for both processes (see below).

By similar experiments with $Ni_2Te_3O_8$ the dissociation reaction was confirmed to be

$$Ni_2Te_3O_8(s) \rightleftharpoons 2NiO(s) + 3TeO_2(g) \qquad (3)$$

corresponding to the endothermic peak observed by separate experiment at 1170 K by DTA in vacuum.

3.2. Measurements of TeO_2 vapour pressure

From the above experiments it could be concluded that $NiTe_2O_5$ and $Ni_2Te_3O_8$ evaporate incongruently, and that TeO_2 vapour pressures for reactions (2) and (3) are the equilibrium pressures at a given temperature.

For the determination of thermochemical data from the ion intensities measured in the mass spectrometer, partial pressures of gases in the Knudsen cell have to be calculated. From the well known correlation [6] between the ion intensity I^+ and the gas pressure p of a neutral molecule, *i.e.* $p = kI^+T$, the constant k could be determined by several methods [7]. For our purposes the total vaporization method was used, where an exactly weighed amount of TeO_2 was evaporated in the Knudsen cell and from the measured ion intensities of $I^+_{TeO_2}$ the constant k was determined as $k = 5.23 \times 10^{-5}$ Pa

V^{-1} K^{-1}. Thus the vapour pressures of TeO_2 obtained at different temperatures and equilibrium constants were calculated according to the relations

$$K_p = p^2_{TeO_2} \qquad \text{and} \qquad K_p = p^3_{TeO_2} \tag{4}$$

for reactions (2) and (3) respectively.

From these experimental results an expression for ln K_p was calculated by least squares fit as

$$\ln K_p = -(32.5 \times 10^3 \pm 0.4 \times 10^3)/T + (24.1 \pm 3) \tag{5}$$

for reaction (2) and

$$\ln K_p = -(10.1 \times 10^4 \pm 0.2 \times 10^4)/T + (71.5 \pm 2) \tag{6}$$

for reaction (3). Some experimental data for both reactions, together with the calculated third law heats of reaction are given in Table 1 and Table 2.

TABLE 1

TeO_2-equilibrium constants (ln K_p) and third law heats of reaction referring to reaction (2)

T (K)	ln K_p	ΔG°_T (kJ mol^{-1})	$\Delta H^{\circ\,\mathrm{III}}_{r,298}$ (kJ mol^{-1})
922	−11.22	86.2	269.4
926	−11.10	85.4	269.9
930	−10.98	84.9	269.9
933	−10.83	84.1	269.9
937	−10.70	83.3	269.9
940	−10.54	82.4	269.9
944	−10.43	82.0	269.9
947	−10.29	81.2	269.4
950	−10.17	80.3	269.4
953	−10.08	79.9	269.9
957	−9.96	79.1	269.9
960	−9.85	78.7	269.9

Mean value $\Delta H^{\circ\,\mathrm{III}}_{r,298} = 269.9 \pm 0.41$ kJ mol^{-1}.

3.3. *Thermodynamic data*

The heats of reaction ΔH°_T referring to reactions (2) and (3) were obtained by second and third law methods. For the second law treatment the van't Hoff relation

$$\Delta H^\circ_T = R\,\frac{\mathrm{d}\ln K_p}{\mathrm{d}(1/T)} \tag{7}$$

and for third law calculations the relation

$$\Delta H^\circ_{298} = -RT\ln K_p - \frac{T\Delta}{T}\,(G^\circ_T - H^\circ_{298}) \tag{8}$$

were used.

TABLE 2

TeO_2-equilibrium constants ($\ln K_p$) and third law heats of reaction referring to reaction (3)

T (K)	$\ln K_p$	ΔG°_T (kJ mol^{-1})	$\Delta H^{\circ\,\mathrm{III}}_{\mathrm{r},298}$ (kJ mol^{-1})
944	−35.56	279.1	850.6
948	−35.07	276.6	850.6
952	−34.71	274.9	851.0
956	−34.27	272.4	851.0
960	−33.87	270.3	850.2
964	−33.31	266.9	850.6
968	−33.04	265.7	851.4
971	−32.67	264.0	850.2
975	−32.27	261.5	850.2
978	−31.79	258.6	851.0
982	−31.37	268.6	850.6
986	−30.84	252.7	849.4
991	−30.27	249.4	849.4
1001	−29.74	249.8	853.5

Mean value $\Delta H^{\circ\,\mathrm{III}}_{\mathrm{r},298} = 851.0 \pm 1.0$ kJ mol^{-1}.

The expression

$$\Delta\{(G^\circ_T - H^\circ_{298})/T\} = \Delta\{-S^\circ_T + (H^\circ_T - H^\circ_{298})/T\}$$

represent the change in the Gibbs free energy function of the corresponding reaction, *i.e.*

$$\Delta\{G^\circ_T - H^\circ_{298})/T\} = \Sigma\{(G^\circ_T - H^\circ_{298})/T\}_{\mathrm{prod}} - \Sigma\{(G^\circ_T - H^\circ_{298})/T\}_{\mathrm{react}}$$

From the slopes of the curves in Fig. 1 and Fig. 2 the second law heats referring to reactions (2) and (3) yield $\Delta H^\circ_{974} = 840.6 \pm 25$ kJ mol^{-1} and $\Delta H^\circ_{944} = 270.7 \pm 13$ kJ mol^{-1} respectively.

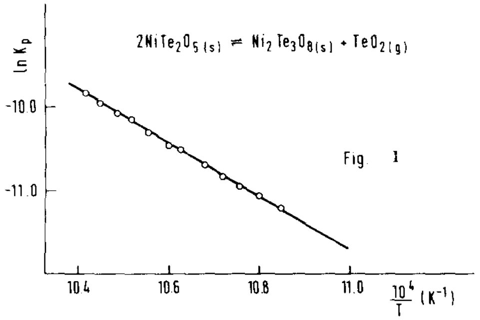

Fig. 1. Equilibrium constant as a function of temperature, *i.e.* $\ln K_p$ *vs.* $1/T$ for the reaction (2).

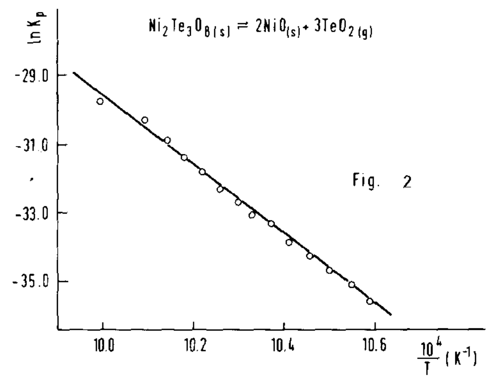

Fig. 2. Equilibrium constant as a function of temperature, *i.e.* ln K_p *vs.* $1/T$ for the reaction (3).

In order to convert second-law enthalpies to 298 K according to relation

$$\Delta H_{298} = \Delta H_T^\circ - \int_{298}^{T} \Delta C_p \, dT1 \qquad (9)$$

ΔC_p as a function of temperature for each reaction was calculated on the basis of data obtained from the literature [8] and results obtained by us by the method described later. Inserting these into eqn. (9), standard heats of reaction at 298 K were calculated to be $\Delta H_{298}^\circ = 283.3 \pm 12.6$ kJ mol^{-1} for reaction (2) and 880.7 ± 25.1 kJ mol^{-1} for reaction (3). The standard heats of formation $\Delta H_{f\,298}^\circ$ for $Ni_2Te_3O_8$ and $NiTe_2O_5$ were obtained from the standard heats of reaction ΔH_{298}° and the standard heats of formation of NiO [9] and TeO_2 [5] as 1549.9 ± 25 kJ mol^{-1} for $Ni_2Te_3O_8$ and 949.3 ± 38 kJ mol^{-1} for $NiTe_2O_5$.

For the application of the third law method according to eqn. (8), entropy values S_T°, S_{298}° and heat capacity C_p as a function of temperature must be calculated for reactants and products.

The entropy and ΔH_{298}° values for TeO_2(g) were obtained from the literature [5]. From the experimental data of $H_T^\circ - H_{298}^\circ$ in the temperature interval between 298 - 2000 K [10] C_p for TeO_2(g) was obtained as a function of temperature.

The entropy for NiO(s) is $S_{298}^\circ = 38.0$ J mol^{-1} K^{-1} [8]. Regarding the transition points of NiO(s), three values for C_p should be considered [11]. Owing to the lack of thermodynamic data for $Ni_2Te_3O_8$ and $NiTe_2O_5$, the S_{298}° of inorganic substances could be estimated to ± 4 J mol^{-1} K^{-1} [11]. According to this the estimated value for S_{298}° yields 272.8 J mol^{-1} K^{-1} for $Ni_2Te_3O_8$ and 166.5 J mol^{-1} K^{-1} for $NiTe_2O_5$. The heat capacities C_p of the substances under investigation could be derived from the additivity rule of Kubaschewski [12], whereas an analytical expression for $C_p = f(T)$ for TeO_2 could be obtained on the basis of literature data [13, 14]. From these considerations, heat capacities C_{p1}, C_{p2} and C_{p3} for $Ni_2Te_3O_8$(s) and $NiTe_2O_5$(s) could be expressed as functions of temperature. Finally, the third law heats of reactions (2) and (3) ΔH°_{298} could be calculated at various temperatures (see Tables 1 and 2) giving an average value $\Delta H^\circ_{298} = 851.0 \pm 8$ kJ mol^{-1} for $Ni_2Te_3O_8$(s) and 269.9 ± 4 kJ mol^{-1} for $NiTe_2O_5$(s). These values are in good agreement with those obtained by the second law method. The heats of reaction determined according to the second law method, $\Delta H^\circ_{298} = 283.3 \pm 12.6$ and 880.7 ± 25.1 kJ mol^{-1}, respectively, are somewhat greater than the third law values. However, if one takes into account the errors associated with the second and third law methods, it becomes clear that the values agree within the limits of the method.

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