Thermochimica Acta, 138 (1989) 47–53
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC STUDY OF THE DEHYDRATION PROCESS OF α-GOETHITE IN VACUO

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(Received 26 February 1988)

ABSTRACT

The decomposition reaction of α-goethite to yield porous α-hematite particles and water, has been investigated in vacuo in the temperature range 423–523K by the Knudsen effusion technique.

Cells with orifices of different diameters were employed and the equilibrium vapour pressure as a function of the temperature was represented by the equation

$$\ln K_p(\text{KPa}) = (13.20 \pm 0.01) - (8095.2 \pm 6.4)/T$$

The enthalpy of reaction, at an average temperature of 473.15K, was found to be $\Delta H^\circ_{473.15} = 67.3 \pm 10.0$ KJ mol^{-1}.

INTRODUCTION

Endothermic decomposition reactions of the type

$$AB(s) = A(s) + B(g) \tag{1}$$

have been the object of several studies [1–6] aimed at determining the kinetics of the process and the effect of different environments on the reaction mechanism.

In particular the kinetics of the endothermic transformation of α-goethite into α-hematite

$$2FeOOH(s) = Fe_2O_3(s) + H_2O(v) \tag{2}$$

has recently been studied in depth and its topotactic nature — with an inhomogeneous mechanism — has been well established [7–11]. According to this model, water is released from certain regions (donors) of the crystal while other parts (acceptors) conserve their oxygen in close-packed structures. In the donor regions, water is lost owing to the combination of the hydroxyl ions with the protons which have migrated from the acceptor

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0040-6031/89/$03.50

regions, and the donor regions are gradually transformed into pores. The microporous structure of the product was observed by high energy transmission electron microscopy and the specific area measured by the liquid nitrogen BET method [11].

In a recent review [12], Volpe and Boudart affirmed that topotactic reactions are non equilibrium processes with a high degree of irreversibility. In particular, they pointed out that during the thermal decomposition of hydroxides into oxides and water in vacuo or in air, the vapour pressure of water is small compared with its equilibrium value. As a consequence, the reaction acquires a large thermodynamic driving force or affinity.

Analogous conclusions were proposed by Darroudi and Searcy [13] for the decomposition of carbonates and sulfates.

The present work was undertaken with the aim of evaluating the vapour pressure of water in the temperature range 423–523K, by means of the Knudsen effusion technique. The enthalpy of reaction was also determined at an average temperature of 473.15K.

EXPERIMENTAL

The acicular goethite employed in the vaporization experiments was supplied by the Bayer Co. and its purity verified by X-ray analysis.

The average dimensions of the particles, which have a cylindrical-like shape, were determined by scanning electron microscopy and were found to be 0.10 ± 0.01 μm for the radius and 1.00 ± 0.10 μm for the length. The specific area was determined by the BET method as 14.1 ± 0.3 m^2 g^{-1}. Details of these experimental techniques and procedure are reported in a previous study [11].

Four stainless steel cylindrical Knudsen cells of 1.0 cm width and 3.0 cm length, with Knudsen orifices of different diameters (designated A, B, C and D), were employed in the decomposition vapour pressure experiments.

In Table 1 the average orifice diameters, measured with a scanning electron microscope, and the cell constants K are reported. They were determined by vaporizing a pure element (mercury) under the same experi-

TABLE 1

Orifice diameters and constants of the cells employed in the determination of vapour pressures

Cell	Orifice diameter d (mm)	Cell constant (Af_C) (cm^2)
A	1.00	29.6×10^{-4}
B	0.57	15.5×10^{-4}
C	0.42	7.78×10^{-4}
D	0.25	4.14×10^{-4}

mental conditions as goethite decomposition and by comparing the obtained vapour pressure with the data reported in the literature [14]. Details of the apparatus and the experimental procedure employed in the dehydration of goethite are also reported elsewhere [11].

In each experiment about 110 mg of dried acicular goethite were loaded into the cell which was suspended from the left arm of a Cahn 1000 computerized microbalance. The vacuum in the quartz apparatus was maintained at below 1×10^{-5} Torr by means of diffusion pumps and liquid nitrogen traps. The cell, in a quartz tube, was immersed in an electronically controlled oil thermostat, and its temperature was determined by a calibrated thermometer.

RESULTS AND DISCUSSION

Two decomposition runs were carried out using cell A (1.00 mm orifice diameter) and one each for cell B (0.57 mm), cell C (0.42 mm) and cell D (0.25 mm). The vapour pressure, as a function of the experimental temperature, was calculated by the Knudsen equation

$$P(\mathrm{KPa}) = \frac{\mathrm{d}W}{\mathrm{d}t} \times \frac{2.286}{K} \times \left[\frac{T}{M}\right]^{1/2}$$

where $\mathrm{d}W/\mathrm{d}t$ is the mass loss in g s^{-1}, T is the temperature in K, M is the molecular weight of the water and K is the cell constant, which is equal to the product of the orifice area (A) and the Clausing factor (f_C) (which takes into account the non-ideality of the holes). The experimental determination of the cell constant was preferred to the geometrical evaluation of the product $A \times f_\mathrm{C}$ since the dimensions of the smallest orifices were rather irregular and did not allow accurate measurements. In Table 2 the temperature – pressure data obtained for each cell are reported, and in Fig. 1 ln P is plotted against $1/T$.

In Table 3 the coefficients of the interpolated straight lines, obtained by least-squares treatment of the data reported in Table 2, are summarized. It will be noticed that the vapour pressure of the water increases as the orifice diameter of the Knudsen cell is reduced, and that it tends to an upper limit, i.e. the equilibrium vapour pressure.

Pairs of ln P as a function of the cell diameter d were obtained through the equations of the straight lines reported in Table 3, at temperatures differing by 10 °C. These data were then interpolated using the equation

$$\ln P(\mathrm{KPa}) = \alpha + \beta \times d(\mathrm{mm})$$

which provides the equilibrium vapour pressure for $d = 0$. The obtained pressure values represent the equilibrium constant (K_P) of reaction (2). They are listed in Table 4 and plotted in Fig. 2. The least square treatment of the

TABLE 2

Water pressure obtained at experimental temperatures and employing different Knudsen orifices

Run	T (°C)	$1/T$ ($\times10^{-3}$ K^{-1})	dW/dt (g s^{-1})	P (KPa)	ln P
Orifice A ($d = 1$ mm)					
A.1	150	2.363	6.667×10^{-8}	0.252×10^{-4}	-8.286
	155	2.336	7.857×10^{-8}	0.297×10^{-4}	-8.121
	170	2.257	2.142×10^{-7}	0.821×10^{-4}	-7.105
	185	2.183	4.081×10^{-7}	1.59×10^{-3}	-6.444
	215	2.047	1.125×10^{-6}	4.52×10^{-3}	-5.399
	230	1.986	1.517×10^{-6}	6.18×10^{-3}	-5.086
	240	1.948	2.375×10^{-6}	9.77×10^{-3}	-4.628
	250	1.910	2.619×10^{-6}	1.08×10^{-2}	-4.524
A.2	160	2.308	1.400×10^{-7}	0.532×10^{-4}	-7.539
	165	2.282	1.447×10^{-7}	0.554×10^{-4}	-7.499
	170	2.257	1.898×10^{-7}	0.721×10^{-4}	-7.235
	180	2.207	3.371×10^{-7}	1.31×10^{-3}	-6.637
	190	2.160	5.583×10^{-7}	2.19×10^{-3}	-6.124
	200	2.112	7.051×10^{-7}	2.80×10^{-3}	-5.879
	210	2.068	7.917×10^{-7}	3.17×10^{-3}	-5.754
	220	2.026	1.042×10^{-6}	4.22×10^{-3}	-5.467
	240	1.948	2.500×10^{-6}	1.03×10^{-2}	-4.574
	250	1.910	2.667×10^{-6}	1.10×10^{-2}	-4.505
Orifice B ($d = 0.57$ mm)					
B.1.	170	2.257	1.476×10^{-7}	1.08×10^{-3}	-6.827
	180	2.207	2.622×10^{-7}	1.94×10^{-3}	-6.244
	190	2.159	5.119×10^{-7}	3.84×10^{-3}	-5.562
	200	2.113	6.403×10^{-7}	4.84×10^{-3}	-5.330
	210	2.070	7.083×10^{-7}	5.41×10^{-3}	-5.219
	220	2.028	9.048×10^{-7}	6.98×10^{-3}	-4.965
	230	1.987	1.359×10^{-6}	1.06×10^{-2}	-4.544
	250	1.911	3.000×10^{-6}	2.38×10^{-2}	-3.736
Orifice C ($D = 0.42$ mm)					
C.1	150	2.363	5.826×10^{-8}	8.30×10^{-4}	-7.094
	165	2.282	1.069×10^{-7}	1.55×10^{-3}	-6.470
	180	2.207	2.238×10^{-7}	3.30×10^{-3}	-5.713
	195	2.136	5.325×10^{-7}	7.98×10^{-3}	-4.831
	210	2.069	8.277×10^{-7}	1.26×10^{-2}	-4.374
	225	2.007	9.380×10^{-7}	1.45×10^{-2}	-4.230
	240	1.949	1.460×10^{-6}	2.29×10^{-2}	-3.776
	250	1.911	2.045×10^{-6}	3.24×10^{-2}	-3.429
Orifice D ($d = 0.25$ mm)					
D.1	150	2.363	7.620×10^{-8}	2.04×10^{-3}	-6.193
	155	2.336	8.541×10^{-8}	2.30×10^{-3}	-6.074
	160	2.309	1.030×10^{-7}	2.79×10^{-3}	-5.882
	175	2.231	1.938×10^{-7}	5.34×10^{-3}	-5.233
	190	2.159	4.250×10^{-7}	1.19×10^{-2}	-4.433
	205	2.091	8.167×10^{-7}	2.32×10^{-2}	-3.762
	220	2.028	1.240×10^{-6}	3.58×10^{-2}	-3.329
	240	1.949	1.458×10^{-6}	4.29×10^{-2}	-3.148

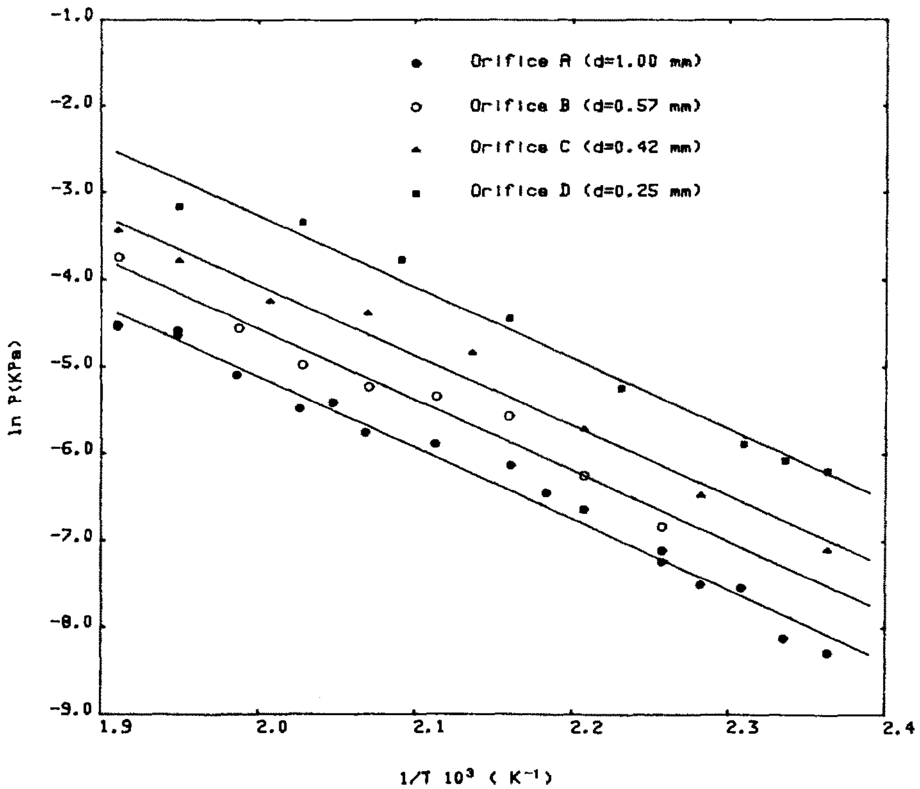

Fig. 1. Vapour pressures of water in the reaction $2FeOOH(s) + Fe_2O_3(s) + H_2O(v)$, obtained using different Knudsen cell orifices.

data reported in Table 4 yielded the equation:

$$\ln K_P(\mathrm{KPa}) = (13.23 \pm 0.01) - (8095.2 \pm 6.4)/T(\mathrm{K})$$

The enthalpy of reaction was found to be $\Delta H^\circ_{473.15} = 67.3 \pm 10.0$ KJ mol^{-1}. The quoted error is an overall evaluation of the associated uncertainties.

TABLE 3

Vapour pressure–temperature equations of the goethite decomposition for different diameters of the Knudsen cell orifice

Exp.	No. of points	ΔT (K)	$\ln P$ (KPa) $= A - B/T$	
			A	$B \times 10^{-3}$
A.1–2	18	523–423	11.28 ± 0.54	8.19 ± 0.25
B.1	8	523–443	11.75 ± 1.23	8.15 ± 0.59
C.1	8	523–423	12.08 ± 0.98	8.07 ± 0.46
D.1	8	513–423	13.08 ± 1.03	8.17 ± 0.47

TABLE 4

Equilibrium water pressure–temperature data

T (°C)	$1/T \times 10^{-3}$ (K^{-1})	K_P (KPa)	$\ln K_P$
150	2.363	2.748×10^{-3}	−5.897
160	2.309	4.275×10^{-3}	−5.455
170	2.257	6.519×10^{-3}	−5.033
180	2.207	9.764×10^{-3}	−4.629
190	2.159	1.436×10^{-2}	−4.243
200	2.113	2.077×10^{-2}	−3.874
210	2.070	2.963×10^{-2}	−3.519
220	2.028	4.163×10^{-2}	−3.179
230	1.987	5.767×10^{-2}	−2.853
240	1.949	7.894×10^{-2}	−2.539
250	1.911	1.068×10^{-1}	−2.237

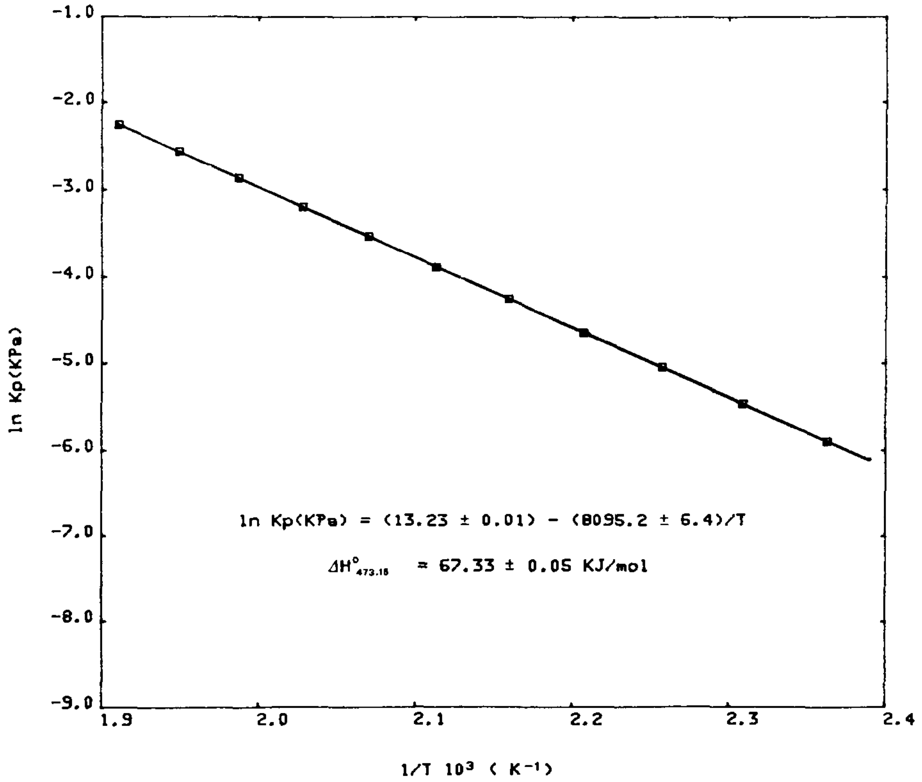

Fig. 2. Plot of the equilibrium vapour pressure of water in the dehydration of α-goethite particles.

This value is in fair agreement with the enthalpy of reaction, $\Delta H^{\circ}_{298} = 52.2$ KJ mol^{-1}, obtained by employing the Hess law and the standard heats of formation of goethite, hematite and $H_2O(v)$ [15].

CONCLUSION

In order that the effusion through an orifice might be considered molecular, one of the Knudsen theory conditions [16], is that the mean free-path of the molecules in the cell at a certain temperature is at least 1/10 of the orifice diameter. All the orifices employed in this study satisfied this requisite.

This allows us to conclude that the increase in the water pressure observed when using the orifices of the smallest diameters, is due to the fact that the phases in the present Knudsen cells are not in thermodynamic equilibrium. The degree of irreversibility of the process is influenced by the experimental conditions in the cell and the modification on the reaction regime due to the particles dimensions must also be evaluated.

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