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Citation: The Journal of Chemical Physics **26**, 1207 (1957); doi: 10.1063/1.1743494 View online: http://dx.doi.org/10.1063/1.1743494 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/26/5?ver=pdfcov Published by the AIP Publishing

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resonance formalism discussed in the case of symmetrical cyanines by Moffitt.⁶ The introduction of the barrier in the first method and the intermediate structures in the second causes a greater change in the ground state than in the excited level. With increasing

⁶ W. E. Moffitt, Proc. Phys. Soc. (London) A63, 700 (1950).

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length of the chain this effect increases in both the methods. For long chains the vinylene shift is constant for the barrier model, but remains nonconvergent in the resonance theory.

A more detailed report on this work will be published in *Acta Physica Polonica*.

VOLUME 26, NUMBER 5

MAY, 1957

Thermodynamics of the Zr-ZrO₂ System: The Dissociation Energies of ZrO and ZrO₂†

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A mass spectrometric analysis of vapors effusing from a Knudsen cell containing either solid ZrO_2 or a mixture of Zr and ZrO_2 powders has been employed to determine the vapor pressures, and hence the heats of sublimation of these species. Combined with published thermodynamic data, these results yield 7.8 ± 0.2 ev and 14.5 ± 0.2 ev for the dissociation energies of ZrO and ZrO₂, respectively. Previous work is shown to be in error due to the volatility of TaO.

I. INTRODUCTION

HE vapor pressure and derived thermodynamic quantities of ZrO₂ have been reported by Hoch, Nakata, and Johnston.¹ These authors employed a Knudsen effusion cell constructed of tantalum, and determined the weight loss under "neutral conditions" $(ZrO_2 alone within the Knudsen cell)$ and "reducing conditions" ($Zr - ZrO_2$ mixture within the effusion cell). Their observation that the vapor pressure appeared to be the same under both conditions led them to conclude that ZrO_2 was the predominant species in the vapor. The fact that $(ZrO_2)^+$ was reportedly observed in a mass spectrometer,² using surface ionization techniques, was used as further support for this conclusion. In view of the possible importance of the ZrO molecule in the $Zr-O_2$ system³ it was deemed advisable to study the system using a combination of Knudsen effusion cell and mass spectrometer in an attempt to detect this molecule in the vapor. As will be seen the analysis has led to a very different interpretation of the $Zr-ZrO_2$ system than that suggested by Hoch, Nakata, and Johnston.

II. EXPERIMENTAL APPARATUS

The experimental arrangement has been described earlier.⁴ In the initial experiments with the $Zr-ZrO_2$

system, a tantalum Knudsen cell was employed under conditions of temperature and concentration similar to those of Hoch, Nakata, and Johnston.¹ Subsequently a thoria crucible was placed within the tantalum cell (which now served merely as an oven) and finally a crucible made of ZrO_2 was used. The orifice was generally *ca* 1 mm diameter, and σ (ratio of inner surface covered by material of interest, to effusion area) was greater than 200 in all cases. Temperatures were measured with an optical pyrometer, and corrections applied for the emissivity of Ta and transmission of the quartz window.

III. EXPERIMENTAL RESULTS

The initial runs revealed that the most volatile species effusing from a tantalum crucible containing ZrO₂ powder were ZrO and TaO. Both the latter species were in evidence at *ca* 1700°C, whereas $ZrO_2(g)$ did not become apparent until ca 1950°C. Addition of Zr powder to the effusion cell increased the ZrO/TaO ratio by less than a factor of 2. The low appearance potential of ZrO (ca 5.5 ev) together with the large ratio of ZrO to ZrO₂ (184 at 2050°C) provides strong evidence for the primary process $ZrO + \bar{e} \rightarrow ZrO^+ + 2\bar{e}$ as the major contributor to the ZrO mass peak. A movable "beam defining slit" between the Knudsen cell and the ionization chamber is used to provide discrimination between peaks arising from residual gases and those due to effusion from the Knudsen cell. This movable slit was used on mass numbers 106 to 112 inclusive, and the net intensity diminutions were in excellent agreement with the isotopic abundance of

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[†] Supported by a joint program of the Office of Ordnance Research and the National Science Foundation.

¹Hoch, Nakata, and Johnston, J. Am. Chem. Soc. 76, 2651 (1954). ²S. V. Starodubtsev and Y. I. Timokhina, Zhur. Tek. Fiz. 19,

² S. V. Starodubisev and Y. I. Thiokinia, Zhui, Tek. Fiz. 17, 606 (1949). ³ G. Herzberg, Molecular Spectra and Molecular Structure. I.

^oG. Herzberg, *Molecular Spectra and Molecular Structure*. 1. Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., New York, 1950).

⁴W. A. Chupka and M. G. Inghram, J. Phys. Chem. 59, 100 (1955).



FIG. 1. Clausius-Clapeyron plot for the sublimation of ZrO₂.

Zr.⁵ Similar results were subsequently obtained for the mass positions corresponding to $(Zr)^+$ and $(ZrO_2)^+$.

These preliminary results yielded vapor pressures in rough quantitative agreement with those of Hoch, Nakata, and Johnston, but indicated that the interpretation given by these authors was in error. The system being studied was apparently being dominated by the reaction:

 $Ta(s)+ZrO_2(s) \rightarrow TaO(g)+ZrO(g).$

In order to minimize the effect of the tantalum oven, a thoria Knudsen cell was placed within the tantalum oven to prevent contact of ZrO2 and tantalum. Subsequently, a Knudsen cell pressed from ZrO₂ powder was placed within the tantalum oven. Even under these conditions the $(ZrO)^+/(ZrO_2)^+$ ratio was about 6.

The reaction $\frac{1}{2}$ Zr(s) $+\frac{1}{2}$ ZrO₂(s) \rightarrow ZrO(g) was more difficult to isolate, because of the ZrO contribution due to reduction by tantalum. In an attempt to minimize extraneous reactions, a ZrO₂ cell containing Zr powder was covered externally with an iridium metal sheet. This assembly was placed within a tungsten crucible. Unfortunately, the iridium alloyed with the tungsten, completely consuming the former and invalidating the experiment.

Two independent methods were employed to extract the heat of sublimation of ZrO and ZrO₂ from the experimental data. It may be shown⁴ that the observed ion intensity, $I^+ = kP/T$ where P = partial pressure of thatparticular isotopic species, T = Absolute temperature, k =Calibration constant for the apparatus. When combined with the Clausius-Clapeyron equation,

$$\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}$$

it becomes evident that the slope of the curve obtained when plotting $\ln(I^+ \cdot T)$ vs 1/T yields $-\Delta H_v/R$, and hence the heat of vaporization.

An alternative procedure is to determine k by completely vaporizing a known weight of material and measuring the integrated current. Silver has generally been used for this purpose. Two additional estimates are necessary in this computation, i.e., (a) the relative ionization cross section of Ag and the species in question, and (b) their relative efficiencies for producing secondary electrons at the first dynode of the electron multiplier. Taking cognizance of these corrections and those due to isotopic abundance, one may calculate the absolute vapor pressures corresponding to the ion intensities observed, and hence ΔF° of vaporization. In the present work we have assumed

$$Ag:Zr:ZrO:ZrO_2: :1:1:1.5:2$$

for relative ionization cross sections and, considering both mass and molecular effects on the secondary electron production rate, unity for relative multiplier efficiencies. From a knowledge of ΔS° of vaporization and the relationship $\Delta F^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}, {}^{4} \Delta H_{v}$ is obtained.

The determination of ΔS° introduces some new difficulties, however. Herzberg's compilation³ provides values for the ground-state frequency of vibration, the internuclear distance and electronic state of the ZrO molecule, but he has reservations regarding the choice of ground electronic state and of internuclear distance. Nevertheless, we have employed these values to determine the third law entropy of ZrO(g). For $ZrO_2(g)$ we have assumed a linear configuration, and have employed a valence-bond approximation to estimate the four frequencies of vibration. The frequencies 865-1 cm, 271^{-1} cm (2), and 1003^{-1} cm were used in the computations. The ground electronic state was assumed to be ${}^{1}\Sigma$.

For $ZrO_2(s)$, the data of Coughlin,⁶ as summarized by Lustman and Kerze⁷ have been used to calculate $S^{\circ}_{2000^{\circ}K}$, and extrapolated by K. K. Kelley's specific

⁵ K. T. Bainbridge and A. O. Nier, "Relative isotopic abun-dances of the elements," Preliminary Report No. 9, Nuclear Science Series, National Research Council (1950).

⁶ J. P. Coughlin, "Contributions to the data on theoretical metallurgy. XII. Heats and free energies of formation of inorganic oxides," U. S. Bur. Mines Bull. 542 (1954). ⁷ B. Lustman and F. Kerze, *The Metallurgy of Zirconium* (McGraw-Hill Book Company, Inc., New York, 1955).

Sample environment	<i>Т</i> , °К	P, atmos	$\Delta F_T \circ \frac{\text{kcal}}{\text{mole}}$	ΔS_T° , eu	ΔH_T° , $\frac{\text{kcal}}{\text{mole}}$	$\Delta H_0^\circ, \frac{\text{kcal}}{\text{mole}}$
$ \begin{array}{c} \operatorname{ZrO:} \operatorname{Zr}(s) + \operatorname{ZrO}_2(s) \text{ in Ta} \\ \operatorname{Zr}(s) + \operatorname{ZrO}_2(s) \text{ in Ta} \\ \operatorname{Calibration} \\ \operatorname{uncertain by} \\ \operatorname{factor 1.5} \end{array} $	2173 2124 2322 2137	6.6 ×10 ⁻⁷ 2.33×10 ⁻⁷ 1.86×10 ⁻⁵ 7.45×10 ⁻⁷	61.4 64.4 50.2 59.9	39.0 39.1 38.8 39.1 Ay	$ 146.1 \\ 147.4 \\ 140.3 \\ 143.5 \\ \overline{144.3} $	151
ZrO_2 : ZrO_2 in Ta ZrO_2 in Ta $Zr+ZrO_2$ in Ta $Zr+ZrO_2$ in ThO_2 $Zr+ZrO_2$ in Ta ZrO_2 crucible $ZrO_2(s)$ in ZrO_2 crucible	2421 2480 2416 2331 2340 2471 2374	$\begin{array}{c} 6.9 \times 10^{-8} \\ 5.9 \times 10^{-8} \\ 4.8 \times 10^{-8} \\ 3.6 \times 10^{-8} \\ 2.1 \times 10^{-7} \\ 1.4 \times 10^{-7} \\ 1.4 \times 10^{-7} \end{array}$	79.3 82.0 80.9 79.4 71.5 77.5 74.4	37.9 37.8 37.9 38.0 38.0 38.0 37.8 37.9 Av	171.1 175.7 172.5 168.0 160.4 170.9 164.4 169.0	186

TABLE I. Heats of sublimation obtained by the absolute pressure method.

heat data.⁸ The thermodynamic data on Zr(s), including its heat of sublimation, have been obtained from Lustman and Kerze, (pp. 360-363) who summarize the data of several investigators. The data and calculations for both ZrO and ZrO₂ are summarized in Table I. Figure 1 shows a typical graph of $\ln P vs 1/T$ from which ΔH_v of ZrO₂ was obtained. Table II summarizes the data obtained by the slope method.

One additional observation was made, which serves as corroborative evidence for the previous results. During two of the experiments, it was possible to simultaneously observe $(Zr)^+$, $(ZrO)^+$, and $(ZrO_2)^+$, and to determine their relative concentration. Taking the reaction

$$Zr(g) + ZrO_2(g) \rightarrow 2ZrO(g)$$

one may compute the equilibrium constant (which is independent of pressure) as a function of ionizing electron voltage. At a temperature of 2408°K, this constant was 0.815×10^3 using 20-volt electrons and 1.16×10^3 using 12-volt electrons. For K=1000,

$$\Delta F_{2408^\circ C} = -33 \text{ kcal/mole}$$

 $\Delta S_{calc} = 9.644 \text{ eu}$

and hence

$$\Delta H_{2408} = -10$$
 kcal/mole

or

 $\Delta H_0^\circ = -14.4$ kcal/mole.

Using the data of Table I, we obtain for the same reaction

$$\Delta H_0^{\circ} = -26 \text{ kcal/mole}$$

which is within the experimental error when allowance is made for the fact that one of the errors is doubled in this calculation.

Sources of Error

For the absolute pressure method, a multiplicative error of a factor of four due to uncertainties in ionization cross section and electron multiplier efficiencies is considered a liberal estimate. This corresponds to an uncertainty of 5–6 kcal in the temperature range under investigation. The necessary estimates of entropy, together with possible errors in the literature, probably do not exceed 2 eu, or 4 kcal. Hence, the maximum error to be expected by this procedure is ± 10 kcal, and the probable error is ± 6 kcal. The error in the slope, estimated by the scatter in the data, is ± 4 kcal, for ZrO₂.

Discussion and Conclusions

It is evident from the data presented here that Hoch, Nakata, and Johnston were observing ZrO(g) and TaO(g) effusing from their Knudsen cell, and hence it is not surprising that the total weight of material leaving the crucible in unit time should be approximately the

TABLE II.	Heats	of sublimation	obtained	by	the slope	method.

	Sample environment	Temp. range, °K	$\Delta H_T^{\circ}, \frac{\text{kcal}}{\text{mole}}$	$\Delta H_0^{\circ} \frac{\text{kcal}}{\text{mole}}$
ZrO ₂	ZrO ₂ in ThO ₂ ZrO ₂ crucible ZrO ₂ (s) in ZrO ₂ crucible	2245–2504 2250–2450 2200–2430 2200–2430	169.5 172.0 169.5 173.7	186.5 189.0 186.5 190.8
			Av	188.2

⁸ K. K. Kelley, "Contributions to the data on theoretical metallurgy. X. High-temperature heat-content, heat-capacity and entropy data for inorganic compounds," U. S. Bur. Mines Bull. 476 (1949).

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same under both their experimental conditions. The earlier mass spectrometric observation of ZrO2 reported by Starodubtsev and Timokhina² also appear rather dubious on two counts:

(1) Zr has a characteristic isotopic structure which is not evident in their mass spectrum, although their quoted resolution should be adequate to observe this.

(2) The appearance potential obtained in our experiments on $(ZrO_2)^+$, 8 ± 0.5 ev, would make surface ionization an extremely inefficient technique for producing these ions.

By appropriate combination of thermodynamic data on the enthalpy of formation of $ZrO_2(s)$,⁶ heat of sublimation of zirconium,⁷ dissociation energy of oxygen,⁹ and the values currently obtained for the

⁹ P. Brix and G. Herzberg, Can. J. Phys. 32, 110 (1954).

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sublimation energies of ZrO₂ and ZrO, we may compute the dissociation energies of these species. For the case of ZrO,

$\frac{1}{2}$ Zr(s) $+\frac{1}{2}$ ZrO ₂ (s) \rightarrow ZrO(g);	$\Delta H_0^{\circ} = 151 \text{ kcal}$
$\frac{1}{2}$ Zr(s) $+\frac{1}{2}$ O ₂ (g) $\rightarrow \frac{1}{2}$ ZrO ₂ (s);	$\Delta H_0 = -131$ kcal
$\operatorname{Zr}(g) \rightarrow \operatorname{Zr}(s);$	$\Delta H_0 = -142$ kcal
$O(g) \rightarrow \frac{1}{2}O_2(g);$	$\Delta H_0 = -59.0 \text{ kcal}$
$\operatorname{Zr}(g) + \operatorname{O}(g) \rightarrow \operatorname{ZrO}(g);$	$\Delta H_0^{\circ} = -181 \frac{\text{kcal}}{\text{mole}}$
	$D_0 = 7.8 \text{ ev}$

If there exists a ZrO(s) phase at elevated temperatures, its heat of formation from Zr(s) and $ZrO_2(s)$ is probably negligible in comparison with other errors in this determination. For ZrO2, a similar calculation yields $D_0 = 14.5$ ev. Hence, the second Zr-O band is weaker than the first by about 1 ev.

VOLUME 26, NUMBER 5

MAY, 1957

Relaxation-Time Model for Free-Radical Concentration*

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The accuracy of the quasi-equilibrium approximation in chemical kinetic studies is examined using a relaxation-time model. Two distinct cases arise: the time-lag case and the diffusion case. In each case, the proposed model leads to exactly the same result as an approximate mathematical treatment.

The kinetic processes in a flame front are examined, and are shown to involve both the time-lag and diffusion cases. Again, the model is justified by an independent approximate method. The model is next examined in that region of the flame where the kinetic processes are most important, that is, near the point of maximum reaction rate. A very simple expression is found for the radical concentration at this point. This expression is justified through numerical examples.

INTRODUCTION

HE concentration of free radicals in a reacting system, and with this an enumeration of the reaction rates, has often been calculated by means of the quasi-equilibrium (steady-state) approximation. The validity of this approximation can be determined only under special circumstances. The obvious approach is to set up and solve the complete chemical change equations. Only a few simple cases have been solved by this method because of severe mathematical limitations.¹ Another approach, more general but not exact, attempts to find the first few correction terms describing the departure from quasi-equilibrium values. Both static reacting systems² and those with mass flow³ (flames) have been treated by this general method.

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¹ S. W. Benson, J. Chem. Phys. 20, 1605 (1952).
² J. O. Hirschfelder, University of Wisconsin Naval Research Laboratory Report ONR-21 (April, 1956).
³ J. C. Giddings and J. O. Hirschfelder, University of Wisconsin Naval Research Laboratory Report SQUID-5 (May, 1956).

As another approach to this problem, we have used a relaxation-time model to formulate equations giving an estimate of the departure from the quasi-equilibrium condition. The model permits the calculation of activeparticle concentration in chemically reacting systems with or without temperature and concentration gradients. The study of radical processes in flames is particularly adaptable to this procedure. If a number of assumptions are made concerning the nature of flame propagation, one needs only the reaction rates of the contributing chemical processes in order to make a good estimation of the free-radical concentration in the reaction zone of a flame front.

The equations which are derived yield a value for the radical's mole fraction under quite general conditions, but two special cases appear. In the time-lag case, one assumes that the radicals do not diffuse away from the surrounding volume element, but the mixture in the volume element is going through both a temperature and a composition change. The diffusion case applies when a given volume element is undergoing no change, but radicals are diffusing from one to another element.

^{*} This work was carried out at the University of Wisconsin Naval Research Laboratory under Contract N6-ori-105 with the Office of Naval Research.

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