

THE DISPROPORTIONATION OF ZIRCONIUM TRICHLORIDE

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[Manuscript received May 28, 1963]

Summary

Equilibrium pressures of the reaction $2\text{ZrCl}_3(\text{c}) \rightarrow \text{ZrCl}_2(\text{c}) + \text{ZrCl}_4(\text{g})$ measured by a cooling curve modification of the dew-point technique are fitted over the range 613–723°K, by the relation

$$\log_{10} p_{\text{mm}} = -6246/T + 11.632 \pm 0.05 \text{ (S.D.)}$$

Derived thermochemical data are $\Delta H_{298} = 30.1 \pm 0.5$ kcal and $\Delta S_{298} = 39.1 \pm 1$ e.u., consistent with estimated $\Delta H_{f298}\text{ZrCl}_3 = -186$ kcal/mole and $\Delta H_{f298}\text{ZrCl}_4 = -136$ kcal/mole, $S_{298}\text{ZrCl}_3 = 36.4$ e.u. and $S_{298}\text{ZrCl}_2 = 28.3$ e.u.

INTRODUCTION

The trihalides of the Group IV and V metals have all been shown to disproportionate on heating, so that their entropy and enthalpy of formation may be found by a study of the equilibrium pressures of the volatile higher halides.

This assumes particular importance for zirconium and hafnium, which may be separated by selective disproportionation of the trichlorides.¹ From preparative studies it appears that ZrCl_3 becomes appreciably converted to ZrCl_2 and ZrCl_4 above 330° (Ruff and Walstein²), 300° (Newnham¹), or 450° (Larsen and Leddy³). The preparation of pure ZrCl_3 by atomic hydrogen reduction (Newnham and Watts⁴) has now enabled a quantitative study of its disproportionation.

Recently, Schläfer and Skoludek⁵ reported the equilibrium pressure of ZrBr_4 over ZrBr_3 . Although equilibrium could only be reached from low pressures and some reaction with the glass vessel was suspected, the pressure-temperature relation appeared to be independent of solid-phase composition within the limits ZrBr_3 to ZrBr_2 , indicating a simple two-phase solid. A similar study of TiCl_3 by Sanderson and MacWood⁶ indicated a two-phase solid in the composition range TiCl_3 to $\text{TiCl}_{2.5}$, but a single-phase solid solution in the range $\text{TiCl}_{2.5}$ to TiCl_2 . For TiBr_3 Hall and Blocher⁷ found solid solution limits of $\text{TiBr}_{3.0}$ to $\text{TiBr}_{2.9}$ at 450° and $\text{TiBr}_{3.0}$ to $\text{TiBr}_{2.0}$ above 600°. Finally, Schäfer and Dohmann⁸ have shown that the equilibrium pressure of NbCl_5 over niobium trichloride varies with composition in the range $\text{NbCl}_{2.67}$ to $\text{NbCl}_{3.13}$ at 355°, indicating again a single-phase region.

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¹ Newnham, I. E., *J. Amer. Chem. Soc.*, 1957, **79**, 20, 5415.

² Ruff, O., and Wallstein, R., *Z. anorg. Chem.*, 1923, **128**, 96.

³ Larsen, E. M., and Leddy, J. J., *J. Amer. Chem. Soc.*, 1956, **78**, 5983.

⁴ Newnham, I. E., and Watts, J. A., *J. Amer. Chem. Soc.*, 1960, **82**, 2133.

⁵ Schläfer, H. L., and Skoludek, H., *Z. Electrochem.*, 1962, **66**, 367.

⁶ Sanderson, B. S., and MacWood, G. E., *J. Phys. Chem.*, 1956, **60**, 316.

⁷ Hall, E. H., and Blocher, J. M., *J. Phys. Chem.*, 1959, **63**, 1525.

⁸ Schäfer, H., and Dohmann, K., *Z. anorg. Chem.*, 1959, **300**, 1.

It is probable that most of the Group IV and V lower halides are derived from the $\text{Cd}(\text{OH})_2$ -type structure. The dihalides consist of hexagonally close-packed arrays with metal atoms occupying alternate layers of octahedral holes, while systematic absence of a third of the metal atoms occurs in the trihalides, e.g. TiCl_3 .⁹ On this model, single phase non-stoichiometric composition ranges due to random metal atom absences appear quite likely, although it is not obvious why such ranges should be found for Nb-Cl and Ti-Br only. Such metal absences are associated with very slight changes in lattice dimensions, so that very precise X-ray measurements are required to reveal them. In the present work, comparison of X-ray powder patterns of $\text{ZrCl}_{3.0}$ and $\text{ZrCl}_{2.67}$ was inconclusive, as also were the X-ray studies of ZrI_3 and $\text{ZrI}_{2.55}$ by Watt and Baker.¹⁰

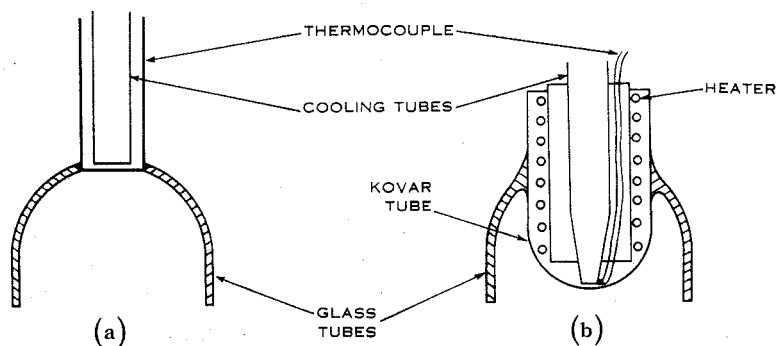


Fig. 1.—Dew-point tubes.

Thus it was of interest to see whether disproportionation pressure studies revealed any single-phase compositions in the ZrCl_3 - ZrCl_2 range.

EXPERIMENTAL

(a) Materials

Finely divided, black ZrCl_3 was prepared by atomic hydrogen reduction of low-hafnium ZrCl_4 followed by vacuum removal of excess ZrCl_4 , H_2 , and HCl at 190° and 5×10^{-3} mmHg for 5-6 hr. Chemical analysis of the four samples used indicated a formula of $\text{ZrCl}_{3.0 \pm 0.02}$, and X-ray powder patterns revealed similar interplanar spacings to those reported by Larsen and Leddy.³

(b) Apparatus

The most successful method used was a cooling curve modification of the dew-point method (runs 1-3).

The sample was transferred in an argon-filled dry box (< 100 p.p.m. water and oxygen) to a long glass ampoule which was subsequently sealed under a vacuum of 10^{-3} mmHg. The other end of this ampoule was closed by a flattened Pt/Pt-13% Rh thermocouple junction (Fig. 1(a)). For a measurement, the temperature of the sample end of the ampoule was controlled to $\pm 0.5^\circ$ while the junction end was slowly cooled. The thermal e.m.f., partly compensated by a potentiometer, was recorded *v. time*. On reaching the saturation temperature corresponding to the ZrCl_4 pressure, condensation on the junction began, causing an inflection (Fig. 2(b)) or a thermal plateau (Fig. 2(a)) in the cooling curve. The lowest detectable pressure was 8 mmHg with a

⁹ Natta, G., Corradini, P., and Allegra, A., *Atti Accad. Lincei*, 1959, **26**, 155.

¹⁰ Watt, G. W., and Baker, W. A., *J. Inorg. Nucl. Chem.*, 1961, **22**, 49.

junction area of 9 mm² and a cooling rate of 3.8°/min. Both dew point and sample thermocouples were checked against a calibrated Pt/Pt-Rh thermocouple, giving temperatures to within ±0.5°, which corresponded to 0.2 mmHg at 290° and 12.5 mmHg at 420°. The ZrCl₄ pressures corresponding to measured dew-point temperatures were found from the vapour pressure relation of Palako, Ryon, and Kuhn¹¹

$$\log p_{\text{mm}} = -5400/T + 11.766 \quad (480-689^{\circ}\text{K}). \quad (1)$$

The heat of sublimation of ZrCl₄ derived from this relation is 24.7 ± 0.3 kcal/mole, which is in close agreement with measurements by Rogers¹² and by Rahlfs and Fisher¹³ by different methods.

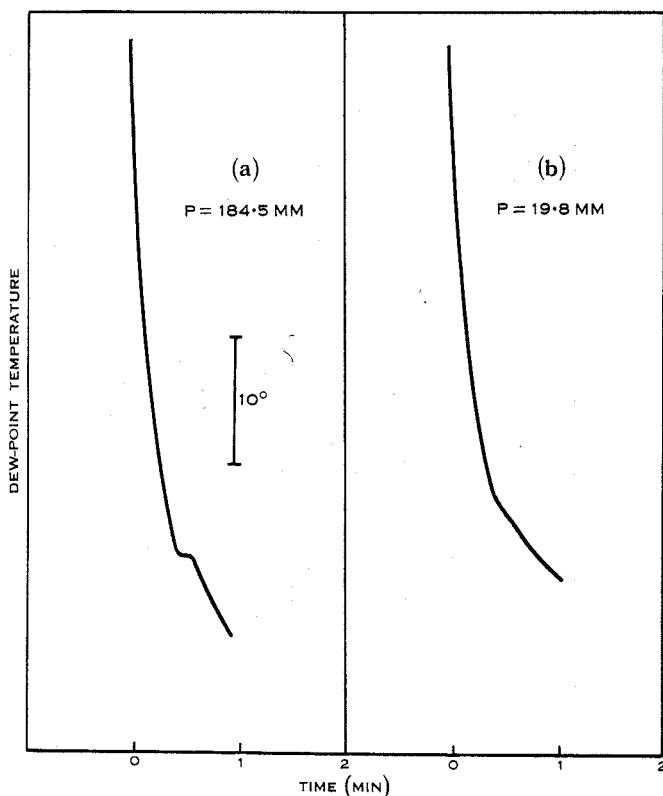


Fig. 2.—Cooling curves.

Condensation on the thermocouple itself avoided the possibility of temperature lags across the glass bulbs often used in dew-point methods (see Kellogg, Howell, and Somers¹⁴). However, it was possible to use an ampoule containing a Kovar bulb (Fig. 1(b)) with the usual visual observation of deposition to check the cooling-curve method (run 4).

Preliminary work with a bismuth-tin manometer method revealed that traces of H₂ or HCl were slowly desorbed from ZrCl₃ made by atomic hydrogen reduction. The dew-point method enabled ZrCl₄ pressures to be measured independently of H₂ or HCl and possible small ZrCl₃

¹¹ Palako, A. A., Ryon, A. D., and Kuhn, D. W., *J. Phys. Chem.*, 1958, **62**, 319.

¹² Rogers, B. A. *et al.*, U.S.A.E.C., 1949, ISC-45.

¹³ Rahlfs, O., and Fischer, W., *Z. anorg. Chem.*, 1933, **211**, 349.

¹⁴ Kellogg, H. H., Howell, L. T., and Sommers, R. C., U.S.A.E.C., 1956, NYO-3108.

pressures. Newnham¹ observed a slight black sublimate above 460° which may have been $ZrCl_3$, but this was not found up to 450° in the present work. Pressures of $TiCl_3$ ¹⁵ and $TiBr_3$ ⁷ are roughly 1/30 of their disproportionation pressures, indicating that $ZrCl_3$ vapour should have negligible effect on the observed condensation temperatures of $ZrCl_4$.

Four disproportionation pressures were also found by heating $ZrCl_3$ in an evacuated tube at fixed temperature for 48 hr and then quenching the $ZrCl_4$ at one end with a gas jet. The perfect gas law was used to find pressure from temperature, bulb volume, and the weight of $ZrCl_4$ found by chemical analysis.

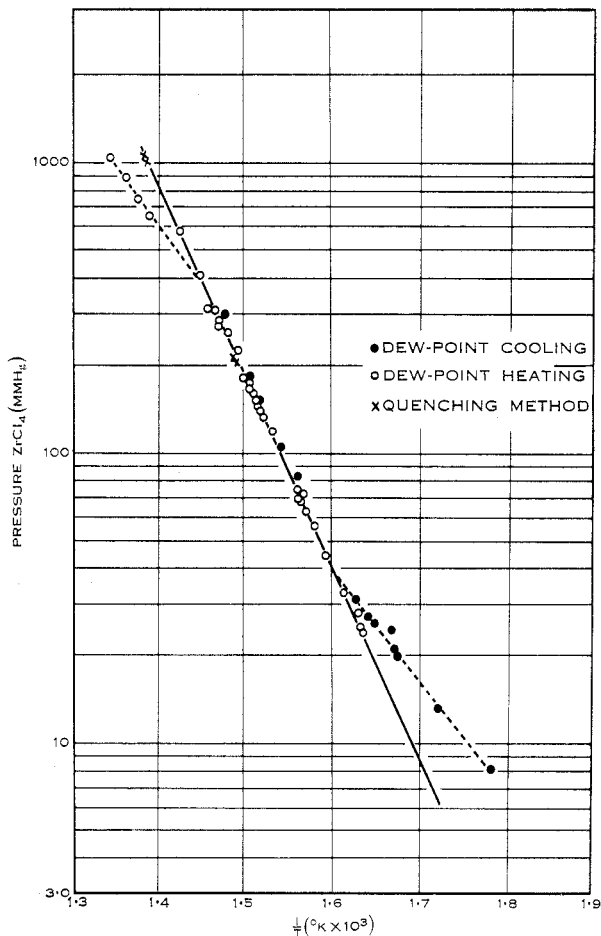


Fig. 3.—Disproportionation pressure of $ZrCl_3$.

RESULTS

Pressures of $ZrCl_4$ measured over the range 8 to 1020 mmHg, corresponding to 290 to 450° sample temperatures, are shown in Figure 3. The majority of the points are fitted by the following least-squares relation, with a standard deviation in log

¹⁵ Farber, M., and Darnell, A. J., *J. Phys. Chem.*, 1955, **59**, 156.

p_{mm} of 0.05,

$$\log_{10} p_{\text{mm}} = -6,246/T + 11.632. \quad (2)$$

It is notable that this equation fits equally well the results from both dew-point methods and the independent quenching method.

On initially heating a ZrCl_3 sample, constant pressures were attained in 3–4 hr at temperatures up to 420° . On subsequent cooling, constant pressures which fell on the same equilibrium line were only attained after some 200 hr. However, below 350° , pressures were still falling at 0.05 mm/hr after 270 hr, and equilibrium could not be attained. Linear rate curves for the ZrCl_4 – ZrCl_2 reaction were obtained by plotting Δp^2 against time, as also found by Busol¹⁶ for the ZrI_4 – Zr reaction. The activation energy obtained was about 45 kcal/mole. This falls within the range of values found for diffusion in metal oxides, 30 to 100 kcal/mole¹⁷ in agreement with rate control by diffusion of Zr through the ZrCl_3 lattice. In comparison, Schläfer and Skoludek⁵ failed to attain ZrBr_4 – ZrBr_2 equilibrium from higher pressures in times of 80 hr below 420° .

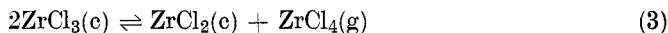
TABLE I
 $2\text{ZrCl}_3(\text{c}) \rightleftharpoons \text{ZrCl}_2(\text{c}) + \text{ZrCl}_4(\text{g})$

T (°K)	ΔG (kcal)	ΔH (kcal)	ΔS (cal/deg)	ΔC_p (cal/deg)
658	6.43 ± 0.3	28.6 ± 0.3	33.7 ± 0.6	–6.7
298	18.45 ± 0.5	30.1 ± 0.5	39.1 ± 1	–6.9

In run 4, divergence from equation (2) was found above 440° , indicating a change in the solid phase from $\text{ZrCl}_3 + \text{ZrCl}_2$ to $\text{ZrCl}_2 + \text{Zr}$ when all the initial ZrCl_3 was disproportionated. The solid phases obtained by quenching at the end of runs 2 and 3, which used larger samples than run 4, were analysed as $\text{ZrCl}_{2.54}$ and $\text{ZrCl}_{2.80}$. Thus, since pressures over solid compositions from ZrCl_3 to ZrCl_2 fit a single equilibrium line, there appears to be only a single two-phase system over this composition range at the temperatures used.

DISCUSSION

The phase-rule considerations of Schläfer and Skoludek⁵ and the assumption of negligible pressures of ZrCl_3 , ZrCl_2 , and Cl_2 indicate that equation (2) must refer to the equilibrium



Thermodynamic data for this reaction (Table I) were derived from the following relations, assuming ZrCl_4 to be an ideal gas.

¹⁶ Busol, F. I., *J. Phys. Chem. USSR*, 1959, **4**, 331, 779.

¹⁷ Kubaschewski, O., and Hopkins, B. E., "Oxidation of Metals and Alloys." (Butterworths: London 1962.)

$$\Delta G_T = RT \ln p \quad (4)$$

$$= \Delta H_T - T\Delta S_T \quad (5)$$

Values of ΔH_T and ΔS_T thus obtained for the average temperature, 658°K, were corrected to 298°K using an estimated ΔC_p for reaction (2). For $\text{ZrCl}_3(\text{c})$, C_p was estimated by substituting its estimated S_{298} into a linear relation between C_p and

TABLE 2
THERMODYNAMICS OF DISPROPORTIONATION

Reaction	ΔH_{298} (kcal)	ΔS_{298} (cal/deg)	Reference
$2\text{TiCl}_3 \rightarrow \text{TiCl}_2 + \text{TiCl}_4(\text{g})$	38.6 ± 0.4	42.5 ± 1.5	6
$2\text{TiBr}_3 \rightarrow \text{TiBr}_2 + \text{TiBr}_4(\text{g})$	34.8 ± 3	39.1 ± 2	7
$2\text{ZrCl}_3 \rightarrow \text{ZrCl}_2 + \text{ZrCl}_4(\text{g})$	30.1 ± 0.5	39.1 ± 1	Present work
$2\text{ZrBr}_3 \rightarrow \text{ZrBr}_2 + \text{ZrBr}_4(\text{g})$	24 ± 2	31 ± 3	5
$2\text{VCl}_3 \rightarrow \text{VCl}_2 + \text{VCl}_4(\text{g})$	33.5 ± 9	48.6 ± 5	22
$2\text{VBr}_3 \rightarrow \text{VBr}_2 + \text{VBr}_4(\text{g})$	40.8 ± 2	31.5 ± 1	23
$2\text{NbCl}_3 \rightarrow \text{NbCl}_2 + \text{NbCl}_4(\text{g})$	43.4 ± 10	42.6 ± 5	24

S_{298} found for TiCl_3 , VCl_3 , and UCl_3 . For $\text{ZrCl}_2(\text{c})$ and $\text{ZrCl}_4(\text{g})$, estimates by Glassner¹⁸ and Kelley¹⁹ were used.

The observed $\Delta H_{298} = 30.1 \pm 0.5$ kcal agrees, within expected errors, with $\Delta H_{298} = 36$ kcal calculated from $\Delta H_{f298} \text{ZrCl}_4(\text{c}) = -234.7$ ²⁰ and recent estimates by Brewer²¹ of $\Delta H_{f298} \text{ZrCl}_3(\text{c}) = 186$ and $\Delta H_{f298} \text{ZrCl}_2(\text{c}) = -130$. It appears that

TABLE 3
THERMODYNAMIC PROPERTIES OF ZIRCONIUM CHLORIDES

Compound	ΔH_{298}° (kcal)	S_{298}° (cal/deg)	C_p (cal/deg)	Reference
$\text{ZrCl}_4(\text{c})$	-234.7 ± 0.4	44.5 ± 0.5	$31.92 - 2.91/T^2$	22
$\text{ZrCl}_4(\text{g})$	-206.2 ± 2	86.5 ± 1.5	$25.60 + 0.16 \times 10^{-3}T$ $-2.04 \times 10^5/T^2$	19, 25
$\text{ZrCl}_3(\text{c})$	-186 ± 5	36.4 ± 2	$23.07 + 4.45 \times 10^{-3}T$	Present work
$\text{ZrCl}_2(\text{c})$	-136 ± 5	28.3 ± 2	$17.3 + 4.2 \times 10^{-3}T$	Present work

¹⁸ Glassner, A., U.S.A.E.C., 1959, ANL-5750.

¹⁹ Kelley, K. K., Bull. U.S. Bur. Min. No. 584.

²⁰ Gross, P., Haymann, C., and Levi, D. L., *Trans. Faraday Soc.*, 1957, **53**, 1601.

²¹ Brewer, L., personal communication, 1962.

²² Kubaschewski, O., and Evans, E. L. I., "Metallurgical Thermochemistry." (Pergamon: London 1959.)

²³ McCarley, R. E., and Roddy, J. W., U.S.A.E.C., 1962, IS-500.

²⁴ Schäfer, H., and Kahlenberg, E., *Z. anorg. Chem.*, 1960, **305**, 291.

²⁵ Kelley, K. K., Bull. U.S. Bur. Min. No. 592.

Zr-Cl bond energies in the three solid zirconium chlorides are quite similar, so that the major part of ΔH_{298} is due to the sublimation heat of ZrCl_4 (28.5 kcal).²²

The observed $\Delta S_{298} = 39.1 \pm 1$ e.u. is in close agreement with $\Delta S_{298} = 42 \pm 5$ e.u. calculated from $S_{298}\text{ZrCl}_4(\text{g}) = 86.5^{19}$, $S_{298}\text{ZrCl}_3(\text{c}) = 36.4$, $S_{298}\text{ZrCl}_2(\text{c}) = 28.3$ estimated from Latimer's rules.²² Once again, almost all of ΔS_{298} is due to the sublimation entropy of ZrCl_4 (Table 3, 42 e.u.).

In Table 2, ΔH_{298} and ΔS_{298} are compared with values for analogous disproportionations, and it is seen that all values lie within relatively narrow limits, $\Delta H_{298} = 35 \pm 10$ kcal and $\Delta S_{298} = 40 \pm 10$ e.u. Also ΔH_{298} and ΔS_{298} values for the chlorides of zirconium and titanium are greater than for the bromides, in agreement with the similar chemical behaviour. The thermochemical properties of zirconium chlorides most consistent with this and other work are collected in Table 3.

ACKNOWLEDGMENTS

The authors are grateful to Professor L. Brewer for his estimates of thermodynamic data.