Standard Free Energy, Enthalpy, and Entropy of Formation of Titanium Hydride

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The standard free energies of formation of titanium hydride TiH_y were determined for $y = 1.252-1.660$ and $T = 673-823$ K from published experimental data on absorption of hydrogen in titanium. The standard enthalpy and entropy of formation of $TiH_{1.66}$ were estimated from the temperature variation of the standard free energies of formation.

The standard properties of formation of titanium hydride have been given few measurements. The heat of combustion of $TiH_{1.73}$ was measured by Sieverts and Gotta.[1] C_p for $TiH_{1.97}$ between 24 and 363 K was measured by Stalinski and Bieganski.[2,3] The heat of dissociation of TiH_y ($y = 1.75-1.93$) was measured by Gibb, McSharry, and Bragdon.[4] The integral heat of mixing for $TiH_{1.73}$ at 723 K was determined from the measurement of equilibrium pressure of hydrogen over titanium-hydrogen by Haag and Shipko.[5] Apparently, no other direct measurements of the standard properties of formation have been reported. So, it is felt that a determination of these properties, in particular the free energy of formation, based on published experimental data is worth reporting. In the following determination of the standard free energy, enthalpy, and entropy of formation of TiH_y ($y = 1.252-1.660$), McQuillan's data[6] on a relationship between the equilibrium pressure of hydrogen and the hydrogen content in titanium were used.

Method for Determining the Standard Free Energy of Formation of TiH_y

The Gibbs–Duhem relationship in the Ti–H system under isothermal isobaric conditions is $X_{Ti} dG_{Ti} + X_H dG_H = 0$, which can be rearranged to

$$X_{Ti} dG_{Ti} + X_H RT d \ln P_{H_2}^{1/2} = 0 \qquad (1)$$

where R is the gas constant, T is the absolute temperature, X_i is the mole fraction of component i, G_i is the partial molar free energy, and P_{H_2} is the pressure of hydrogen gas equilibrated with the solid system. In deriving the last equation, we used the equality $G_H(\text{in solid}) = G_{H_2}/2$ ($=$ constant $+ RT \ln P_{H_2}^{1/2}$) (in ideal gas), by virtue of the second law of thermodynamics. Upon dividing by X_{Ti} ($= 1 - X_H$) and integrating eq 1, we obtain

$$G_{Ti} - G_{Ti}^\circ = -RT \int_0^{P_{H_2}^{1/2}} \frac{X_H dP_{H_2}^{1/2}}{(1 - X_H)P_{H_2}^{1/2}} \qquad (2)$$

The standard free energy of formation of TiH_y is defined as

$$\begin{aligned}
\Delta G_f^\circ &= \sum_{\text{prod}} G_p^\circ - \sum_{\text{reac}} G_r^\circ \\
&= (G_{Ti} + yG_H) - (G_{Ti}^\circ + yG_{H_2}^\circ/2) \\
&= (G_{Ti} - G_{Ti}^\circ) + y(G_H - G_{H_2}^\circ/2) \qquad (3)
\end{aligned}$$

where the standard state for Ti is hydrogen-free pure α-titanium under 1 atm and the standard state for hydrogen gas is pure hydrogen gas of 1 atm pressure. With the aid of eq 2 and G_H

$- G_{H_2}^\circ/2 = (G_{H_2} - G_{H_2}^\circ)/2 = RT \ln P_{H_2}^{1/2}$ on the assumption that hydrogen gas be ideal, eq 3 becomes

$$\Delta G_f^\circ = -RT \int_0^{P_{H_2}^{1/2}} \frac{X_H dP_{H_2}^{1/2}}{(1 - X_H)P_{H_2}^{1/2}} + yRT \ln P_{H_2}^{1/2} \qquad (4)$$

Note that P_{H_2} in the second term of the right-hand side of eq 4 should be measured in the unit of atmospheres because of the 1 atm standard state of hydrogen gas. The standard enthalpy and entropy of formation can be estimated from the relations

$$\Delta H_f^\circ = \partial(\Delta G_f^\circ/T)/\partial(1/T) \qquad (5)$$

$$\Delta S_f^\circ = -\partial \Delta G_f^\circ/\partial T \qquad (6)$$

Calculated Results and Discussion

In Figure 1, the integrand of eq 4 is plotted against $P_{H_2}^{1/2}$ for $T = 773$ K, whose data points were taken from ref 6 and are tabulated in Table I. In Table I, McQuillan's data for other temperatures, which were used to make a graphical integration by eq 4, are also listed. Table II lists the values of ΔG_f° of TiH_y at 773 K, calculated by integration along the smoothed curve in Figure 1. Table III lists the values of ΔG_f° of $TiH_{1.66}$ between 673 and 823 K, which are plotted in Figure 2. For $T = 673$ and 723 K, McQuillan's data on the variation of log P_{H_2} with $1/T$ were linearly extrapolated to lower temperatures in order to make a graphical integration by eq 4. Table III also lists the values of ΔH_f° and ΔS_f° of $TiH_{1.66}$, which were calculated from the temperature variation of ΔG_f°, according to eq 5 and 6. In Tables II and III, the errors of ΔG_f° represent the difference between the ΔG_f° value shown therein and that value which was obtained from integration along straight lines tying two neighboring data points in Figure 1 and Table I. In addition to these errors, errors in the measurement of X_H and P_{H_2} should be included. According to a simple calculation in which eq 4 is treated as a function of two independent variables X_H and P_{H_2}, the ΔG_f° error associated with the measurement errors of X_H and P_{H_2} for $TiH_{1.66}$ at 773 K is estimated to be $90\delta X_H^{\beta/\alpha}$ (kJ/mol), where $\delta X_H^{\beta/\alpha}$ is the error in the measurement of X_H in the β phase equilibrated with the α phase. In the above estimation, no error of X_H has been assumed in the α phase. Therefore, if $\delta X_H^{\beta/\alpha}$ is 2% of $X_H^{\beta/\alpha}$ for $X_H^{\beta/\alpha} = 0.277$, then $\delta \Delta G_f^\circ = \pm 0.5$ kJ/mol, which is comparable with the errors listed in Table I.

In Table III, other measurements[1,3,5] of ΔH_f° and ΔS_f° are also listed. In ref 1 and 3, the values for 298 K are based on measurements of the heat of combustion and the C_p°, respectively. Reference 7 has estimated the high-temperature C_p° values of $TiH_{1.97}$ by using the C_p° data[1,3] below 360 K. If one neglects the small difference[1,3] in C_p° between $TiH_{1.97}$ and $TiH_{1.66}$, ΔC_p° from ref 7 allows the estimation of ΔH_f° and ΔS_f° for $TiH_{1.66}$ at 773 K from the corresponding quantities[3] at 298 K in the following manner. From ref 3, ΔH_f° and ΔS_f° for $TiH_{1.66}$ at 298 K are estimated to be 116 kJ/mol and 109 J/(mol K). From ref 7, $\int_{298}^{773} \Delta C_p^\circ$ $dT = -1.8$ kJ/mol and $\int_{298}^{773} \Delta C_p^\circ$ d ln $T = -5.4$ J/(mol K). Accordingly, ΔH_f°, ΔS_f°, and ΔG_f° for $TiH_{1.66}$ at 773 K are -118 kJ/mol, -114 J/(mol K), and -29.5 kJ/mol, respectively. These values are in fair agreement with

Table I. Tabulation of McQuillan's Data[6] Used for Integration in Equation 4[a-e]

T/K	X_H	$(P_{H_2}/Pa)^{1/2}$	$\dfrac{X_H/(1-X_H)\cdot}{(P_{H_2}/Pa)^{1/2}}$	phase
673	0	0	0.0284	α
673	0.081	2.85	0.0309	α/β
673	0.334	2.85	0.1759	β/α
673	0.350	3.31	0.1626	β
673	0.410	4.94	0.1406	β
673	0.441	5.80	0.1360	β
673	0.465	7.10	0.1224	β/γ
673	0.519	7.10	0.1519	γ/β
673	0.593	14.48	0.1006	γ
673	0.613	34.08	0.0465	γ
673	0.624	72.29	0.0230	γ
723	0	0	0.0163	α
723	0.083	5.09	0.0177	α/β
723	0.304	5.09	0.0859	β/α
723	0.350	7.12	0.0756	β
723	0.410	10.64	0.0653	β
723	0.441	12.76	0.0618	β
723	0.471	16.51	0.0539	β
723	0.486	19.71	0.0480	β/γ
723	0.541	19.71	0.0598	γ/β
723	0.593	37.55	0.0388	γ
723	0.613	73.04	0.0217	γ
723	0.624	128.9	0.0129	γ
773	0	0	0.0100	α
773	0.083	8.30	0.0109	α/β
773	0.277	8.30	0.0461	β/α
773	0.287	9.18	0.0438	β
773	0.350	13.75	0.0391	β
773	0.410	20.58	0.0337	β
773	0.441	25.38	0.0311	β
773	0.471	33.30	0.0267	β
773	0.490	47.47	0.0202	β/γ
773	0.556	47.47	0.0264	γ/β
773	0.593	79.05	0.0184	γ
773	0.613	131.4	0.0120	γ
773	0.624	199.6	0.0083	γ
823	0	0	0.0065	α
823	0.086	13.12	0.0071	α/β
823	0.249	13.12	0.0253	β/α
823	0.287	16.73	0.0241	β
823	0.350	24.94	0.0216	β
823	0.410	37.41	0.0186	β
823	0.441	42.02	0.0188	β
823	0.471	61.38	0.0145	β
823	0.490	86.47	0.0111	β
823	0.492	106.9	0.0091	β/γ
823	0.574	106.9	0.0126	γ/β
823	0.593	136.7	0.0107	γ
823	0.613	209.6	0.0076	γ
823	0.624	274.2	0.0061	γ

[a] α/β means "α in equilibrium with β". [b] For 673 and 723 K, the $(P_{H_2}/Pa)^{1/2}$ values in the β and γ phases have been obtained by linear extrapolation of McQuillan's data from higher temperatures. [c] The α-phase data are based on McQuillan's formulation, $P_{H_2}/mmHg = (9.616 \times 10^7)(X_H)^2 \exp(-21600/1.987T)$, where 1 mmHg = 133.3 Pa. [d] Except in footnote c, the data were taken from Figures 2, 3, and 4 of McQuillan. [e] McQuillan used iodide-decomposed Ti of >99.93% purity and H_2 produced by heating titanium hydride.
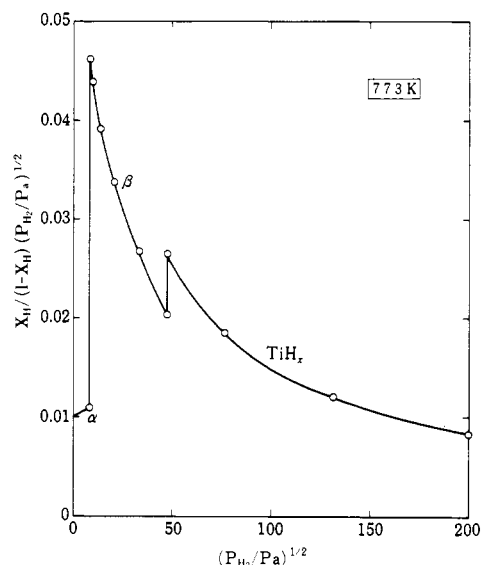
Table II. Standard Free Energy of Formation of TiH_y at 773 K

y	$\Delta G_f^\circ/(kJ/mol)$
1.252	-23.4 ± 0.1^a
1.457	-25.6 ± 0.2^a
1.584	-26.6 ± 0.3^a
1.660	-26.9 ± 0.4^a
2.000	-38.8^b

[a] See the text for the definition of errors. [b] Reference 7.

the present determination in Table III.

In ref 5, the ΔH_f° value for 723 K is based on the measurements (their own and McQuillan's[6]) of the equilibrium

Figure 1. Replotting of McQuillan's data[6] on hydrogen absorption in titanium at 773 K.
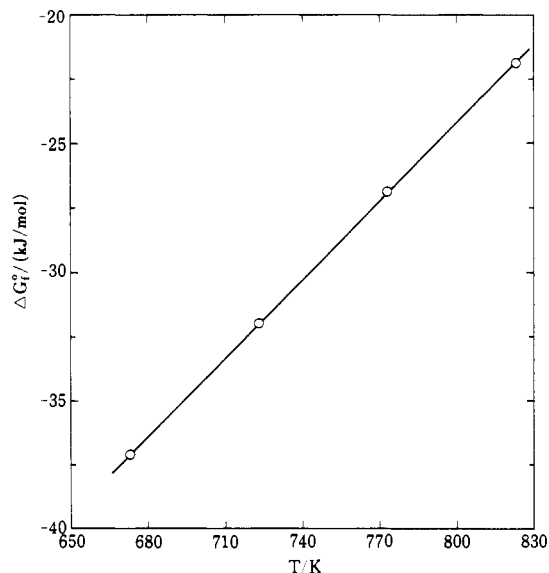
Figure 2. Temperature dependence of ΔG_f° of $TiH_{1.66}$.

Table III. Temperature Dependence of ΔG_f° of $TiH_{1.66}$ and Estimations of ΔH_f° and ΔS_f° of $TiH_{1.66}$

T/K	$\Delta G_f^\circ/(kJ/mol)$	$\Delta H_f^\circ/(kJ/mol)$	$\Delta S_f^\circ/(J/mol\ K)$
673	-37.2 ± 0.7^a		
723	-32.0 ± 0.5^a	$(-112)^c$	
773	-26.9 ± 0.4^a		
823	-21.9 ± 0.4^a		
673–823		-106 ± 4^b	-102 ± 5^b
298		$(-123),^d (-114)^e$	$(-105)^e$

[a] See the text for the definition of errors. [b] Maximum errors associated with the errors of ΔG_f° for 673 and 823 K calculated by use of eq 5 and 6. [c] Reference 5 for $TiH_{1.66}$. [d] Calculation by ref 7 based on the heat of combustion data for $TiH_{1.73}$ by ref 1. [e] Reference 3 for $TiH_{1.607}$.

pressure of hydrogen and is close to the present determination, though the method of determining ΔH_f° is somewhat different from the present method, eq 5.

The JANAF thermochemical tables[7] list ΔG_f° values for $TiH_{2.00}$, which are based on the data in ref 1, 2, and 4. The ΔG_f° value for the 773 K in the JANAF Tables is -38.8 kJ/mol, which considerably differs from the present determination for $TiH_{1.66}$. This large difference is considered to be attributed partly to the

difference in the number of hydrogen atoms in the compound formula and partly to inaccurate estimation of the difference between ΔH_f° for $TiH_{2.00}$ and that for $TiH_{1.73}$ in the JANAF tables.

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Ultrasound Study of Binary Mixtures of Acetone with Ethylene Glycol, Benzene, and Toluene

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Ultrasonic velocity, density, isentropic compressibility, and molecular association have been determined for binary liquid mixtures of acetone with ethylene glycol (I), benzene (II), and toluene (III) at different compositions. The temperatures of study were 23 °C in the former and 27 °C in the latter two. Excess density values are positive in each case. Excess compressibility is negative, except in the case of acetone and ethylene glycol in which it is negative in a mixture rich in ethylene glycol but becomes positive at compositions quite rich in acetone. Excess properties have been used to discuss the molecular interaction taking place between the components of mixtures. The associating nature of ethylene glycol leads to a stronger interaction in I while π electrons of aromatic rings are possibly involved in the interaction in II and III.

An ultrasound study of binary liquid–liquid mixtures has been made by some workers (9–11). The nonlinear behavior of ultrasound velocities and isentropic compressibilities with changing mole fractions are attributed to the difference in size of the molecule and the strength of interaction. Lagemann and Corry (4) discussed sound property as bond property while Fort and Moore (3) have compared the excess compressibility with excess volume. Prakash et al. (5) and Bhatgadde and Deshpande (2) discussed molecular interaction on the basis of excess free volume. This paper deals with the results obtained from the study of binary liquid mixtures acetone + ethylene glycol (I), acetone + benzene (II), and acetone + toluene (III) with regards to the ultrasound velocity, density, isentropic compressibility, and molecular association. Excess values of density and compressibility also have been reported.

Experimental Section

Materials. All chemicals used were AR (BDH) grade and were redistilled and further purified by standard methods described by Weissberger (12). The calculated volumes of liquids were added to one another to get mixtures of different known compositions. The mixtures were kept for 2 h and then they were used for velocity measurements. Water at fixed temperature was circulated around the ultrasound cell for maintaining the temperature within ±0.05 °C during the experiment.

Sound Velocity Measurements. The ultrasound velocities were measured at 5 MHz by using the Debye–Sears (1) light diffraction method. The details of instrumental technique have

been described previously (6). The maximum uncertainty in the velocity measurements was ±0.18%. The maximum error in the compressibility values is ±0.4% and the error in mole fraction is not more than 0.05%.

Density Measurements. The densities of pure liquids and liquid mixtures were determined in a 10-mL calibrated density bottle. To avoid temperature variation, we kept the solution bottles in a container with a thermostat maintaining constant temperature through an electric relay system. The densities were reproducible to 1 part in 10^4.

Results and Calculations

For any homogeneous nondissipative liquid system, the velocity (v) for the compressed acoustic wave is related to the density (ρ) and isentropic compressibility (β_s) of the medium by the well-known equation

$$v = (\rho \beta_s)^{-1/2} \qquad (1)$$

Molecular association was determined by Prakash et al. (7) by using the expression

$$\text{molecular assocn} = [(v^2_{exptl}/v^2_{calcd}) - 1] \qquad (2)$$

where v_{calcd}, velocity in the mixture, is given by

$$\left(\frac{1}{x_1 M_1 + x_2 M_2}\right)\frac{1}{v^2_{calcd}} = \left(\frac{x_1}{M_1 v_1^2} + \frac{x_2}{M_2 v_2^2}\right) \qquad (3)$$

where x_1 and M_1 are mole fraction and molecular weight, respectively, for acetone and x_2 and M_2 are the same properties for the second component of the mixtures.

The excess properties are given by the relation

$$A^E = A_{exptl} - A_{id} \qquad (4)$$

where $A_{id} = (x_1 A_1 + x_2 A_2)$ and A^E represents the excess property under consideration.

The mole fractions, ultrasound velocities, densities, isentropic compressibilities, molecular association, and excess values of compressibilities and densities are listed in Table I. Each set of results was fitted with a Redlich–Kister (8) form of the type

$$A^E = x(1 - x)\sum_{j=1}^{n} a_j(1 - 2x)^{j-1} \qquad (5)$$

where a_j = polynomial coefficients and n = polynomial degree.