

A TEST OF THE APPLICABILITY OF THE SIMPLE STATISTICAL-THERMODYNAMIC APPROACH TO EQUILIBRIUM CONSTANTS OF GAS-PHASE REACTIONS*

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Equilibrium constants of 33 chemical reactions, with components in the gas phase or in both gas and solid phases, were calculated by means of partition functions according to the rigid rotator and harmonic oscillator approximations. The form of the partition functions was so chosen as to suit molecular parameters given by quantum chemical methods. The agreement of calculated with observed equilibrium constants proves the utility of the simple statistical-thermodynamic treatment.

Equilibrium constants of gas-phase reactions, K_p , can be determined in the well-known way¹⁻⁴, making use of partition functions based on the experimentally estimated zero-point energy and molecular constants inferred from spectroscopic data. This procedure becomes independent of experiment if molecular constants can be estimated from a theoretical potential function. Such treatments, making use of empirical, semiempirical, or *ab initio* potential energy functions, have, however, been very rare⁵⁻⁹. Quantum chemical methods make it possible to calculate molecular constants^{10,11} that are associated with the potential function proper (heats of formation, barriers to internal rotation), its first derivative (molecular geometry), and its second derivative (harmonic modes of vibration). Finer effects, however, such as those giving rise to anharmonicity of vibrations are inaccessible by present quantum chemical methods; the inadequacy both of method and of numerical techniques prohibit the necessary evaluation of the third and higher derivatives of a potential-energy function. For the present the source of theoretical partition functions is thus restricted to the rigid rotator and harmonic oscillator assumptions (hereafter referred to as RRHO). This circumstance dictates the use of the simple RRHO model, in spite of the availability of a more advanced statistical-thermodynamic apparatus.

The goal of this paper is to estimate the accuracy attainable by current quantum chemical methods in calculations of equilibrium constants of gas-phase reactions. As limiting values we consider the K_p 's given by the RRHO model, making use of recent observed molecular characteristics (theoretically these values are attainable in an ideal case if quantum chemical methods closely reproduce the observed molecular characteristics). Calculations of this type have of course been performed³ rather frequently,

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but they lack uniformity in both the partition function approximation used and in the reliability of molecular constants adopted. In this paper we present the comparison between experimental equilibrium constants and those calculated by the RRHO approximation, making use of recently obtained molecular constants.

CALCULATIONS

The theoretical approach to the equilibrium constant, K_p , of a chemical reaction between the gas-phase reactants A_i with stoichiometric factors ν_i

$$\sum_i \nu_i A_i(g) = 0, \quad (1)$$

and the approximations used for partition functions in the present paper have been described in the Appendix of ref.⁸. Reaction components are considered as ideal gases. The standard state is chosen as a state of a pure component at 1 atm pressure. Assuming ideal behaviour, the equilibrium constant is determined by the partial pressures of the components:

$$K_p = \prod_i p_i^{\nu_i}. \quad (2)$$

In terms of partition functions of components, Q_i^0 , the K_p can be expressed as follows:

$$K_p = \prod_i (Q_i^0/N_A)^{\nu_i} \exp(-\Delta H_0^0/RT). \quad (3)$$

Here Q_i^0 is a partition function of the A_i component at the standard pressure ($p = 1$ atm) within the RRHO approximation (see Appendix of ref.⁸), N_A is the Avogadro number, R is the gas constant and ΔH_0^0 stands for the reaction enthalpy at absolute zero. The reaction enthalpy at any temperature T can be evaluated by the following formula:

$$\Delta H_T^0 = \Delta H_0^0 + RT^2 \sum_i \nu_i (\partial \ln Q_i^0 / \partial T)_p. \quad (4)$$

With heterogeneous reactions (components in gas or solid phase) the partition function for a solid-state component was simulated by means of its experimental thermodynamic potential, $\phi_{T,i}^0$, by making use of the following formula

$$\phi_{T,i}^0 = - \frac{G_{T,i}^0 - H_{0,i}^0}{T} = R \ln (Q_i^0/N_A). \quad (5)$$

$\phi_{T,i}^0$ was expressed on the basis of experimental data in the form of expansion of T .

Molecular characteristics for the components of the systems studied were taken from the literature, as stated in Table I. In constructions of partition function, we used the harmonic frequencies throughout; if they were not available we used the fundamental ones. For molecules with hindered rotation (CH_3OH , C_2H_6 , $\text{C}_2\text{H}_5\text{OH}$) we made use of the potential function with three equivalent minima; the corresponding torsion frequencies for $\text{C}_2\text{H}_5\text{OH}$ were determined from the heights of barriers of hindered rotation¹². With the gas-phase reactions the ΔH_0^0 values were inferred from the observed ΔH_{298}^0 through Eq. (4) by making use of the same partition functions as in

calculations of K_p . The ΔH_0^0 's for solid-phase components were determined from the heats of formation at absolute zero.

RESULTS AND DISCUSSION

The calculations undertaken cover 33 reactions, 26 of them being gas-phase reactions and 7 having components in both gas and solid phases. The reactions chosen are limited to those in which ΔH_0^0 could be determined by a method other than the temperature dependence of the corresponding $\log K_p$. For the comparison of experimental and calculated equilibrium constants, we selected the following coefficient

TABLE I

References to Molecular Characteristics Used in Calculations

G molecular geometry, ω vibrational frequencies, V_0 barrier to internal rotation, ϵ electronic energy levels, ΔH_{f298}^0 heat of formation, Φ_T^0 thermodynamic potential.

Compound	G	ω	ϵ	ΔH_{f298}^0	Compound	G	ω	ΔH_{f298}^0
H(g)	—	—	—	14	HBr(g)	17	16	14
F(g)	—	—	15	14	HI(g)	17	16	14
Cl(g)	—	—	16	14	IBr(g)	16	16	14
Br(g)	—	—	16	14	CO(g)	16	16	14
I(g)	—	—	16	14	H ₂ O(g)	17	16	14
H ₂ (g)	17	16	—	—	H ₂ S(g)	15	16	14
D ₂ (g)	17	16	—	—	CO ₂ (g)	17	15	14
N ₂ (g)	17	16	—	—	SO ₂ (g)	17	16	16
O ₂ (g)	17	16	16	—	NH ₃ (g)	17	16	14
F ₂ (g)	17	16	—	—	P ₄ (g)	16	16	14
P ₂ (g)	17	16	—	14	SO ₃ (g)	17	16	16
Cl ₂ (g)	15	15	—	—	CH ₄ (g)	16	16	14
S ₂ (g)	16	16	16	14	CH ₃ Cl(g)	17	16	14
Br ₂ (g)	16	16	—	14	CH ₃ Br(g)	17	16	14
I ₂ (g)	16	16	—	14	C ₂ H ₄ (g)	16	18	14
HD(g)	17	16	—	14	CH ₃ OH(g) ^a	19	18	14
HCl(g)	17	16	—	14	C ₂ H ₆ (g) ^b	17	18	14
DCl(g)	16	16	—	14	C ₂ H ₅ OH(g) ^c	22	23	14

Compound	Φ_T^0	Compound	ΔH_{f298}^0	Φ_T^0	Compound	ΔH_{f298}^0	Φ_T^0
C(s)-graphite	16	CaO(s)	16 ^d	16	β -Fe ₃ O ₄ (s)	25 ^d	25
α -Fe(s)	24	FeO(s)-wüstite	25 ^d	25	CaCO ₃ (s)-calcite	26	27

^a For CH₃OH(g) V_0 ref.²⁰; ^b C₂H₆(g) V_0 ref.²¹; ^c C₂H₅OH(g) V_0 ref.²³; ^d ΔH_{f0}^0 .

TABLE II
Comparison of Experimental and Calculated Equilibrium Constants

No	Reaction	Number of experimental values <i>n</i>	Temperature range, K	Average difference ^a , %
1	$\text{H}_2(\text{g}) \rightleftharpoons 2 \text{H}(\text{g})$	9 ²⁸	1800–2600	–10.2
2	$\text{H}_2(\text{g}) + \text{D}_2(\text{g}) \rightleftharpoons 2 \text{HD}(\text{g})$	6 ²⁹	298–741	0.05
3	$\text{F}_2(\text{g}) \rightleftharpoons 2 \text{F}(\text{g})$	36 ^{30,31}	513–1155	0.06
4	$\text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{Cl}(\text{g})$	5 ³²	1335–1973	18.4
5	$\text{Br}_2(\text{g}) \rightleftharpoons 2 \text{Br}(\text{g})$	6 ³³	1073–1323	–4.6
6	$\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g})$	35 ^{34–37}	732–1473	1.7
7	$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{g})$	1 ³⁸	1829	4.9
8	$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$	3 ³⁹	1297–1495	–2.3
9	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$	4 ⁴⁰	553–793	1.6
10	$2 \text{IBr}(\text{g}) \rightleftharpoons \text{I}_2(\text{g}) + \text{Br}_2(\text{g})$	5 ^{41–43}	388–1495	15.9
11	$\text{H}_2(\text{g}) + \text{DCl}(\text{g}) \rightleftharpoons \text{HD}(\text{g}) + \text{HCl}(\text{g})$	11 ⁴⁴	388–944	4.3
12	$4 \text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{g}) + 2 \text{Cl}_2(\text{g})$	7 ⁴⁰	625–923	3.5
13	$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{g})$	10 ¹³	1200–3000	–0.06
14	$2 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{S}_2(\text{g})$	9 ^{45,46}	1023–1667	1.4
15	$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$	7 ⁴⁷	600–1200	5.0
16	$3 \text{H}_2(\text{g}) + \text{SO}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{g}) + \text{H}_2\text{S}(\text{g})$	5 ⁴⁶	1160–1645	–3.6
17	$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$	5 ¹³	600–1400	1.4
18	$\text{P}_4(\text{g}) \rightleftharpoons 2 \text{P}_2(\text{g})$	4 ^{48,49}	1173–1473	–5.8
19	$2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g})$	10 ¹³	1200–3000	–5.9
20	$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$	59 ⁵⁰	568–1259	–8.2
21	$\text{CO}(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$	6 ⁴⁰	1133–1325	–8.2
22	$\text{CO}_2(\text{g}) + 4 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$	4 ⁴⁰	681–773	–8.5
23	$\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$	14 ⁵¹	531–602	2.8
24	$\text{C}_2\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g})$	6 ⁵²	673–973	–6.0
25	$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(\text{g})$	10 ^{53,54}	418–548	10.2
26	$\text{HCl}(\text{g}) + \text{CH}_3\text{Br}(\text{g}) \rightleftharpoons \text{HBr}(\text{g}) + \text{CH}_3\text{Cl}(\text{g})$	3 ⁵⁵	357–606	27.5
27	$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	7 ⁵⁶	773–1473	9.3
28	$\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g})$	9 ¹³	600–2000	–6.0
29	$\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO}(\text{g})$	5 ¹³	900–1600	6.4
30	$\text{Fe}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{FeO}(\text{s}) + \text{H}_2(\text{g})$	10 ⁵⁷	907–991	42.0
31	$3 \text{FeO}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + \text{H}_2(\text{g})$	13 ⁵⁷	971–1335	13.3

TABLE II
(Continued)

No	Reaction	Number of experimental values n	Temperature range, K	Average difference ^a , %
32	$\text{Fe(s)} + \text{CO}_2(\text{g}) \rightleftharpoons \text{FeO(s)} + \text{CO(g)}$	7 ⁵⁸	973–1273	17.2
33	$\text{Fe}_3\text{O}_4(\text{s}) + \text{CO(g)} \rightleftharpoons 3 \text{FeO(s)} + \text{CO}_2(\text{g})$	7 ⁵⁸	973–1273	19.8

$$^a \frac{1}{n} \sum_{i=1}^n \frac{\log K_{p_i}^{(\text{calc.})} - \log K_{p_i}^{(\text{exp.})}}{|\log K_{p_i}^{(\text{exp.})}|} 100,$$

$$\Delta = \frac{1}{n} \sum_{i=1}^n \frac{\log K_{p_i}^{(\text{calc.})} - \log K_{p_i}^{(\text{exp.})}}{|\log K_{p_i}^{(\text{exp.})}|} 100, \quad (6)$$

where n is the number of experimental values. It should be emphasized that coefficient (6) overestimates errors for $K_{p_i}^{(\text{exp.})}$ close to 1 and, on the contrary, it may underestimate errors for $K_{p_i}^{(\text{exp.})}$ considerably different from 1.

The systems studied and the comparison of experimental and calculated equilibrium constants are summarized in Table II. The determining term in calculation of K_p is ΔH_0^0 , which is associated with the largest experimental error (for many of our systems of the order of tens of kcal/mol). An error of 0.1 kcal/mol in ΔH_0^0 corresponds to an error of 0.07 in $\log K_p$ at 300 K. For most systems studied the $\log K_{p_i}^{(\text{exp.})}$ used was taken directly from experiment, but for reactions 13, 17, 19, 28, and 29, the values used were obtained by interpolating and averaging the results of several authors¹³.

More than 80% in the group of 26 gas-phase reactions give a coefficient (6) of the order of a few per cent, which is a very satisfactory result for chemical purposes. This finding justifies the RRHO approximation and, in conjunction with quantum chemical methods as sources of molecular constants, confirms its utility for determination of equilibrium constants of gas-phase reactions, in complete independence of experiment.

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