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Thermodynamics of Hydrogen-Isotope-Exchange Reactions. 3. An Experimental Test of the Born–Oppenheimer Approximation

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This paper reports the results of an experimental electrochemical test of the Born–Oppenheimer approximation for the hydrogen-isotope-exchange reaction $D_2(g) + 2HCl(g) \rightleftharpoons H_2(g) + 2DCl(g)$. The reaction was investigated in electrochemical double cells of the type shown in eq 2, in which the vertical arrows represent equilibria between the cell electrolyte solutions and the respective gas phases. The experimental value of the equilibrium constant for the reaction is 1.959 ± 0.011 at 20.0 ± 0.1 °C. Assuming that the Born–Oppenheimer approximation holds, the calculated value of K at 20 °C is 2.024, whereas the calculated value of K is 1.965, if Wolfsberg and Kleinman's predicted corrections for the Born–Oppenheimer approximation failure are applied. The results obtained provide strong quantitative support for Kleinman and Wolfsberg's theoretical analysis which predicts that the use of the Born–Oppenheimer approximation can introduce significant errors in calculated values of equilibrium contants for certain hydrogen-isotope-exchange reactions.

Introduction

On the basis of a suggestion by Wolfsberg that our electrochemical double-cell technique for the study of the thermodynamics isotope-exchange reactions[1] might provide a direct experimental test of the applicability of the Born–Oppenheimer approximation[2] to the statistical thermodynamic theory of hydrogen-isotope-exchange reactions, we devised a cell to study the reaction

$$D_2(g) + 2HCl(g) \rightleftharpoons H_2(g) + 2DCl(g) \tag{1}$$

Kleinman and Wolfsberg[2-6] predict that the equilibrium constants for hydrogen-isotope-exchange reactions, calculated by using statistical thermodynamic theory which invokes the Born–Oppenheimer approximation, can be in error by as much as 15%. The predicted correction to the Born–Oppenheimer approximation in the calculation of K for reaction 1 is about 3%. Therefore an experimental determination of K to within about 0.5% should be sufficient to test Kleinman and Wolfsberg's predicted Born–Oppenheimer approximation failure for reaction 1.

Reaction 1 is a gas-phase reaction and as such presents a unique problem in electrochemical cell design. No purely gas-phase *reactions have been investigated to date in electrochemical cells.* The cell diagram for the electrochemical double cell that we devised to study reaction 1 is

$$\begin{array}{ccc} \mathrm{DCl(g), D_2(g), D_2O(g)} & \qquad & \mathrm{HCl(g), H_2(g), H_2O(g)} \\ \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\ \end{array} \tag{2}$$
$$\mathrm{Pt(s)|D_2(g)|DCl(daq)|Hg_2Cl_2(s)|Hg(l)|Hg_2Cl_2(s)|HCl(aq)|H_2(g)|Pt(s)}$$

where the vertical arrows denote equilibria between gas phases and the respective cell electrolyte solutions and (daq) and (aq) denote the solvents D_2O and H_2O, respectively. The postulated electrode reactions for the double cell (2) are

$$D_2(g) \rightleftharpoons 2D^+(daq) + 2e^-$$

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(daq)$$

$$2Hg(l) + 2Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

Addition of the electrode reactions yields the net cell reaction

$$D_2(g) + 2HCl(aq) \rightleftharpoons H_2(g) + 2DCl(daq) \tag{3}$$

The cell is setup such that the cell electrolyte solutions are in equilibrium with their respective gas phases. Thus we have the independently established equilibria

$$2HCl(g) \rightleftharpoons 2HCl(aq) \tag{4}$$

$$2DCl(daq) \rightleftharpoons 2DCl(g) \tag{5}$$

Addition of reactions 3, 4, and 5 yields reaction 1. Because $\Delta G_4 = \Delta G_5 = 0$, we have

$$\Delta G_3 = \Delta G_1 = \Delta G_1{}^\circ + RT \ln \left\{ \frac{a_{H_2(g)} a^2{}_{DCl(g)}}{a_{D_2(g)} a^2{}_{HCl(g)}} \right\} \tag{6}$$

Using the relation $\Delta G = -nF\epsilon$ in eq 6 yields

$$\epsilon_3 = \epsilon_1{}^\circ - \frac{RT}{2F} \ln \left\{ \frac{P_{H_2} P^2{}_{DCl}}{P_{D_2} P^2{}_{HCl}} \right\} \tag{7}$$

where we have taken $a_i = P_i$, because the corrections for nonideality in the gas phases are negligible, as will be shown. Equation 7 shows that a measurement of the voltage ϵ_3 of cell 2, together with simultaneous measurements of the equilibrium gas pressures P_{H_2}, P_{HCl}, P_{D_2}, and P_{DCl} over the cell solutions, yields $\epsilon_1{}^\circ$ for reaction 1, from which the equilibrium constant is obtained: $K_1 = \exp(2F\epsilon^\circ/RT)$.

Experimental Section

Because of the need to control the composition of the gas phases in the cell and to exclude oxygen and water vapor, the entire cell system was setup and studied as a closed system on a vacuum line. The hydrogen electrodes were prepared as described previously.[7] The calomel electrodes were prepared according to the procedure recommended by Hills and Ives.[8] The DCl(daq) and HCl(aq) solutions were prepared in reservoirs on the vacuum line by reaction of $PCl_5(s)$ with $D_2O(l)$ (99.8 atom % D, Bio-Rad Laboratories) and $H_2O(l)$, respectively, followed by dissolution of the gas in the appropriate water.[7] The $H_2O(l)$ used was purified by distillation of deionized water from alkaline $KMnO_4$ solution. Many of the details of the vacuum line system have been described previously.[7,9,10]

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(1) Rock, P. A. *ACS Symp. Ser.* **1975**, *No. 11*, 131.
(2) Born, M.; Oppenheimer, R. *Ann. Phys.* (*Leipzig*) **1927**, *84*, 457.
(3) Kleinman, L. I.; Wolfsberg, M. *J. Chem. Phys.* **1973**, *59*, 2043.
(4) Kleinman, L. I.; Wolfsberg, M. *J. Chem. Phys.* **1974**, *60*, 4740.
(5) Kleinman, L. I.; Wolfsberg, M. *J. Chem. Phys.* **1974**, *60*, 4749.
(6) Wolfsberg, M.; Kleinman, L. I. *ACS Symp. Ser.* **1975**, *No. 11*, 64.
(7) Silvester, L. F.; Kim, J. J.; Rock, P. A. *J. Chem. Phys.* **1972**, *56*, 1863.
(8) Hills, G. J.; Ives, D. J. G. *J. Chem. Soc.* **1951**, 305.
(9) Contreras-Ortega, C. H.; Nash, C. P.; Rock, P. A. *J. Soln. Chem.* **1976**, *5*, 133.

0022-3654/88/2092-1308$01.50/0

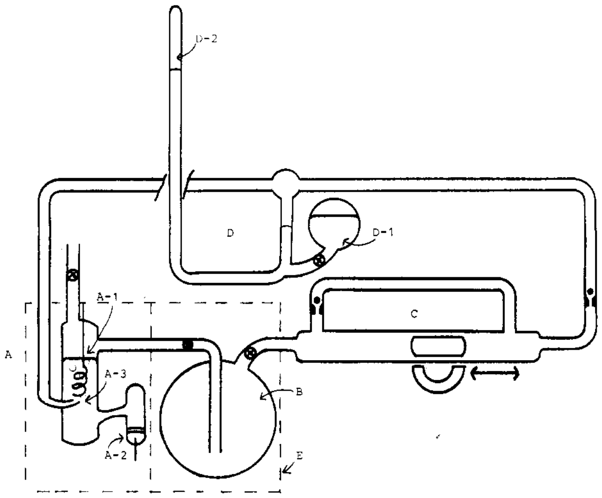

Figure 1. Schematic diagram of half of the double cell system (scale distorted): (A) the H-side of the electrochemical double cell; (A-1) the hydrogen electrode; (A-2) the calomel electrode; (A-3) the hydrogen gas bubbler; (B) the gas-sampling flask; (C) the gas-circulating pump; (D) the fixed-zero manometer; (D-1) the mercury reservoir; (D-2) the upper manometer arm (under vacuum); (E) the constant temperature bath.

The double cell and gas sampling flasks (Figure 1), which are attached to the cell, are thermostated in a water bath maintained below room temperature, to prevent the cell solutions from distilling to other regions of the vacuum line. Bath temperatures were measured with a certified Leeds and Northrup platinum resistance thermometer and G-2 Mueller Bridge. The $D_2(g)$ (99.5 atom %) and $H_2(g)$, both obtained from the Matheson Chemical Co., were first run through DEOXO hydrogen purifiers (Englehard Industries) to remove traces of oxygen, and then through $CaSO_4$ drying towers to remove traces of water vapor. The $D_2(g)$ and $H_2(g)$ were then bubbled through the respective cell solutions and circulated continuously through the respective halves of the double cell (Figure 1), using special noncorrodable pumps with Teflon-covered pistons.[10]

The composition of the respective gas phases ($H_2 + H_2O + HCl$) and ($D_2 + D_2O + DCl$) was determined as follows. Before $H_2(g)$ was introduced to the cell, the equilibrium between HCl(aq) and $H_2O(g)$ + HCl(g) was established. Concentrated (~12–16 *m*) solutions were used to obtain appreciable (~6–120 Torr) pressures of HCl(g). The pressure $P_{H_2O} + P_{HCl}$ was monitored periodically by use of manometers with a fixed zero-point on the lower manometer arm to maintain a fixed gas volume. A phototransistor detector, coupled by a system of cams to a mercury reservoir, was used to maintain a constant mercury height in the lower manometer arm. The manometer systems were enclosed in Plexiglas to minimize thermal gradients. Temperature compensation corrections and gravitational corrections were made for the pressure measurements. The manometers were checked by measuring the vapor pressures of $H_2O(l)$ and $CH_2Cl_2(l)$ as a function of temperature. Accepted values of the vapor pressure were reproduced with a least-squares correlation ≥0.999. When the liquid–vapor equilibrium was established, $H_2(g)$ was added and the pressure $P_{H_2} + P_{H_2O} + P_{HCl}$ was monitored periodically. The two pressure measurements give the values of P_{H_2} and $P_{H_2O} + P_{HCl}$. Following the determination of the cell voltage, the gas-sampling flask is closed off and removed. The HCl content of the flask is determined by reaction with excess standardized NaOH(aq), which is introduced into the flask from another flask without allowing exposure of the sampling flask contents to the atmosphere. The excess NaOH(aq) is back titrated with standardized HCl(aq) prepared from constant-boiling HCl(aq), which was standardized against primary standard potassium acid phthalate. From the known volume and temperature of the gas-sampling flask, together with the measured number of moles of HCl, the pressure is calculated from the ideal gas equation. The procedure for the deuterium half of the cell is analogous to that described for hydrogen. All voltages were measured with an NBS traceable, certified, Leeds and Northrup K-3 potentiometer (±0.5 μV).

TABLE I: Experimentally Determined Values of $\epsilon°$ at 20.0 °C for the Reaction $D_2(g) + 2HCl(g) \rightleftharpoons H_2(g) + 2DCl(g)$

P_{HCl}/Torr	P_{DCl}/Torr	P_{H_2}/Torr	P_{D_2}/Torr	$\epsilon°$/mV
10.7	6.4	477.0	501.2	8.35 (±0.027)
10.1	9.5	470.5	486.2	8.32 (±0.023)
118.2	127.9	387.3	372.1	8.33 (±0.018)
37.8	31.8	175.5	180.1	8.27 (±0.014)

Results

The results of measurements on double cells of type 2 (eq 2) are shown in Table I. The average of the $\epsilon°$ values given in Table I yields $\epsilon° = 8.32 \pm 0.024$ mV at 20.0 °C, which corresponds to an equilibrium constant for reaction 1 of $K = 1.932 \pm 0.011$ at 20.0 °C.

Because of small pressure fluctuations, it is more accurate to calculate an $\epsilon°$ value for each set of voltage and pressure measurements, taken at 30-min intervals during the life of the cell (typically 10 h), and then average the results to obtain the resulting set of $\epsilon°$ values given in Table I. Cell stability was excellent with voltage fluctuations usually less than 0.02 mV and often less than 0.005 mV over 2-h periods. Reversibility tests (current vs voltage plots) of the cells showed no evidence of hysteresis, which is strong evidence for reversible cell operation. The excellent agreement of the $\epsilon°$ values for the various cells calculated by using eq 7 substantiates the postulated cell reaction.

In the calculation of the $\epsilon°$ values given in Table I, we assumed (1) that ideal-gas behavior and Dalton's law of partial pressures applied and (2) that the addition of up to 500 Torr of $H_2(g)$ or D_2 does not affect significantly the values of $P_{H_2O} + P_{HCl}$ and $P_{D_2O} + P_{DCl}$, respectively. The solubility[11] of $H_2(g)$ in aqueous solutions around 25 °C and 1 atm of H_2 is less than 8×10^{-4} M; consequently the effect of dissolved H_2 on $a_{H_2O(l)}$ and $a_{HCl(aq)}$ is less than 0.01 mV and is cancelled (to within 0.001 mV) by the corresponding effect of D_2 on $a_{H_2O(l)}$ and $a_{DCl(aq)}$. The effect of $H_2(g)$ on the values of P_{HCl} and P_{H_2O} is estimated by using the Gibbs equation $(\partial \ln P_i/\partial P)_T = \bar{V}_i/RT$, where $\bar{V}_i$ is the partial molal volume of *i* in the solution. The value of $\bar{V}_{HCl}$ is[12] 22 $cm^3 \cdot mol^{-1}$, and thus the addition of 500 Torr of $H_2(g)$ to the vapor phase increases the value of P_{HCl} by 0.05 Torr when the initial value of P_{HCl} is about 100 Torr, which corresponds to a relative error of 0.05%. The corresponding error in the ratio P_{DCl}/P_{HCl} is less than 0.005%, which corresponds to an error of less than 0.0013 mV in the measured $\epsilon°$ value for reaction 1.

We used virial coefficient data for $H_2(g)$ and $D_2(g)$[13] to calculate the activity coefficients of $H_2(g)$ and $D_2(g)$. At 25 °C and 1 atm we compute $\gamma_{D_2} = 1.00055$ and $\gamma_{H_2} = 1.00053$. These deviations from ideality contribute less than 0.0003 mV to $\epsilon°$. The contributions to $\epsilon°$ from deviations from ideality in HCl(g) and DCl(g) are of similar magnitude. There is no evidence for the association of HCl and H_2O in the gas phase. We ran infrared spectra on samples of the gas phase from our cells and compared the resulting spectra with the spectra obtained after freezing out the water. No detectable difference in the infrared spectrum of HCl was found. Our analytical technique for the determination of P_{HCl} and P_{DCl} was checked by comparison of our results with the independent pressure measurements on HCl(aq) solutions of Fritz and Fuget.[14] The two sets of data agree within experimental error.

The limit of pressure measurements on the monometers used is ±0.025 Torr. However, the $H_2(g)$ and $D_2(g)$ pressures are

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[10] Contreras-Ortega, C.; Silvester, L. F.; Rock, P. A. *J. Appl. Electrochem.* **1980**, *10*, 665.

[11] Weast, R. C. *Handbook of Chemistry and Physics*; The Chemical Rubber Co.: Cleveland, OH, 1967, p B-280.

[12] Wirth, H. E. *J. Am. Chem. Soc.* **1940**, *60*, 1128.

[13] Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Gases*; Claredon: Oxford, 1969.

[14] Fritz, J. J.; Fuget, C. R. *Ind. Eng. Chem.* **1956**, *1*, 10.

determined by subtracting the equilibrium pressures of the cell solutions before the H_2 and D_2 were added from the respective total equilibrium pressures in the cell. The precision of the total pressure measurements limits the accuracy of the $H_2(g)$ and $D_2(g)$ pressure measurements. The limits of the error in the determinations of P_{H_2} and P_{D_2} were usually less than ±0.1 Torr and never more than ±0.2 Torr which corresponds to a relative error of ±0.05%.

The calculation of the errors in the P_{HCl} and P_{DCl} values is involved because of the double back-titration. The accuracy of the buret used (±0.03 mL), the reproducibility of the titration (±0.02 mL), and the accuracy of the volume measurements for the gas-sampling flasks all contribute to the error. Error propagation calculations yield a total error in the values P_{HCl} and P_{DCl} that ranges from ±0.2 Torr at the highest pressures used to less than ±0.05 Torr for the lowest pressures. The accumulated error in each determination of ϵ° ranges from ±0.04 to ±0.07 mV. However, this is the maximum error expected and does not take into account cancellation of errors that occur as a result of the double cell technique.

The actual deuterium content of the nominally deuterium species would be expected to be that of the deuteriated materials from which they were prepared ($D_2O(l)$, 99.8 atom % D and $D_2(g)$, 99.5 atom % D). The error introduced into the value of K_1 by assuming 100.0 atom % D is about 1% and thus is significant at the desired level of accuracy. Consequently, we have independently determined the H content of our deuterium cell solutions by proton magnetic resonance. For solutions with a high (>90%) D content, the integrated area under the peaks due to the H resonance is proportional to the number of H atoms in the field. The relative area of the sample peaks was compared to the area of the H peaks in standard solutions ($D_2O + H_2O$ prepared gravimetrically) to obtain the H content of the sample. A Perkin-Elmer EM 360 NMR spectrometer was used. The peak-area ratio is not a direct measure of the percent H content because the standard and the sample are in different NMR tubes and the solutions have different densities. Densities of the reference standard and the cell solutions were determined gravimetrically. The atom fraction of H in the cell solutions was determined to be 0.011. Samples of the $D_2O(l)$ used to prepare the cell solutions were analyzed by NMR and found to contain 99.67 atom % D which is close to the supplier's stated D content of 99.8%. The increase in H content in the cell solutions over that in the $D_2O(l)$ used is probably due to traces of water in the very hydroscopic $PCl_5(s)$ used in the solution synthesis.

In our correction of K_1 for isotope mixing to a value of K_1 corresponding to 100.0 atom % D, we assumed (1) that H had equilibrated with the D-containing species DCl, D_2, and D_2O and (2) that no significant H/D partitioning occurs between the solution and the gas phases. These assumptions are supported (1) by the platinum-catalyzed equilibrium of H and D on the platinized hydrogen electrode and (2) by the fact that Henry's law constants of HCl and DCl are approximately equal.[15]

Assuming equilibrium of H and D, the ratio DCl(g)/HCl(g) in the deuterium cell is determined by the mole fraction ratio X_D/X_H, that is, $X_{DCl}/X_{HCl} = X_D/X_H$. The H atoms in the gas phase are partitioned between HD, H_2, and D_2 by the equilibrium

$$H_2(g) + D_2(g) \rightleftharpoons 2HD(g) \tag{8}$$

From the equilibrium constant expression for reaction 8

$$K_8 = X_{HD}^2/X_{H_2}X_{D_2} \tag{9}$$

and the mass balances on H and D

$$2X_{H_2} + X_{HD} = 2X_H \tag{10}$$

$$2X_{D_2} + X_{HD} = 2X_D \tag{11}$$

the values of X_{H_2}, X_{HD}, and X_{D_2} can be determined. Solving eq 9–11 for X_{HD} yields

$$X_{HD} = \frac{-(K_8/2) + \{K_8^2((1/4) - X_H + X_H^2) + 4K_8(X_H - X_H^2)\}^{1/2}}{2 - (K_8/2)} \tag{12}$$

The value of K_8 at 20.00 °C was calculated as 3.248 by the methods described in the Discussion. We note, as pointed out by Wolfsberg and Kleinman,[6] that the correction to the Born–Oppenheimer approximation value for reaction 8 is zero.

The measured value of the equilibrium constant for reaction 1, $K_{1,exp}$, is the weighted geometric mean of the equilibrium constants for the three reactions that occur in the cell, because of the isotopic dilution on the deuterium side of the double cell. The three reactions are

$$D_2(g) + 2HCl(g) \rightleftharpoons H_2(g) + 2DCl(g) \tag{1}$$

$$HD(g) + 2HCl(g) \rightleftharpoons H_2(g) + HCl(g) + DCl(g) \tag{13}$$

$$H_2(g) + 2HCl(g) \rightleftharpoons H_2(g) + 2HCl(g) \tag{14}$$

The weighting factors are the mole fractions of D_2, HD, and H_2 in the deuterium cell

$$K_{1,exp} = (K_1)^{X_{DD}}(K_{13})^{X_{HD}}(K_{14})^{X_{HH}} \tag{15}$$

The value of K_{14} is unity. The value of K_{13} can be expressed in terms of K_1 and K_8

$$K_{13} = (K_1/K_8)^{1/2} \tag{16}$$

Substitution of eq 16 into eq 15, together with the values $K_8 = 3.248$, $K_{14} = 1$ (exactly), $X_{DD} = 0.987\,15$, and $X_{HD} = 0.021\,70$, yields $K_1 = 1.959$ at 20.0 °C.

Discussion

We have calculated the equilibrium constant for the reaction

$$D_2(g) + 2HCl(g) \rightleftharpoons H_2(g) + 2DCl(g)$$

at 19.00, 20.00, and 21.00 °C at various levels of approximation, to illustrate the significance of the errors introduced by the various assumptions. With the exception of the corrections for the Born–Oppenheimer approximation,[3-6] the calculations are based on well-established methods.[16-19]

One aspect that influences the calculations at all levels is the isotopic abundances of the species involved. The composition of the chlorine-containing species is assumed to be that of naturally occurring chlorine, namely, 75.53 atom % ^{35}Cl and 24.47 atom % ^{37}Cl. For hydrogen-containing species (99.985% ^1H and 0.015% ^2H), the effect can be neglected because of isotopic purity. For the deuterium-containing species, we have corrected the 98.9% D experimental results to 100.0% D, as already described. The calculated equilibrium constants are corrected for the chlorine isotopic mixture by geometrically weighting the partition functions of each isotopic specie to obtain the partition function for the actual samples used. Thus we have

$$q(\text{natural abundance HCl}) = \{q(H^{35}Cl)\}^{0.7753}\{q(H^{37}Cl)\}^{0.2447}$$

Table II summarizes the data used in the calculations. All spectroscopic data used are based on the spectra[20,21] of H_2 and $H^{35}Cl$. The spectroscopic quantities for species not given in Table II were calculated by using the reduced mass relations given by Herzberg,[22] together with the data in Table II. For the rigid-rotor approximation (A) in Table II we used

$$q_{rot} = \frac{1}{\sigma}\left\{\frac{kT}{hcB_e} + \frac{1}{3} + \frac{hcB_e}{15kT}\right\}$$

for the rotational partition function. For the direct-summation

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(15) Gary, R.; Bates, R. G.; Robinson, R. A. *J. Phys. Chem.* **1964**, *68*, 1186.

(16) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261.

(17) Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962; Chapters 8 and 9.

(18) Lewis, G. N.; Randall, M. *Thermodynamics*, 2nd ed.; revised by Pitzer, K. S., Brewer, L.; McGraw-Hill: New York, 1961; Chapter 27.

(19) Wolfsberg, M. *Adv. Chem. Ser.* **1967**, *89*, 185.

(20) Stoicheff, B. P. *Can. J. Phys.* **1957**, *35*, 730.

(21) Rank, D. H.; Eastman, D. P.; Rao, B. S.; Wiggins, T. A. *J. Opt. Soc. Am.* **1962**, *52*, 1.

(22) Herzberg, G. *Spectra of Diatomic Molecules*, 2nd ed.; D. Van Nostrand: New York, 1965; p 553.

TABLE II: Results of Calculations of the Equilibrium Constant for the Reaction $D_2(g) + 2HCl(g) \rightleftharpoons H_2(g) + 2DCl(g)$[a]

	temp/°C		
assumption level	19.00	20.00	21.00
A. harmonic oscillator, rigid rotor	2.037	2.035	2.021
B. harmonic oscillator, rigid rotor (direct summation)	2.033	2.029	2.019
C. anharmonic oscillator, nonrigid vibrating rotor (direct summation)	2.059	2.052	2.045
D. Wolfsberg's G_0 correction to zero-point energy[b]	2.031	2.024	2.017
E. Kleinman and Wolfsberg's Born–Oppenheimer electronic correction[c]	1.967	1.961	1.954
F. Kleinman and Wolfsberg's secondary Born–Oppenheimer failure effects[d]	1.971	1.965	1.958

[a] Atomic mass: ^1H, 1.007 825; ^2H, 2.014 102; ^{35}Cl, 34.968 851 (75.53%); ^{37}Cl, 36.965 898 (24.47%). Spectroscopic constants in cm^{-1} (H_2, $^1H^{35}Cl$): ω_e (4400.390, 2991.0676); $\omega_e x_e$ (120.8148, 52.845 79); $\omega_e y_e$ (0.724 19, 0.256 34); B_e (60.8407, 10.593 580); D (4.6841×10^{-2}, 5.32019×10^{-4}); H(5.21×10^{-5}, 6.53×10^{-6}); α (3.017 74, 0.307 139 4); β (1.706×10^{-3}, 3.022×10^{-4}); γ (0.028 55, 0.007 148). [b] Calculated values of Wolfsberg G_0 factors in cm^{-1}: H_2, 8.6325; D_2, 4.3196; $H^{35}Cl$, 1.5934; $H^{37}Cl$, 1.5910; $D^{35}Cl$, 0.8196; and $D^{37}Cl$, 0.8172. All G_0 values are ±0.0001 based on the accuracy of the spectroscopic data. The values of G_0 for natural-abundance chlorine-containing species are the weighted average of those for the isotopic species. [c] Kleinman and Wolfsberg's corrections in cm^{-1} to the electronic energy: H_2, 101.31; D_2, 50.69; HCl, 1346.96; DCl, 1324.89. Thus $\Delta C = C(H_2) + 2C(DCl) - C(D_2) - 2C(HCl) = 6.48\ cm^{-1}$. [d] Secondary correction terms due to failure of the Born–Oppenheimer approximation obtained from the results of Kleinman and Wolfsberg: $K_{(BOELE)_{\Delta r}} = 1.000\,03$; $(MMI)_{corr} = 1.000\,12$; $(EXC)_{corr} = 0.999\,999\,96$; $(ZPE)_{corr} = 1.001\,84$; $(AZPE)_{corr} = 1.000\,045\,4$; and $(QMRC)_{corr} = 0.9995$. Thus, $K_{corr} = K_{(BOELE)_{\Delta r}}(MMI)_{corr}(EXC)_{corr}(ZPE)_{corr}(AZPE)_{corr}(QMRC)_{corr} = 1.001\,99$.

rigid-rotor approximation (B), the combined nuclear and rotational partition functions, $q_{nuc-rot}$, were used for H_2 and D_2. The nonrigid-vibrating-rotor direct-summation approximation (C) involves the evaluation of the combined nuclear–vibrational–rotational partition functions $q_{nuc}q_{vib}q_{rot}$. The degeneracy of each state is given by the product of the nuclear degeneracy terms and the rotational degeneracies. For H_2, $g_{H_2} = (1)(1/2)(2J + 1)$ for even J and $g_{H_2} = (3)(1/2)(2J + 1)$ for odd J values. For D_2, $g_{D_2} = (6)(1/2)(2J + 1)$ for even J values and $g_{D_2} = (3)(1/2)(2J + 1)$ for odd J values. For HCl and DCl the rotational symmetry numbers are unity and the nuclear degeneracy is 8 for all J values in both $H^{35}Cl$ and $H^{37}Cl$ and 12 for DCl species resulting in the total degeneracies: $g_{HCl} = 8(2J + 1)$ and $g_{DCl} = 12(2J + 1)$.

The vibrational–rotational energy levels for the anharmonic-oscillator, nonrigid vibrating rotor are given by

$$\epsilon_{v,J} = \omega_e(v) - \omega_e x_e(v)^2 + \omega_e y_e(v)^3 + B_e J(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 - \alpha(v + 1/2)J(J + 1) + \gamma(v + 1/2)^2 J(J + 1) - \beta J^2(J + 1)^2(v + 1/2) + \delta(v + 1/2)^2 J^2(J + 1)^2$$

where the zero-point energy has been substracted out into the term

$$\epsilon_{0,0} = \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8$$

The combined nuclear-vibration-rotation partition functions are calculated from

$$q_{nuc-vib-rot} = \sum_{v=0}^{\infty}\sum_{J=0}^{\infty} g_J \exp(-hc\epsilon_{v,J}/kT)$$

and the zero-point contribution to K from

$$K_{zp} = \exp[-hc(\Delta\epsilon_{0,0})/kT]$$

where

$$\Delta\epsilon_{0,0} = \epsilon_{0,0}(H_2) + 2\epsilon_{0,0}(DCl) - \epsilon_{0,0}(D_2) - 2\epsilon_{0,0}(HCl)$$

The zero-point energies of the mixed-isotopic species HCl and DCl are the weighted averages of the zero-point energies of the individual-isotopic species, for example

$$\epsilon_{0,0}(HCl) = 0.7553[\epsilon_{0,0}(H^{35}Cl)] + 0.2447[\epsilon_{0,0}(H^{37}Cl)]$$

An additional correction term (G_0) to the zero-point energy needs to be considered, as shown by Wolfsberg[23]

$$G_0 = \frac{B_e}{4} + \frac{\alpha_e\omega_e}{12B_e} + \frac{\alpha_e^2\omega_e^2}{144B_e^3} + \frac{\omega_e x_e}{4}$$

The correction term (K_{Wf}) to the equilibrium constant arising from G_0 is

$$K_{Wf} = \exp[-hc(\Delta G_0)/kT]$$

where

$$\Delta G_0 = G_0(H_2) + 2G_0(DCl) - G_0(D_2) - 2G_0(HCl)$$

The calculated values of G_0 for each molecule in the isotope-exchange reaction (1) are given in Table II. The calculated value of $\Delta G_0 = 2.765\,32\ cm^{-1}$ gives rise to a correction term to the equilibrium constant of $K_{Wf} = 0.986\,519$ at 20 °C.

The calculated value of the equilibrium constant for reaction 1 that incorporates all of the appropriate correction terms within the framework of the Born–Oppenheimer approximation, including cubic terms in anharmonicity and quartic term vibration–rotation interaction, is

$$K = K_{elec}K_{trans}K_{nuc-vib-rot}K_{zp}K_{Wf} = (1)(0.384\,096\,7) \times (1.957\,88)(2.278\,28)(0.986\,519) = 2.024\,06 \text{ at } 20\ °C$$

Kleinman and Wolfsberg[3-6] have calculated correction terms to the ground-state electronic wave functions for diatomic hydrides and deuterides and have shown that the potential energy surfaces are not identical for isotopically substituted molecules. These correction terms (abbreviated C) arise from the derivatives of the electronic wave function with respect to R, the internuclear distance. Actual wave functions are needed for the determination of these C terms, so the calculations are quite involved for HCl and DCl which have 18 electrons. The C terms represent energy that must be added to the Born–Oppenheimer approximation electronic energy. Thus the C correction influences the ground-state vibrational energy and hence the equilibrium constant.

Table II summarizes Kleinman and Wolfsberg's results for H_2, D_2, HCl, and DCl. The value of ΔC for reaction 1 was calculated from

$$\Delta C = C(H_2) + 2C(DCl) - C(D_2) - 2C(HCl)$$

The correction to the equilibrium constant, K_{BOELE} (after Kleinman and Wolfsberg), arising from ΔC is given by

$$K_{BOELE} = \exp[-hc(\Delta C)/kT]$$

which has the value $K_{BOELE} = 0.9687 \pm 0.0001$ at 20 °C.

The calculated value of the equilibrium constant for the isotope exchange reaction (1) is $K = 1.9607$ at 20 °C when the Born–Oppenheimer electronic correction (K_{BOELE}) is multiplied by the result of the equilibrium constant calculated under the Born–Oppenheimer conditions for the direct-summation, anharmonic oscillator, nonrigid vibrating rotor.

In their studies of the Born–Oppenheimer approximation failure, Kleinman and Wolfsberg have pointed out other factors that must be considered in the equilibrium constant calculation. All of these factors arise from a secondary result of the so-called adiabatic correction. Because the isotopically related molecules do not lie on identical potential energy surfaces, the equilibrium internuclear separation, r_e, is not identical for the two molecules. The Born–Oppenheimer correction terms (C) calculated by Kleinman and Wolfsberg are functions of the internuclear separation. Each of the quantities ω_e, $\omega_e x_e$, and G_0 will also be affected by the slight shift in the equilibrium internuclear separation (Δr_e) from the Born–Oppenheimer potential-energy surface.

Kleinman and Wolfsberg have calculated several correction terms arising from Δr_e. They include (following Kleinman and

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(23) Wolfsberg, M. *Isotope Effects in Chemical Processes*; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1969; p 185.

Wolfsberg's notation): (1) $K_{(\mathrm{BOELE})\Delta r}$, a correction to the Born–Oppenheimer electronic correction term; (2) $(\mathrm{MMI})_{\mathrm{corr}}$, a correction to the rotational contribution due to Δr_e; (3) $(\mathrm{EXC})_{\mathrm{corr}}$, a correction term for vibrational energy shifts due to Δr_e for vibrational levels with $v \geq 1$; (4) $(\mathrm{ZPE})_{\mathrm{corr}}$, a factor similar to $(\mathrm{EXC})_{\mathrm{corr}}$ for the ground-state vibrational level ($v = 0$); (5) $(\mathrm{AZPE})_{\mathrm{corr}}$, a correction to the anharmonic term in the zero-point energy for the Δr_e shift; (6) $(\mathrm{QMRC})_{\mathrm{corr}}$, a correction for shifts in K due to the effects of Δr_e on quantum-mechanical rotation.

From values reported in ref 5, the value of each of the corrections (1–6) has been calculated, either from the shift in energy ($\Delta\epsilon$) values given or from the equilibrium constant corrections given for the reaction

$$\mathrm{HD + HX \rightleftharpoons DX + H_2}$$

where X can be D or Cl.

The values of each of the correction factors to the equilibrium constant of reaction 1 are listed in Table II. Because some of the correction terms are greater than one, and others less, the net effect is rather small. The product of all of these correction terms (K_{corr}) is $K_{\mathrm{corr}} = 1.00199 \pm 0.00003$, where the error limit has been inferred from the number of significant figures reported by Kleinman and Wolfsberg.

The final, calculated equilibrium constant, which takes into account anharmonicity, coupling of vibration and rotation, as well as the failure of the Born–Oppenheimer approximation, is $K = 1.965$ at 20 °C. The agreement between the calculated and measured values of the equilibrium constant for reaction 1 using Kleinman and Wolfsberg's corrections for Born–Oppenheimer approximation failure (1.965 vs 1.959 ± 0.011) is within the experimental error and is much better than that between the calculated and measured values (2.024 vs 1.959) when the Born–Oppenheimer approximation is invoked. Consequently, we conclude that our experimental results support the theory of isotope-exchange reactions of Kleinman and Wolfsberg in which the Born–Oppenheimer approximation is not adequate for the most precise calculations of equilibrium constants for certain hydrogen-isotope-exchange reactions.

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Thermodynamics of Hydrogen-Isotope-Exchange Reactions. 4. Determination of *K* and $\Delta S°$ for the Reaction $D_2(g) + H_2O(l) \rightleftharpoons H_2(g) + D_2O(l)$

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This paper reports our results for the direct experimental determination of the equilibrium constant and its temperature dependence for the hydrogen-isotope-exchange reaction $D_2(g) + H_2O(l) \rightleftharpoons H_2(g) + D_2O(l)$. The reaction was studied in an electrochemical double cell without liquid junction of the type Pt(s)|D_2(g)|NaOD(daq,m)|HgO(s)|Hg(l)|HgO(s)|NaOH(aq,m)|H_2(g)|Pt(s), where (daq,m) denotes a D_2O solution. The experimental value of the equilibrium constant at 25.0 °C for the reaction is $K = 12.30 \pm 0.09$; the experimental value of $\Delta S°$ at 25.0 °C for the reaction is -8.1 ± 1.7 J·K^{-1}. The experimental results are compared with theoretical calculations within the framework of the Born–Oppenheimer approximation. The comparison suggests a failure of the Born–Oppenheimer approximation of about 4% in the value of the calculated equilibrium constant for the reaction. When Kleinman and Wolfsberg's corrections for the failure of the Born–Oppenheimer approximation are taken into account, the experimental result for the equilibrium constant is in excellent agreement with the calculated value.

Introduction

This paper reports part of a continuing investigation of the thermodynamics of hydrogen-isotope-exchange reactions[1-3] directed toward (1) providing experimental data to test the theoretical predictions of Kleinman and Wolfsberg[4] that the Born–Oppenheimer approximation can introduce an error of several percent in the calculated value of the equilibrium constant for certain hydrogen-isotope-exchange reactions and (2) providing direct experimental data to assess the operational effectiveness of the Girdler–Spevack sulfide process for the industrial-scale separation of hydrogen isotopes.[5]

We have used the electrochemical double cell[2]

$$\mathrm{Pt(s)|D_2(g)|NaOD(daq,m)|HgO(s)|Hg(l)|HgO(s)|NaOH(aq,m)|H_2(g)|Pt(s)} \quad (1)$$

for the direct experimental determination of the equilibrium constant and the entropy change for the reaction

$$\mathrm{D_2(g) + H_2O(l) \rightleftharpoons H_2(g) + D_2O(l)}$$

The results obtained suggest a failure of the Born–Oppenheimer approximation of about 4% in the equilibrium constant for this reaction.

Experimental Section

Details of our general experimental procedures have been published.[1-3] Thus, we confine our discussion to those aspects that are unique to the experiments described in this paper. The double-cell system was set up such that H_2(g) and D_2(g) were supplied continuously by electrolysis of 0.7 M Na_2CO_3 in H_2O(l) and D_2O(l), respectively, in specially constructed self-contained gas generators.[6] Oxygen was removed by passing the gases over hot Ni–Cr wire coils. The H_2 and D_2 generators are connected in series to a constant-current power supply. Therefore, H_2 and D_2 have the same flow rate, which is regulated to the desired value by adjusting the current. Appropriate experiments showed that the cell voltage is constant over the electrolysis current range of 0.2–1.0 A in the generators.

The H_2O used in the experiments was prepared by distillation of deionized water to which dilute NaOH(aq) and $KMnO_4$ were

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(1) Silvester, L. F.; Kim, J. J.; Rock, P. A. *J. Chem. Phys.* **1972**, *56*, 1863.

(2) Rock, P. A. *ACS Symp. Ser.* **1975**, *No. 11*, 131.

(3) Contreras-Ortega, C. H.; Nash, C. P.; Rock, P. A. *J. Solution Chem.* **1976**, *5*, 133.

(4) Kleinman, L. I.; Wolfsberg, M. *J. Chem. Phys.* **1974**, *60*, 4740, 4749; **1973**, *59*, 2043. Wolfsberg, M.; Kleinman, L. *ACS Symp. Ser.* **1975**, *No. 11*, 64.

(5) Rae, H. K. *ACS Symp. Ser.* **1978**, *No. 68*, 1.

(6) Zhang, R.-S.; Chang, O.-K.; Rock, P. A., submitted to *J. Appl. Electrochem.*