

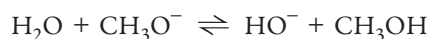
Acidities of Water and Methanol in Aqueous Solution and DMSO

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Acidities and basicities are among the most important concepts in college chemistry. Thus, there have been a number of publications in this *Journal* dealing with these topics (1–6). However, owing to the lack of accurate experimental and theoretical data of solvation Gibbs energies for neutral molecules and ions, several previous publications could only provide conceptual explanations on acidities of molecules in aqueous solution (7–9). For example, the acidities and the experimental procedures of determining the pK_a values of methanol and water in aqueous solution were reviewed by Abrash (10). It is difficult to measure the activities of methanol, methoxide, and hydroxide anions in dilute aqueous solution (10). One could not use the reported pK_a values of methanol ($pK_a = 15.5$) based on approximate activities and water ($pK_a = 15.7$) based on concentrations in aqueous solution as evidence to indicate that methanol is slightly more acidic than water in aqueous solution because the pK_a value (15.7) for water is not thermodynamically valid (3, 4).

A preponderance of experimental measurements of the equilibrium constant for the proton-transfer reaction,



in various water–methanol solutions supports that methanol is about twice as acidic as water (10). But the factors that govern the relative acidities of methanol and water remain unresolved (10). The acidity of molecules in solution is determined by both the intrinsic gas-phase acidity and solvent effects, including the solvation Gibbs energies of the neutral acid, its anion, and the proton. Thus, the values of accurate solvation Gibbs energies of these species are essential to understand the nature of the acidities of molecules in solution. It has been difficult to obtain the absolute solvation Gibbs energy of the proton both experimentally and theoretically (11–13). The value for aqueous solvation Gibbs energy of the proton, ranging from 1050 to 1090 kJ/mol, had been reported in the past and summarized by Pliego and Riveros (11). With the advance of experimental techniques of cluster pair approximation, an accurate and reliable value of 1112.5 kJ/mol for the absolute aqueous solvation Gibbs energy of the proton was obtained by Tissandier et al. in

1998 (12). This solvation Gibbs energy of the proton is regarded as “the most accurate value for this quantity and that it should not be changed unless/until it is superseded by better measurements” (13, 14). The value of aqueous solvation Gibbs energy of the proton was further justified and used to determine the solvation Gibbs energies of a number of ions by Cramer and Truhlar and co-workers (14, 15). These latest developments can help decipher the factors that control the relative acidities of methanol and water in solution.

To help students develop a better quantitative understanding of the acidity concept, we present a detailed analysis of the relative acidities of methanol and water in the gas phase and water using both experimental data and computations. We also discuss the relative acidities of methanol and water in the organic solvent DMSO because an accurate solvation Gibbs energy of the proton in DMSO was also obtained in 2007 (15).

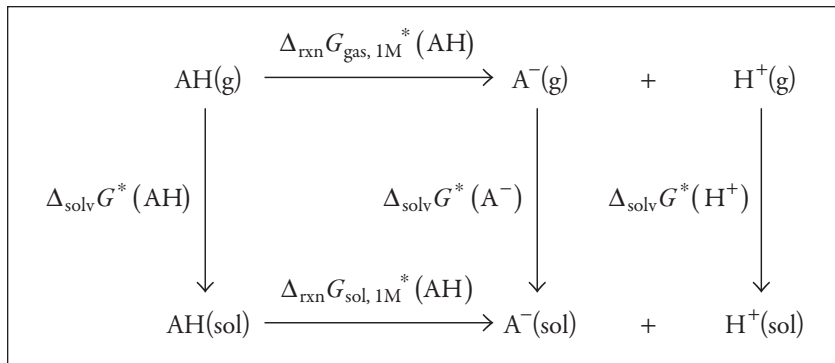
The thermodynamic cycle shown in Figure 1 is usually used to determine the pK_a value of an acid AH in solution (16, 17). The pK_a value of an acid AH in solution is related to the basicity of the conjugate base A^- or the solution-phase acidity $\Delta_{\text{rxn}}G_{\text{sol}, 1\text{M}}^*(\text{AH})$; gas-phase acidity $\Delta_{\text{rxn}}G_{\text{gas}, 1\text{M}}^*(\text{AH})$; and the solvation Gibbs energies for AH, A^- , and the proton H^+ :

$$pK_a(\text{AH}) = -\log K_a(\text{AH}) = \frac{\Delta_{\text{rxn}}G_{\text{sol}, 1\text{M}}^*(\text{AH})}{2.303 RT} \quad (1)$$

$$\begin{aligned} \Delta_{\text{rxn}}G_{\text{sol}, 1\text{M}}^*(\text{AH}) \\ = \Delta_{\text{rxn}}G_{\text{gas}, 1\text{M}}^*(\text{AH}) + \Delta_{\text{solv}}G^*(A^-) \\ + \Delta_{\text{solv}}G^*(\text{H}^+) - \Delta_{\text{solv}}G^*(\text{AH}) \end{aligned} \quad (2)$$

In eqs 1 and 2, the standard state of the concentration of 1 M (mol/L) (denoted by a superscript asterisk) for both the gas phase and solution phase is used to calculate the Gibbs energy changes at 298.15 K. This is a common convention in experimental solution chemistry and computational chemistry (14–17). The relationship between the gas-phase standard state of 1 atm (denoted by a superscript degree symbol) and the gas-phase standard state of 1 M is given by

Figure 1. Thermodynamic cycle for evaluating the solution-phase acidity.



$$\Delta_{\text{rxn}} G_{\text{gas}, 1\text{M}}^{\circ}(\text{AH}) = \Delta_{\text{rxn}} G_{\text{gas}, 1\text{atm}}^{\circ}(\text{AH}) + RT \ln(24.46) \quad (3)$$

This conversion is derived following the standard procedures in the Atkins and de Paula textbook (18) and can be used as an exercise for students in a physical chemistry class.

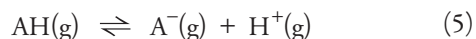
From eqs 1 and 2, students learn that the pK_a value of the acid AH in solution is controlled by four factors: the gas-phase acidity, $\Delta_{\text{rxn}} G_{\text{gas}, 1\text{M}}^{\circ}(\text{AH})$ and the solvation Gibbs energies for the neutral acid AH, its anion, A^- , and the proton H^+ . Thus, the $pK_a(\text{AH})$ is determined by both the intrinsic property of AH ($\Delta_{\text{rxn}} G_{\text{gas}, 1\text{atm}}^{\circ}$) and solvent effects. When one needs to compare the relative acidities of structurally similar acids such as CH_3OH and H_2O , the accurate solvation Gibbs energies of different components and the gas-phase acidities are warranted. One common flaw is that students often emphasize the gas-phase ionization process such as the stability of CH_3O^- versus HO^- in the gas phase when discussing the solution-phase acidities. In this article, we help classify some confusion regarding the solution-phase acidities by using the latest, accurate experimental data.

Acidities in the Gas Phase

Since methanol and water are common and affordable species in both experimental and computational chemistry, their gas-phase acidities, $\Delta_{\text{rxn}} G_{\text{gas}, 1\text{atm}}^{\circ}(\text{AH})$, can be obtained by three methods. Firstly, students can use the standard G2, G3, and the complete basis sets (CBS) procedures in Gaussian 03 program to evaluate the gas-phase ionization Gibbs energies of the two molecules in less than one hour by using any current desktop or laptop computers with 1 GB memory (19). These highly automated procedures, which were implemented in Gaussian 03, incorporate a series of electron correlation energy calculations, including extrapolation of basis sets, based on an initial optimized geometry (20). To calculate the gas-phase acidity,

$$\Delta_{\text{rxn}} G_{\text{gas}}^{\circ}(\text{AH}) = G_{\text{gas}}^{\circ}(\text{A}^-) + G_{\text{gas}}^{\circ}(\text{H}^+) - G_{\text{gas}}^{\circ}(\text{AH}) \quad (4)$$

for the ionization reaction of



the absolute value of Gibbs energy of the proton,

$$G_{\text{gas}}^{\circ}(\text{H}^+) = H - TS \quad (6)$$

at 1 atm and 25 °C is needed, while the Gibbs energies of A^- and AH are calculated by the standard statistical mechanics methods. Using the Sackur–Tetrode equation (21), students can obtain the entropy

$$S_{\text{gas}}^{\circ}(\text{H}^+) = 13.1R \quad (7)$$

where R is the universal gas constant. Therefore,

$$\begin{aligned} G_{\text{gas}}^{\circ}(\text{H}^+) &= H_{\text{gas}}^{\circ}(\text{H}^+) - TS_{\text{gas}}^{\circ}(\text{H}^+) \\ &= E_{\text{gas}, \text{t}}^{\circ}(\text{H}^+) + PV_{\text{gas}}^{\circ}(\text{H}^+) - TS_{\text{gas}}^{\circ}(\text{H}^+) \\ &= \frac{3}{2}RT + RT - 13.1RT = -10.6RT \quad (8) \\ &= 26.3 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Secondly, interested advanced physical chemistry students can be encouraged to do more in-depth work to evaluate the gas-phase ionization Gibbs energies by performing customized calculations such as MP2/aug-cc-pVTZ//HF/6-311+G(d,p). In this situation, students need to evaluate the reaction enthalpy of the gas-phase ionization process of $\text{AH} \rightarrow \text{A}^- + \text{H}^+$ by

$$\begin{aligned} \Delta_{\text{rxn}} H^{298} &= \Delta_{\text{rxn}} E_{\text{e}}^0 + \Delta_{\text{rxn}} E_{\text{v}}^0 \\ &+ \Delta_{298 \leftarrow 0}(\Delta_{\text{rxn}} E_{\text{v}}) + \Delta_{\text{rxn}} E_{\text{t}}^{298} \quad (9) \\ &+ \Delta_{\text{rxn}} E_{\text{r}}^{298} + \Delta_{\text{rxn}}(PV)^{298} \end{aligned}$$

where $\Delta_{\text{rxn}} E_{\text{e}}^0$ is the change of electronic energy including correlations between products and reactant at 0 K; $\Delta_{\text{rxn}} E_{\text{v}}^0$ is the change in vibrational zero-point energy; and $\Delta_{298 \leftarrow 0}(\Delta_{\text{rxn}} E_{\text{v}}^0)$ is the change in zero-point energy from 0 to 298.15 K. The final three terms in eq 9 are for changes in translational and rotational energies and the work term. The gas-phase acidity at $T = 298$ K was calculated by

$$\Delta_{\text{rxn}} G^{298} = \Delta_{\text{rxn}} H^{298} - T\Delta_{\text{rxn}} S^{298} \quad (10)$$

It is shown that the enthalpic contribution fully predominates the entropic component ($T\Delta_{\text{rxn}} S$) in the gas-phase Gibbs energy change (Table 3 in the online material). The detailed expression to calculate the entropy can be found in standard textbooks (22, 23). These calculations can be done by a small Fortran program in which some statistical mechanics formulas are used. The program employs harmonic frequencies, temperature, and the principal moments of inertia of the molecules that are available from the frequency calculations in Gaussian 03. The two approaches of evaluating gas-phase acidities are recommended activities for students who are taking a physical or computational chemistry course. Some students doing computational chemistry research at this college completed the exercise. These students now understand how the thermodynamic properties can be obtained by combinations of quantum mechanics and statistical mechanics. The related formulas, an example calculation for water, the Fortran program, and the Excel spreadsheet are provided in the online material.

Thirdly, reliable experimental data for the $\Delta_{\text{rxn}} G_{\text{gas}, 1\text{atm}}^{\circ}(\text{AH})$ can be obtained from the NIST Chemistry Webbook (24). Experimental values of the gas-phase acidity for methanol, $\Delta_{\text{rxn}} G_{\text{gas}, 1\text{atm}}^{\circ}(\text{methanol}) = 1569.4$ kJ/mol, and water, $\Delta_{\text{rxn}} G_{\text{gas}, 1\text{atm}}^{\circ}(\text{water}) = 1605.4$ kJ/mol, are listed in Table 1 (1 M standard state was used for both the gas and solution-phase acidities). In gas phase, methanol is more acidic than water by 36.0 kJ/mol.

Acidities in Water

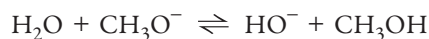
To comprehend the magnitude of the factors that govern the acidities of methanol and water in aqueous solution, we list the experimental gas-phase acidities of methanol and water (24), aqueous solvation Gibbs energies of methanol (11, 25) and water (11, 25), and the anions, CH_3O^- (14) and HO^- (13, 26), the latest aqueous solvation Gibbs energy of the proton, 1112.5 kJ/mol (12–15), and the experimental pK_a values for methanol (27) and water (based on concentrations) (28) in Table 1. Note that the uncertainties of solvation Gibbs energies were often given in an estimated manner in previous publications (11–14, 26, 27). To help students obtain a sense of error

Table 1. Experimental Data for Methanol and Water in Aqueous Solution at 1 M Standard State

AH	$\Delta_{\text{rxn}}G_{\text{gas},1\text{M}}^*(\text{AH})/\text{kJ/mol}$	$\Delta_{\text{solv}}G^*(\text{AH})/\text{kJ/mol}$	$\Delta_{\text{solv}}G^*(\text{H}^+)/\text{kJ/mol}$	$\text{p}K_{\text{a}}$	$\Delta_{\text{rxn}}G_{\text{sol},1\text{M}}^*(\text{AH})/\text{kJ/mol}$	$\Delta_{\text{solv}}G^*(\text{A}^-)/\text{kJ/mol}$
CH ₃ OH	1577.3 ± 2.5 ^a	-21.3 ± 0.8 ^b	-1112.5 ± 8.4 ^c	15.5 ± 0.2 ^d	88.5 ± 1.1 ^f	-397.6 ± 8.9 ^g
H ₂ O	1613.3 ± 1.3 ^a	-26.4 ± 0.8 ^b		15.7 ± 0.1 ^e	89.6 ± 0.6 ^f	-437.6 ± 8.6 ^h

^aRef 24. ^bRefs 11 and 25. ^cRefs 12 and 14. ^dRef 27. ^eRef 28. ^fCalculated from eq 1 based on the experimental $\text{p}K_{\text{a}}$ value. ^gCalculated from eq 2 and refs 11 and 14. ^hCalculated from eq 2 and refs 13 and 26.

bars on these experimental values and have an opportunity to evaluate the error propagations as a rigorous training on error analysis, we derived the aqueous solvation Gibbs energies of the two anions, CH₃O⁻ and HO⁻, with the inclusion of a detailed calculation of the uncertainties. We first calculated the solution-phase acidities ($\Delta_{\text{rxn}}G_{\text{sol},1\text{M}}^*$) of methanol and water based on eq 1 and the experimental $\text{p}K_{\text{a}}$ values of 15.5 for methanol and of 15.7 for water according to the standard rules for propagation of uncertainty (29). The calculated aqueous solution-phase acidities ($\Delta_{\text{rxn}}G_{\text{sol},1\text{M}}^*$) of methanol and water are 88.5 kJ/mol and 89.6 kJ/mol with the uncertainties of 1.1 kJ/mol and 0.6 kJ/mol, respectively (Table 1). By use of eq 2, we then obtained the aqueous solvation Gibbs energies of CH₃O⁻ and HO⁻ as -397.6 ± 8.9 kJ/mol and -437.6 ± 8.6 kJ/mol, respectively. These solvation Gibbs energy values of CH₃O⁻ and HO⁻ are consistent with those derived by four other groups based on eq 2 and the same new proton solvation Gibbs energy (11, 13, 14, 26). Note that the uncertainties of these ion solvation Gibbs energies were suggested to range from 2 to 13 kJ/mol by those workers. Independently, Tissandier et al. determined a value of -438.7 kJ/mol (corrected to 1 M gas-phase standard state) for the aqueous solvation Gibbs energy of HO⁻ by the cluster pair approximation, which is in excellent agreement with the value of -437.6 kJ/mol for HO⁻ in Table 1. This renders some support of the common practice of deriving the solvation Gibbs energies of the anions by use of the experimental $\text{p}K_{\text{a}}$ values and the thermodynamic cycle in Figure 1. Moreover, it is not surprising that the aqueous solution-phase acidities ($\Delta_{\text{rxn}}G_{\text{sol},1\text{M}}^*$) of methanol and water are almost identical in Table 1, which are based on the experimental $\text{p}K_{\text{a}}$ values of 15.5 for methanol and of 15.7 for water. Use of these two $\text{p}K_{\text{a}}$ values of methanol and water in eq 1 is supported by the observation that the experimental measurements of the equilibrium constant for the proton-transfer reaction,



in various water–methanol solutions indicate that methanol is about twice as acidic as water (10).

It is observed that both the absolute and relative acidities of methanol and water undergo dramatic changes on going from the gas phase to aqueous solution. Particularly, methanol is more acidic than water by 36.0 ± 2.8 kJ/mol in the gas phase; however, the acidities are almost identical in an aqueous solution with only a difference of 1.1 ± 1.3 kJ/mol. The virtually identical aqueous acidities of methanol and water are controlled by a combination of factors: the intrinsic gas-phase acidities and the solvation Gibbs energies of the neutral molecules and the anions. In gas phase, the greater acidity of methanol than

water can be explained because the negative charge of the resulting anion of the ionization reaction is more delocalized in CH₃O⁻ than HO⁻ owing to polarization and the anionic hyperconjugation effect (30–32). In aqueous solution, the difference between the solvation Gibbs energy of the neutral CH₃OH and H₂O is 5.1 kJ/mol, while HO⁻ is better solvated than CH₃O⁻ by 40.0 kJ/mol. The 36.0 kJ/mol of more favorable acidity of methanol than water in the gas phase is reduced to about 1.1 kJ/mol in aqueous solution. The relative contributions from the intrinsic (gas-phase) acidity difference and the solvent effects to the acidity difference between methanol and water in aqueous solution are shown in Figure 2.

The favorable solvation (40.0 kJ/mol) of HO⁻ over CH₃O⁻ in aqueous solution plays the largest role in the nearly identical acidities of water and methanol in water, as compared to the gas-phase acidity difference of 36.0 kJ/mol. The origin of the better solvation of HO⁻ than CH₃O⁻ in water is investigated by high-level ab initio calculations. The ion–molecule bonding complexes, HO⁻⋯H₂O, CH₃O⁻⋯H₂O, HO⁻⋯(H₂O)₂, CH₃O⁻⋯(H₂O)₂, and the individual anions and water molecules were optimized at the MP2/6-311++G(d,p) level. The key structural and energetic features are available in the online material (Figures 1 and 2 and Tables 4 and 5). It is found that the HO⁻⋯H₂O is better bonded than CH₃O⁻⋯H₂O, with a more favorable bonding Gibbs energy of 15.5 kJ/mol. When the ion interacts with two explicit water molecules, the HO⁻⋯(H₂O)₂ is better bounded than CH₃O⁻⋯(H₂O)₂ by 21.8 kJ/mol. Thus, the HO⁻ anion forms stronger H-bonding complexes with water molecules than CH₃O⁻ in aqueous solution. The favorable

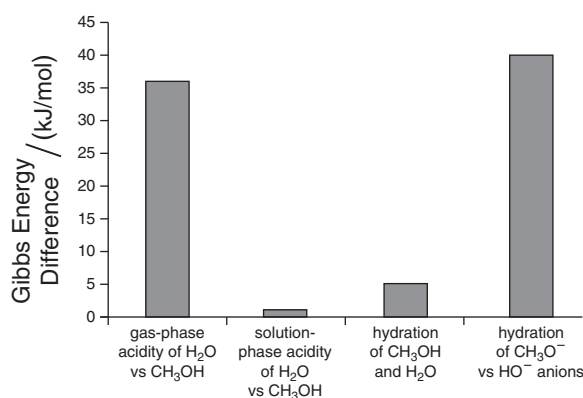


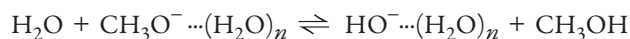
Figure 2. The differences in acidity between methanol and water in the gas phase and in aqueous solution. The differences in hydration Gibbs energy between methanol and water and between methoxide and hydroxide anions.

Table 2. Experimental Data for Methanol and Water in DMSO at 1 M Standard State

AH	$\Delta_{\text{rxn}} G_{\text{gas}, 1\text{M}}^* (\text{AH}) / \text{kJ/mol}$	$\Delta_{\text{solv}} G^* (\text{AH}) / \text{kJ/mol}$	$\text{p}K_{\text{a}}$	$\Delta_{\text{solv}} G^* (\text{H}^+) / \text{kJ/mol}$	$\Delta_{\text{solv}} G^* (\text{A}^-) / \text{kJ/mol}$
CH ₃ OH	$1577.3 \pm 2.5^{\text{a}}$	$-21.3 \pm 0.8^{\text{b}}$	$29.0 \pm 0.1^{\text{d}}$	$-1143.5 \pm 8.4^{\text{e}}$	$-289.5 \pm 8.8^{\text{f}}$
H ₂ O	$1613.3 \pm 1.3^{\text{a}}$	$-26.4 \pm 0.8^{\text{c}}$	$31.4 \pm 0.1^{\text{d}}$		$-316.9 \pm 8.6^{\text{f}}$

^aRef 24. ^bRefs 15 and 33. ^cRefs 15 and 34. ^dRef 35. ^eRef 15. ^fCalculated from eqs 1 and 2 based on the experimental values.

electrostatic interaction in the hydroxide–water complexes is reflected in the Mulliken population analysis at the MP2/6-311++G(d,p) level with the hydroxide oxygen carrying more negative charge than the oxygen in methoxide. Moreover, for the proton-transfer reaction,



the reaction Gibbs energies from the MP2/6-311++G(d,p) calculations are -34.1 kJ/mol, -18.5 kJ/mol, and -12.3 kJ/mol when $n = 0, 1$, and 2 , respectively, while the experimental Gibbs energy of the reaction in bulk water (corresponding to $n = \infty$) is -1.1 kJ/mol (Table 1). Thus, inclusion of one explicit water in the proton-transfer reaction of the relative acidities of methanol and water can account for 47% of the solvent effects of the reaction in bulk water. Inclusion of two explicit water molecules in the calculation can recover 66% of the solvent effects. This is mainly due to the more favorable electrostatic interaction of hydroxide anion with solvent water molecules than the methoxide anion with water.

Acidities in DMSO

Since most organic reactions take place in non-aqueous solution, it is interesting to see how the acidities of methanol and water change on going from aqueous solution to a typical organic solvent. This exercise helps students further appreciate how differential solvent effects affect the chemical reactivity. Fortunately, the latest solvation Gibbs energy of the proton in DMSO was derived by Cramer and Truhlar and co-workers through a statistical analysis procedure (15). This value of -1143.5 kJ/mol for the proton solvation Gibbs energy in DMSO, along with the experimental solvation Gibbs energies of the neutral methanol (11, 33) and water (11, 34), and Bordwell's $\text{p}K_{\text{a}}$ values of methanol and water in DMSO (35), are used to calculate the solvation Gibbs energies of the anions CH_3O^- and HO^- in DMSO from eqs 1 and 2. All the experimental data, uncertainties, and the calculated solvation Gibbs energies of the anions in DMSO are listed in Table 2.

Employing eqs 1 and 2, we obtain the predicted value of -289.5 ± 8.8 kJ/mol for the solvation Gibbs energy of CH_3O^- and a value of -316.9 ± 8.6 kJ/mol for the solvation Gibbs energy of HO^- in DMSO. Our predicted solvation Gibbs energy of -289.5 kJ/mol for CH_3O^- is slightly different from the value of -288.3 kJ/mol obtained by Cramer and Truhlar and co-workers because these investigators obtained their value based on a theoretically computed solvation Gibbs energy of -20.1 kJ/mol for the neutral methanol, rather than the experimental value of -21.3 kJ/mol used in this work (11, 15). The pre-

dicted solvation Gibbs energy of CH_3O^- in this work and that of Cramer and Truhlar's work differ by 11.7 kJ/mol from the value of -301.2 kJ/mol determined by Pliego and Riveros who used a different value (-1123.8 kJ/mol) for the proton solvation Gibbs energy in DMSO (11). While there is no report on the solvation energy of HO^- in DMSO in Cramer and Truhlar and co-workers' work (15), our predicted solvation Gibbs energy of -316.9 ± 8.6 kJ/mol for HO^- in DMSO differs by 13.6 kJ/mol from the value of -330.5 kJ/mol obtained by Pliego and Riveros (11). These are the only two values of solvation Gibbs energy of HO^- in DMSO in the literature. We believe that our predicted solvation Gibbs energy of -316.9 kJ/mol for the HO^- anion in DMSO is more reliable. It is based on the latest proton solvation Gibbs energy in DMSO (15).

Interpretation of Findings

In DMSO, methanol is more acidic than water by a factor of 250 ($\Delta\text{p}K_{\text{a}} = 2.4$) as compared to the factor of 2 in aqueous solution. Since there is little change for the solvation Gibbs energies of the neutral methanol and water in DMSO and water, the difference in acidity comes from differential solvation of the anions. In water, HO^- is better solvated than CH_3O^- by 40.0 ± 12.4 kJ/mol, whereas this value is reduced to 27.4 ± 12.3 kJ/mol in DMSO. This results because HO^- in water is better solvated through stronger hydrogen bonding interactions with the solvent water molecules than the large, diffuse CH_3O^- anion that also contains a large cavitation penalty. In the dipolar, aprotic DMSO solution, the solute and solvent interaction is a charge and dipole interaction. The preferential solvation of HO^- decreases by 12.6 kJ/mol on going from aqueous solution to DMSO, making methanol more acidic than water by a factor of 250 in DMSO. Moreover, the solvation Gibbs energies of CH_3O^- and HO^- in the hydrogen-bonding aqueous solvent are much larger than the values in the dipolar aprotic DMSO solvent by 105–125 kJ/mol. The relatively smaller solvation Gibbs energies of the CH_3O^- and HO^- anions lead to a much greater $\text{p}K_{\text{a}}$ values for the two acids, methanol ($\text{p}K_{\text{a}} = 29$) and water ($\text{p}K_{\text{a}} = 31.4$) in DMSO. In other words, methanol is more acidic in water than in DMSO by a factor of 10^{14} ! Thus, solvent effects play an important role in both the absolute and relative acidities of methanol and water in solution.

In addition, with the availability of the accurate absolute solvation Gibbs energies of the two anions, CH_3O^- and HO^- in both water and DMSO solution, we obtain the Gibbs energy of transfer ($\Delta_{\text{trans}} G = \Delta_{\text{solv}} G - \Delta_{\text{hyd}} G$) for the two anions on going from water to DMSO (Figure 3). The predicted $\Delta_{\text{trans}} G(\text{CH}_3\text{O}^-)$ is 108.1 ± 12.5 kJ/mol, and $\Delta_{\text{trans}} G(\text{HO}^-)$ is 120.7 ± 12.2 kJ/mol. Knowledge of the Gibbs energy transfer of

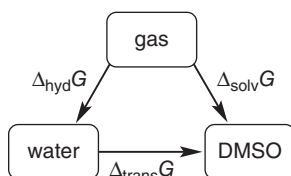


Figure 3. Gibbs energy transfer.

anions from water to organic solvents is essential in understanding the organic reactivity in solution. For example, the large positive values for the Gibbs energy transfer of CH_3O^- and HO^- on going from water to DMSO indicate that the anions are much less solvated in DMSO than in water. This is consistent with the enhanced nucleophilicity of anions in aprotic solvents such as DMSO. This is the basis for a widely used strategy for speeding up nucleophilic substitution reactions. The CH_3O^- and HO^- anions are better nucleophiles in DMSO than in water. For a comprehensive review on this important topic, readers are referred to a recent review article by Marcus (36).

Conclusion

We have presented a detailed quantitative analysis of the factors that govern the relative acidities of methanol and water in water and DMSO. Both the intrinsic property (gas-phase acidity) and solvent effects play an important role in determining the absolute and relative acidities of the two acids in solution. The materials presented here can be used by instructors as a special topic in a physical or general chemistry class, which will help students better appreciate the importance of solvent effects in chemistry.

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Supplement

Details of calculating the gas phase acidity (Gibbs free energy) at the MP2/aug-cc-pVTZ//HF/6-311+G(d,p), G2, G3, and CBS-APNO levels, the related formulas, the Fortran program, the Excel spreadsheet, and the optimized ion molecule complexes