Korean J. of Chem. Eng., 3(1) (1986) 67−72

IONIZATION AND HENRY'S LAW CONSTANTS FOR VOLATILE, WEAK ELECTROLYTE WATER POLLUTANTS

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(Received 14 November 1985 • accepted 12 February 1986)

Abstract— Data base on ionization and Henry's law constants up to 673 K are presented by temperature dependent equations for volatile, weak electrolyte water pollutants; ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide and hydrogen cyanide. In the fitting of ionization constants, various recent sources of experimental isothermal data are mainly utilized, however, Henry's constants are correlated by two steps: first the vapor pressures, the partial molar volumes at infinite dilution, and the vapor and liquid phase nonidealities based on the vapor-liquid equilibrium conditions are calculated from P-T-x data. And then the calculated Henry's constants at different isotherms are treated as a function of temperature. Both correlations reproduce actual data accurately up to high temperatures for reliable phase equilibrium calculations.

INTRODUCTION

Chemical and related industries frequently utilize water to cool and wash process streams and as a result produce complex problems of adequate handling of waste water. Furthermore, increasingly stringent governmental regulations have been acted, making the water decontamination more difficult. Fore examples, in coal gasifications, steam-based enhanced oil recoveries, and biological systems, water absorbs sizable quantities of ammonia, carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen cyanide. To design any type of water purification equipment. it is necessary to describe the phase distribution of these species through the entire process sequence.

In recent years, several molecular thermodynamic frameworks [1-10] are proposed for calculating equilibrium properties of aqueous weak electrolyte solutions. However, most of the theories are based on the virial expansion of Debye-Hückel electrostatic theory with several adjustable parameters. The accuracy and reliability of the models are severely limited by a need for pertinent equilibrium data and predetermined reliable ionization and Henry's constants to yield required molecular and/or ionic interaction parameters in the models.

Toward the reliable phase equilibrium calcualtion by such models, present work has given primary attention to provide exclusive and accurate database of both ionization and Henry's constants. A literature search and critical examination of existing ionization and Henry's constant data used in the molecular thermodynamic frameworks indicated that there exist inconsistencies in utilizing the data and correlation sources [5-7]. In addition, a large number of new experimental ionization and P-T-m data for Henry's constant become available.

In the present study, recent new experimental data coupled with existing correlation sources have been used to present most reliable database of both ionization and Henry's constants with particular emphasis on high temperature region. In addition, molecule-molecule interaction parameters for activity coefficients at dilute concentration are estimated as a function of temperature.

THERMODYNAMIC FRAMEWORKS

In various molecular thermodynamic frameworks of aqueous weak electrolyte systems [1-10], several phase equilibrium principles are usually based. A detailed discussion of basic principles are inappropriate here. In stead, only the fundamental concepts are briefly presented to provide quantitative understanding of the need of reliable database of ionization and Henry's constants.

For the molecular solute, phase equilibrium between the vapor phase and the liquid phase is given by

$$y_m \phi_m P = m_m \gamma_m^* H^s \exp\left\{\frac{\bar{v}_m^\infty (P - P_w^s)}{RT}\right\} \quad (1)$$

where, the subscript m refers to the molecular species of solute, y the mole fraction, P the pressure, m the molality, the activity coefficient $\gamma^* \rightarrow 1$ as $\Sigma m_i \rightarrow 0$, and H^s the Henry's constant which has taken into account the effect of pressure given by Krichevsky and Kasarnovsky's Poynting correction factor [13], $\bar{v}_m^\infty$ the partial molar

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Table 1. Ionization Constants.

Systems	ln K(T) = A+B.T+C.ln T+D/T, g-mole/Kg and T in Kelvin					Data Sources
	A	B	C	D	Temperature Range	
H_2O	-16.6190	-0.039254	4.5573	8983.4	273-673	12, 15, 16, 17, 21, 28
NH_3	4.5927	-0.39449	1.4919	-3658.2	273-623	2, 13, 20, 24, 28
H_2S	0.3979	-0.050763	3.4882	-6342.2	273-423	20, 29, 35
HCN	-12.1960	-0.031482	3.7658	-6340.7	273-423	20, 14, 26
SO_2	-0.7717	-0.00977	-0.7227	1032.7	273-423	27, 31, 32
CO_2	235.4820	0.00000	-36.7816	-12431.7	273-573	23, 25, 30, 33
C_6H_5OH	-174.1328	0.00000	147.0015	11669.5	298-423	18, 19, 20
HCO_3^-	220.067	0.00000	-35.4819	-12431.7	273-473	7
HS^-	$\ln K_{H_2O} - 2.76$					22, 34

volume at infinite dilution, and P^s_w the vapor pressure of saturated water. Also, similar expression with Poynting correction can be used for solvent water.

Several ionic equilibria exist in these weak electrolyte systems. Each is given by the ionization equilibrium constant, K, which is the ratio of molecular to ionic concentrations of the weak electrolytes

$$K = \prod_i (m_i \gamma_i^*)^{\nu_i} \quad (2)$$

where ν_i is positive for molecular species and negative for ionic species, and subscript i refers to all solute species.

Activity coefficients describe physical interactions between solute species in the liquid phase. These are the types of molecule-molecule, molecule-ion and ion-ion. In dilute solutions with low ionization cosntants, the concentration of ions is so small that Pitzer's theory [8-11] reduce to

$$\ln \gamma_m^* = 2\beta^\circ_{mm} m_m \quad (3)$$

where β° is the characteristic binary interaction parameter.

DATA REGRESSION

Ionization Constants

The temperature dependence of ionization constants can be described in terms of the standard enthalpy and the heat capacity of the reaction. The temperature dependent ionization constant can readily be expressed by van't Hoff equation with a linear heat capacity function.

$$\ln K(T) = A + BT + C \ln T + D/T \quad (4)$$

where K(T) is the ionization constant with unit of moles of solute per kilogram of water. Equation [4] implies that a quadratic behavior would be needed to describe its temperature dependence. Parameters A,B,C, and D are given in Table 1, which summarizes our current recommendation of K(T) values of the weak electrolytes such as ammonia, carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen cyanide. Detailed literature data sources utilized in the present regression were cited in Table 1 and in the reference section.

Table 2. Characteristic binary interaction coefficients in Peng-Robinson equation of state.

System (i-j)	Coefficient, τ_{ij}
$NH_3 - H_2O$	-0.26
$CO_2 - H_2O$	$-0.5572+0.001879*T-1.274\times10^{-6}*T^2$
$SO_2 - H_2O$	0.87
$H_2S - H_2O$	$-0.3897+0.001565*T-1.142\times10^{-6}*T^2$
$HCN - H_2O$	0.00

Table 3. Partial molar volumes in dilute aqueous solution.

Systems	Partial molar volumes, cm^3/g-mole		
	Temperature, K		
	273	298	323
NH_3	28.11	28.81	29.56
CO_2	31.76	32.56	33.87
SO_2	39.33	40.49	42.24
H_2S	34.10	34.94	36.55
HCN	41.37	42.62	44.41

Table 4. Henry's constants evaluated at saturation pressure.

Systems	ln H(T) = A + B. T + C. ln T + D/T, in Kg-atm/mole					Data Sources
	A	B	C	D	Temperature Range	
NH_3	5. 6024	− 0. 020262	2. 5647	− 5441. 6	273 − 623	1, 2, 4, 7, 43, 46, 47, 52
CO_2	13. 7750	− 0. 024950	1. 8090	− 3955. 5	273 − 623	2, 5, 7, 45, 48, 50, 53
H_2S	8. 3325	− 0. 019254	1. 7928	− 3137. 4	273 − 573	2, 44, 49, 51
SO_2	7. 2068	− 0. 018880	2. 1423	− 4158. 5	273 − 423	27, 32, 52
HCN	9. 5850	− 0. 03147	3. 1704	− 6302. 0	273 − 373	2, 54

Henry's Law Constants: From Equations (1) and (3), the equation of phase equilibrium for a single solute is,

$$\ln\left(\frac{y_m \phi_m P}{m_m}\right) - \left\{\frac{\bar{v}_m^\infty (P - P_w^s)}{RT}\right\} = \ln H^s + 2\beta^\circ_{mm} m_m \qquad (5)$$

Henry's constant and molecule-molecule interaction parameters may be evaluated from Equation (5) if all other necessary physical properties such as ϕ_m, $\bar{v}_m^\infty$, and P_w^s are provided. These additional properties for the estimation of Henry's constant are briefly presented in the following sections.

Vapor Phase Fugacity Coefficients: Owing to the strong polar character of the components, the fugacity coefficients may differ appreciably from unity even at low to moderate pressures. In the present work, the fugacity coefficients were calculated using Peng-Robinson equation of state [7, 39, 40]. In applying this equation, the characteristic binary interaction parameter, τ_{ij}, were assigned different values in the fitting and is given in Table 2.

Here, we note that Peng and Robinson [40] used a slightly different expression for the temperature dependence of k for water below $T_R^{1/2} < 0.85$. The difference is negligible in the gas phase at the pressures interest here. Also, the parameter, $\alpha^{1/2}$ $(1-T_R^{1/2}) = 0.37464 + 1.54226\omega - 0.26992\omega^2$ is used in the present work.

Partial Molar Volumes at Infinite Dilution; The correlations of Brelvi and O'Connell [38], and Moore et. al [41] were utilized to estimate the partial molar volume of molecular solute at infinite dilution. Estimated results are given in Table 3. In addition, the saturation pressures of water at system temperatures are calculated by usual Antoine's equation [42].

Finally, Henry's constants and molecular interaction parameters in Equation (5) are calculated at each system temperature, where the interaction parameter is determined by the slope; the intercept determines the molecular Henry's constant H.

Using literature data of total pressure or relative

Table 5. Characterstic molecule-molecule interaction parameters.

Systems (m_i − m_j)	β°_{mm} = E + F/T, in Kg/mole		
	E	F	Temperature Range, K
NH_3 − H_2O	− 0. 097623	39. 161	273 − 623
CO_2 − H_2O	− 3. 42420	844. 82	273 − 623
H_2S − H_2O	− 1. 8251	469. 82	273 − 573
SO_2 − H_2O	0. 26877	62. 46	273 − 423

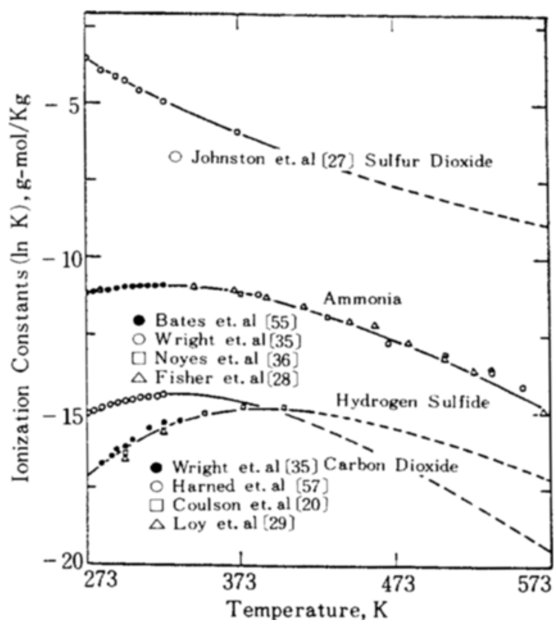

Fig. 1. Comparison of ionization constants with literature data for systems of sulfur dioxide, ammonia, hydrogen sulfide and carbon dioxide.

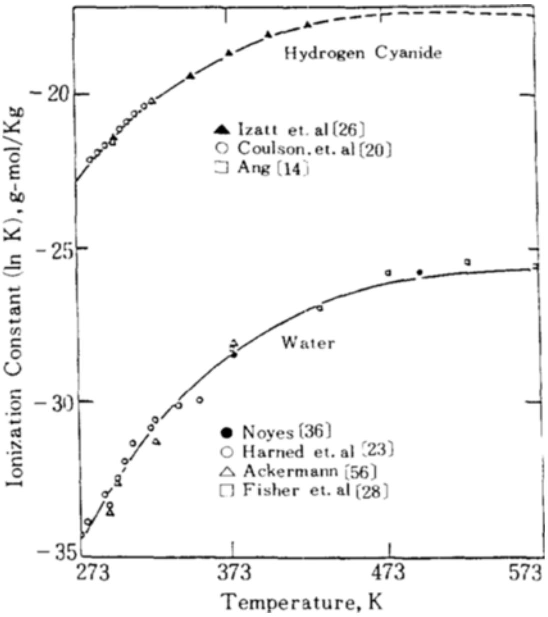

Fig. 2. Comparison of ionization constants with literature data for systems of hydrogen cyanide and water.

volatility, Henry's constants and interaction parameters were determined by several plots. These results are shown in Tables 4 and 5, where both calculated constants are represented by the semiempirical equation correlated in the ionization constants.

RESULTS AND DISCUSSION

The ionization constants in Table 1 and Figures 1 and 2 were all derived from experimental data sources; direct measurements, standard enthalpy, and heat capacity data. Over a wide range of temperature, present correlation reproduce experimental data well within the limited accuracy of the data now available. The dotted lines in Figures 1 and 2 represent uncertain regions of our fitting. The pressure dependence of ionizations are too weak to be of any significance and were neglected in the present correlation [36].

Pressure independent Henry's constants in Table IV were all estimated from experimental total pressure or relative volatility data using fugacity coefficients from the Peng-Robinson equation of state. The fitting results for systems under consideration are also shown in Figures 3, 4 and 5, where existing correlations of Edwards et al. [2], and Roberts et al. [7] are compared for systems of carbon dioxide, ammonia and hydrogen sulfide in water. Over a wide range of temperature, present correlation reproduce Henry's constant accurately.

The two body, molecule-molecule interaction parameter, β^{0}_{mm} is a function of temperature as shown in Table 5. These values provide an approximation for the same temperature reange as that used for Henry's constants. Having determined such parameters as H^{s}, and β^{0} for single solute systems, we can now calcualte vapor-liquid equilibria for dilute weak electrolyte water contaminant abatement work.

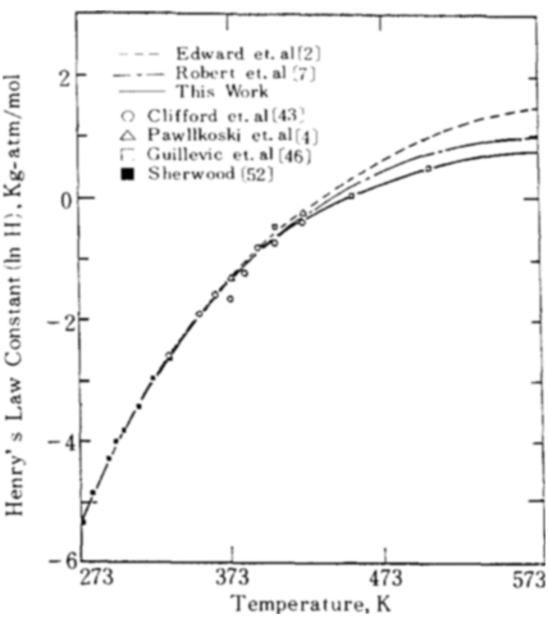

Fig. 3. Henry's law constant for carbon dioxide in water.

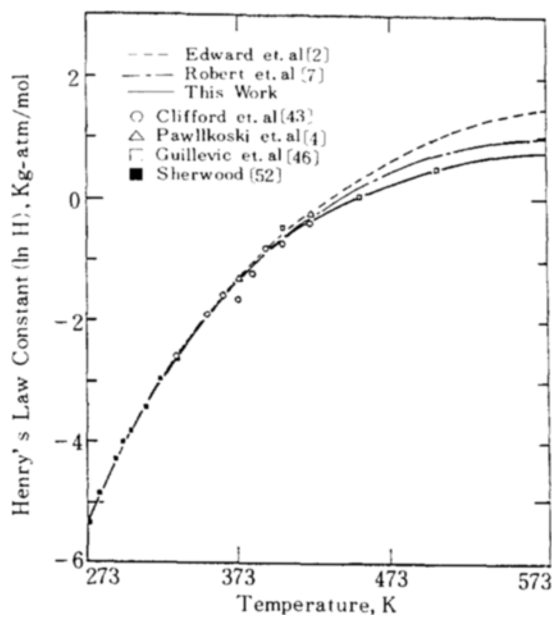

Fig. 4. Henry's law constant for ammonia in water.

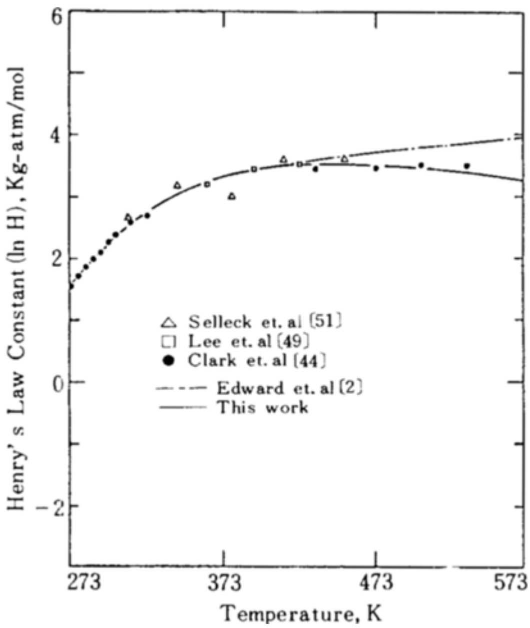

Fig. 5. Henry's law constant for hydrogen sulfide in water.

CONCLUSION

We have presented exclusive database for ionization constants, molecular interaction parameters, and Henry's law constants for aqueous solution containing single weak electrolytes such as ammonia, sulfur dioxide, carbon dioxide, hydrogen sulfide, and hydrogen cyanide. The databases and calculation methods of other equilibrium properties presented here is readily applicable to reliable vapor-liquid equilibrium calculation of dilute weak electrolyte systems.

ACKNOWLEDGEMENT

The authors KPY and SYL are grateful to Sogang University Research Foundation for the financial support on this work.

NOMENCLATURE

A : adjustable parameter in Equation (4)
B : adjustable parameter in Equation (4)
C : adjustable parameter in Equation (4)
D : adjustable parameter in Equation (4)
E : coefficient in molecular interaction parameter
F : coefficient in molecular interaction parameter
H^s : Henry's constant evaluated at saturation pressure, atm-Kg/mole
K : ionization equilibrium constant, mole/Kg
m : concentration, molality, mole/Kg
P : pressure, atm
P_w^s : saturation pressure of water at system temperature, atm
R : gas constant, J/Mol-K
T : temperature, K
$\bar{V}_m^\infty$: partial molar volume of molecular solute at infinite dilution, cm^3/mole
y : vapor phase mole fraction

Greek Letters

α : Peng-Robinson parameter
β^o : characteristic interaction parameter of a given molecular solute
γ : molar activity coefficient
ϕ : vapor phase fugacity coefficient
κ : Peng-Robinson paramter
τ : binary interaction coefficient in Peng-Robinson equation
ν : stoichiometric coefficient
ω : Pitzer's acentric factor

Superscripts

s : saturation
— : partial
* : unsymmetric convention
∞ : infinite dilution

Subscripts

m : molecular
mm : molecule-molecule
ij : species
w : water

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