SUPPORTING INFORMATION FOR

Dissociation Constants of Perchloric and Sulfuric Acids in Aqueous Solution

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The Supporting Information contains:
Brief Description of the Methods for Evaluation of Apparent Dissociation Constants and Limiting Activity Coefficients from Reference Data, the Input Data and Results of the Calculations

Method No.1. The Henry's law constant K_H is computed with the expression

$$K_H = \exp(-\frac{1}{RT}(\Delta_f G^{ø}_{298}(A^-,aq) - \Delta_f G^{o}_{298}(HA,gas))), \quad (19)$$

where $\Delta_f G^{ø}_{298}(A^-,aq)$ and $\Delta_f G^{o}_{298}(HA,gas)$ are standard Gibbs energies of formation of A^- ions in aqueous solution and HA molecules in the gas phase at 298.15 K. Hereafter, the equation numbers in the Supporting Information are the same as in the text of the article.

The apparent dissociation constant is calculated by the formula

$$K'_a \equiv K_H \times p^*_{HA} / 55.51, \quad (17)$$

where p^*_{HA} is the saturated vapor pressure (or fugacity) of pure liquid acid HA.

Table S1. The input data and results of calculation of the apparent dissociation constants at 298.15 K using Method No.1.

HA	$\Delta_f G°_{298}$(HA,gas), kJ/mol	$\Delta_f G^{ø}_{298}(A^-,aq)$, kJ/mol	K_H, mol^2 kg^{-2} bar^{-1}	p*, bar	K'_a, mol kg^{-1}
$HClO_4$	91.37 [1]	−3.397 [1]	4.01×10^{16}	0.0471 [2, 3]	3.40×10^{13}
$HClO_4$	85.14 [4]	−8.52 [5]	2.57×10^{16}	0.0471 [2, 3]	2.18×10^{13}
H_2SO_4	−662.91 [1]	−756.97 [1]	3.01×10^{16}	1.88×10^{-8} [6]	1.02×10^{7}
H_2SO_4	−653.37 [7]	−755.91 [5]	9.25×10^{17}	7.58×10^{-8} [8]	1.26×10^{9}

Method No.2. The apparent dissociation constant is calculated by the formula

$$K'_a = \frac{1}{55.51}\exp(-\frac{1}{RT}(\Delta_f G^{ø}(A^-,aq) - \Delta_f G^*(HA,liq))). \quad (25)$$

where $\Delta_f G^{ø}_{298}(A^-,aq)$ and $\Delta_f G^*(HA,liq)$ are standard Gibbs energies of formation of A^- ions in aqueous solution and pure liquid acid HA at 298.15 K.

Table S2. The input data and results of calculation of the apparent dissociation constants at 298.15 K using Method No.2.

HA	$\Delta_f G^*$(HA,liq), kJ/mol	$\Delta_f G^{ø}_{298}(A^-,aq)$, kJ/mol	K'_a, mol kg^{-1}
$HClO_4$	83.972 [1]	−3.397 [1]	3.65×10^{13}
H_2SO_4	−690.29 [1]	−756.97 [1]	8.66×10^{9}
H_2SO_4	−690 [5]	−755.91 [5]	6.34×10^{9}

Method No.3. The limiting activity coefficient is calculated by the formula

$$f_X^{\infty} = \frac{55.51}{H_X\ p^*_X}, \quad (26)$$

where H_X is the Henry's law constant of substance X, and is p^*_X is the saturated vapor pressure (or fugacity) of pure substance X.

Table S3. The values of Henry's law constants (mol kg^{-1} bar^{-1}) for CO_2, SO_2, HCOOH, CH_3COOH, C_2H_5COOH, CF_3COOH, together with the literature references, taken from review of Sander (2015)[10] and used for the calculation of the limiting activity coefficients by Method No.3.

CO_2	
3.3×10^{-2}	Sander et al. (2011)
3.3×10^{-2}	Sander et al. (2006)
3.3×10^{-2}	Fernández−Prini et al. (2003)
3.4×10^{-2}	Carroll et al. (1991)
3.4×10^{-2}	Crovetto (1991)
3.4×10^{-2}	Yoo et al. (1986)
3.4×10^{-2}	Edwards et al. (1978)
3.3×10^{-2}	Wilhelm et al. (1977)
3.4×10^{-2}	Weiss (1974)
3.6×10^{-2}	Zheng et al. (1997)
3.5×10^{-2}	Bohr (1899)
3.4×10^{-2}	Chen et al. (1979)
3.1×10^{-2}	Chameides (1984)
3.5×10^{-2}	Scharlin (1996)
3.4×10^{-2}	Perry and Chilton (1973)
3.4×10^{-2}	Lelieveld and Crutzen (1991)
3.4×10^{-2}	Pandis and Seinfeld (1989)
4.5×10^{-2}	Yaws (1999)
3.3×10^{-2}	Dean (1992)
4.5×10^{-2}	Yaws and Yang (1992)
3.4×10^{-2}	Seinfeld (1986)
3.3×10^{-2}	Hoffmann and Jacob (1984)
SO_2	
1.3	Sander et al. (2011)
1.3	Sander et al. (2006)
1.2	Yoo et al. (1986)
1.2	Maahs (1982)
1.2	Edwards et al. (1978)
1.4	Wilhelm et al. (1977)
1.2	Johnstone and Leppla (1934)
1.1	Terraglio and Manganelli (1967)
1.2	Chameides (1984)
1.3	Young (1983)
1.2	Pandis and Seinfeld (1989)
CF_3COOH	
8900	Sander et al. (2011)
5700	Kutsuna and Horia (2008)
8800	Bowden et al. (1996)

HCOOH	
8800	Sander et al (2011)
8800	Sander et al (2006)
6700	Staudinger and Roberts (2001)
8800	Johnson et al (1996)
5400	Khan et al (1995)
5400	Khan and Brimblecombe (1992)
1500	Hwang et al (1992)
3700	Jacob (1986)
5500	Keene and Galloway (1986)
7500	Johnson (1990)
5900	Gaffney and Senum (1984)
5100	Johnson et al (1996)
5100	Keene et al (1995)
5300	Keene et al (1995)
3700	Lelieveld and Crutzen (1991)
3500	Pandis and Seinfeld (1989)
CH_3COOH	
4000	Sander et al. (2011)
4000	Sander et al. (2006)
4600	Staudinger and Roberts (2001
1400	von Hartungen et al. (2004)
4000	Johnson et al. (1996)
5400	Khan et al. (1995)
5400	Khan and Brimblecombe (199
9200	Servant et al. (1991)
910	Hwang et al. (1992)
8700	Jacob et al. (1989)
8700	Keene and Galloway (1986)
970	Goldstein (1982)
9900	Gaffney and Senum (1984)
5100	Johnson et al. (1996)
5200	Keene et al. (1995)
8500	Keene et al. (1995)
C_2H_5COOH	
1500	von Hartungen et al. (2004)
5600	Khan et al. (1995)
5500	Khan and Brimblecombe (1992)
6100	Servant et al. (1991)
2200	Butler and Ramchandani (1935)

Table S4. The input data and results of calculation of the limiting activity coefficients at 298.15 K using Method No.3.

X	H_X, mol kg^{-1} bar^{-1}	p^*_X, bar	f_X^∞	lg f_X^∞
CO_2	0.031 - 0.045 [10]	44.3 [8]	27.8 - 40.4	1.44 - 1.61
SO_2	1.1 - 1.4 [10]	3.98 [11]	9.97 - 12.7	1.00 - 1.10
HCOOH	1500 - 8800 [10]	0.0567 [8]	0.111 - 0.652	−0.954 - −0.186
CH_3COOH	910 - 9900 [10]	0.0208 [8]	0.270 - 2.94	−0.569 - 0.468
C_2H_5COOH	1500 - 6100 [10]	5.38×10^{-3} [11]	1.69 - 6.88	0.228 - 0.837
CF_3COOH	5700 - 8900 [10]	0.144 [11]	0.0432 - 0.0674	−1.36 - −1.17

Method No.4. The Henry's law constant H_X is computed with the expression

$$H_X = \exp(-\frac{1}{RT}(\Delta_f G^{ø}_{298}(X,aq) - \Delta_f G^{o}_{298}(X,g))), \quad (27)$$

where $\Delta_f G^{ø}_{298}(X,aq)$ and $\Delta_f G^{o}_{298}(X,g)$ are standard Gibbs energies of formation of substance X in aqueous solution and in the gas phase at 298.15 K.

The limiting activity coefficient is calculated by the formula

$$f_X^\infty = \frac{55.51}{H_X\ p^*_X}, \quad (26)$$

where p^*_X is the saturated vapor pressure (or fugacity) of pure substance X.

Table S5. The input data and results of calculation of the limiting activity coefficients at 298.15 K using Method No.4.

X	$\Delta_f G°_{298}$(X, gas), kJ/mol	$\Delta_f G^{ø}_{298}$(X, aq), kJ/mol	H_X, mol kg^{-1} bar^{-1}	p^*_X, bar	f_X^∞	lg f_X^∞
CO_2	−394.379 [1]	−386.02 [1]	3.43×10^{-2}	44.3 [8]	36.5	1.56
CO_2	−394.359 [5]	−385.98 [5]	3.40×10^{-2}	44.3 [8]	36.8	1.57
SO_2	−300.194 [5]	−300.676 [5]	1.21	3.98 [11]	11.5	1.06
HF	−272.809 [1]	−296.185 [1]	1.25×10^4	1.20 [8]	3.73×10^{-3}	−2.43
HF	−273.2 [5]	−296.82 [5]	1.37×10^4	1.20 [8]	3.38×10^{-3}	−2.47
HCOOH	−351.389 [1]	−372.961 [1]	6.02×10^3	0.0567 [8]	0.163	−0.789
CH_3COOH	−373.61 [1]	−396.517 [1]	1.03×10^4	0.0208 [8]	0.259	−0.586
CH_3COOH	−374 [5]	−396.46 [5]	8.61×10^3	0.0208 [8]	0.310	−0.508
HNO_3	−74.847 [1]	−102.845 [12, 13]	8.04×10^4	0.0752 [8]	9.19×10^{-3}	−2.04
HNO_3	−74.72 [5]	−102.299 [12, 14]	6.79×10^4	0.0752 [8]	0.0109	−1.96

Method No.5. The limiting activity coefficient is calculated by the formula

$$f_X^{\infty} = 55.51 \times \exp\left(-\frac{1}{RT}\left(\Delta_f G^*(X,liq) - \Delta_f G^{ø}(X,aq)\right)\right). \quad (29)$$

where $\Delta_f G^{ø}_{298}(A^-,aq)$ and $\Delta_f G^*(HA,liq)$ are standard Gibbs energies of formation of A^- ions in aqueous solution and pure liquid acid HA at 298.15 K.

Table S6. The input data and results of calculation of the limiting activity coefficients at 298.15 K using Method No.5.

X	$\Delta_f G^*(X,liq)$, kJ/mol	$\Delta_f G^{ø}(X,aq)$, kJ/mol	f_X^{∞}	lg f_X^{∞}
HCOOH	−362.2 [1]	−372.961 [1]	0.723	−0.141
HCOOH	−361.35 [5]	−372.3 [5]	0.670	−0.174
CH_3COOH	−389.358 [1]	−396.517 [1]	3.09	0.490
CH_3COOH	−389.9 [5]	−396.46 [5]	3.94	0.595
H_3PO_4	−1119.107 [1]	−1136.54 [1]	0.0490	−1.31
H_3PO_4	−1119.1 [5]	−1142.54 [5]	4.34×10^{-3}	−2.36
HNO_3	−80.843 [1]	−102.845 [12, 13]	7.76×10^{-3}	−2.11
HNO_3	−80.71 [5]	−102.299 [12, 14]	9.17×10^{-3}	−2.04

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