Estimation of Gas Solubilities in Salt Solutions at Temperatures from 273 K to 363 K

S. Weisenberger
Technische Chemie I, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany

A. Schumpe
Institut für Technische Chemie, Technische Universität Braunschweig, D-38106 Braunschweig, Germany

The solubilities of gases in electrolyte solutions are important in chemical and biochemical reaction engineering. For example, the estimation of gas-liquid mass-transfer rate requires not only the volumetric mass-transfer coefficient but also the equilibrium liquid-phase concentration to be known. With increasing salt concentration, gas solubility is nearly always found to decrease ("salting-out" effect). At moderately high salt concentrations, the effect can be described in the form of the Sechenov relation:

$$\log(c_{G,o}/c_G) = K c_s \tag{1}$$

Here $c_{G,o}$ and c_G denote the gas solubility in pure water and the salt solution, respectively, and c_s is the molar concentration of the salt. The relation usually holds well up to salt concentrations of about 2 kmol/m^3 and sometimes more than 5 kmol/m^3. At higher salt concentrations, the gas solubility c_G tends to be underestimated. One of the reasons for this trend is concentration-dependent dissociation of the salt. The parameter K ("Sechenov constant") is specific to the gas as well as the salt, as shown in Figure 1, and shows a moderate temperature dependency.

Several models have been suggested for the prediction of Sechenov constants. Based on these models, estimates can be obtained for systems that never have been studied experimentally. This includes cases where a chemical reaction of the gas prevents the direct experimental determination of physical gas solubility. The van Krevelen-Hoftijzer type models (Danckwerts, 1970; Onda et al., 1970) have been used extensively, but are inconsistent when applied to solutions of more than just one salt (Schumpe et al., 1982). Recently, Schumpe (1993) suggested a consistent model for mixed electrolyte solutions:

$$\log(c_{G,o}/c_G) = \Sigma(h_i + h_G)c_i \tag{2}$$

For a single salt, the Sechenov constant K is then given by the following relation:

$$K = \Sigma(h_i + h_G)n_i \tag{3}$$

where n_i is the index of ion i in the formula of the salt. With this model, the standard deviation was only half as compared to the van Krevelen-Hoftijzer model when both models were fitted to the same set of 163 experimental Sechenov constants for 5 gases at 298.15 K (Schumpe, 1993). Hermann et al. (1995) extended the parameter set by considering 319 experimental Sechenov constants for 22 gases at the same temperature. The standard deviation of the predicted Sechenov constants for this data set was 0.026.

The objective of this article is to extend the model of Schumpe (1993) to a wider temperature range. To this end, solubility data reported in the literature for temperatures from 273.15 K to 363.15 K were analyzed to obtain a set of 892 Sechenov constants for different gas/salt/temperature combinations. Gas solubility was expressed in the form of the

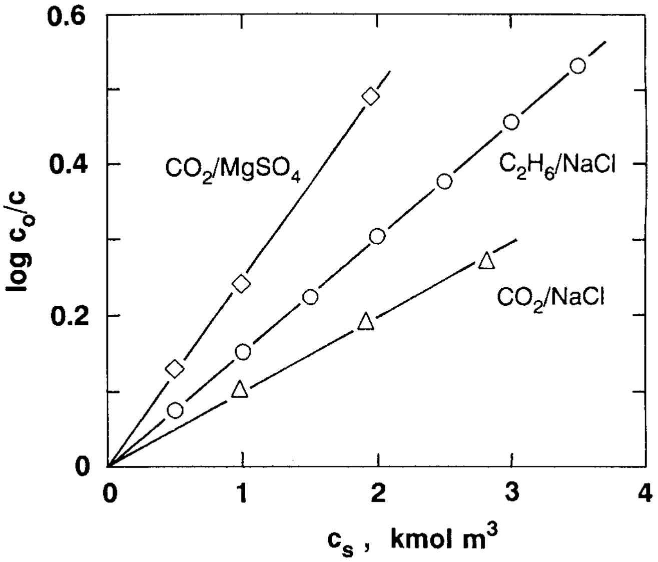

Figure 1. Sechenov plots for various gas/salt systems at 313.15 K (Markham and Kobe, 1941; Mishnina et al., 1961).

Correspondence concerning this article should be addressed to A. Schumpe.

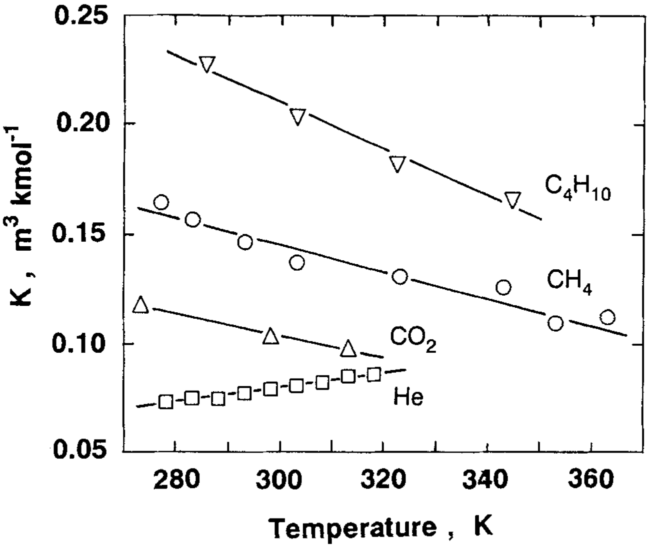

Figure 2. Temperature effect on salting-out of various gases by sodium chloride (Markham and Kobe, 1941; Mishnina et al., 1961, 1962; Morrison and Billet, 1952).

Bunsen coefficient (volume of gas, reduced to 273.15 K and 101.3 kPa, absorbed per unit volume of solvent at 101.3-kPa partial pressure). Note that only the relative solubility is considered and any out of various proportional measures (Schumpe et al., 1982) could be used. The full list of references (321 entries) is available from the authors.

Results and Discussion

The Sechenov constants usually decrease with increasing temperature. The temperature effect tends to become weaker at high temperature but the trend is rather close to linear. The temperature dependency was found gas-specific. This is most obvious for helium and sulfur dioxide, where the Sechenov constants even increase with increasing temperature. These trends are exemplified in Figure 2.

When extending the model of Schumpe (1993) to the temperature range of 273 to 363 K, the gas-specific constant was assumed to be a linear function of the temperature:

$$h_G = h_{G,o} + h_T(T - 298.15\ \text{K}) \tag{4}$$

The temperature of 298.15 K was used as the reference to keep the $h_{G,o}$ parameters comparable with the parameter values suggested for this temperature by Schumpe (1993) and Hermann et al. (1995). As in these previous studies, the h_i parameters for the hydrogen ion and the $h_{G,o}$ parameter for oxygen were arbitrarily set to zero to obtain one parameter set out of an unlimited number of equivalent sets.

The optimum parameter values obtained by nonliner regressin (Marquardt's method) are listed in Table 1. As compared to the results of Hermann et al. (1995) for 298.15 K, more parameters are available and some ion-specific parameters h_i(Cs^+, Ba^{2+}, I^-) and some gas parameters $h_{G,o}$ (*Rn*, C_3H_8, $n\text{-}C_4H_{10}$) show rather different values. The present results are based on much more experimental information and should be preferred even when salting-out effects at 298.15 K are to be estimated. The standard deviation of the predicted

Table 1. Model Parameters

Cation	h_i $m^3 \cdot kmol^{-1}$		Anion	h_i $m^3 \cdot kmol^{-1}$		Gas	$h_{G,o}$ $m^3 \cdot kmol^{-1}$		$10^3 \times h_T$ $m^3 \cdot kmol^{-1} \cdot K^1$	Temp.* K
H^+	$\equiv 0$	(57)**	OH^-	0.0839	(51)**	H_2	−0.0218	(75)**	−0.299	273-353
Li^+	0.0754	(73)	HS^-	0.0851	(1)	He	−0.0353	(20)	+0.464	278-353
Na^+	0.1143	(261)	F^-	0.0920	(7)	Ne	−0.0080	(57)	−0.913	288-303
K^+	0.0922	(226)	Cl^-	0.0318	(421)	Ar	0.0057	(79)	−0.485	273-353
Rb^+	0.0839	(21)	Br−	0.0269	(58)	Kr	−0.0071	(14)	n.a.†	298
Cs^+	0.0759	(36)	I^-	0.0039	(88)	Xe	0.0133	(5)	−0.329	273-318
NH_4^+	0.0556	(51)	NO_2^-	0.0795	(2)	Rn	0.0447	(10)	−0.138	273-301
Mg^{2+}	0.1694	(32)	NO_3^-	0.0128	(109)	N_2	−0.0010	(38)	−0.605	278-345
Ca^{2+}	0.1762	(17)	ClO_3^-	0.1348	(1)	O_2	$\equiv 0$	(162)	−0.334	273-353
Sr^{2+}	0.1881	(2)	BrO_3^-	0.1116	(1)	NO	0.0060	(1)	n.a.	298
Ba^{2+}	0.2168	(30)	IO_3^-	0.0913	(1)	N_2O	−0.0085	(78)	−0.479	273-313
Mn^{2+}	0.1463	(14)	ClO_4^-	0.0492	(4)	NH_3	−0.0481	(27)	n.a.	298
Fe^{2+}	0.1523	(4)	IO_4^-	0.1464	(1)	CO_2	−0.0172	(50)	−0.338	273-313
Co^{2+}	0.1680	(6)	CN^-	0.0679	(1)	CH_4	0.0022	(60)	−0.524	273-363
Ni^{2+}	0.1654	(6)	SCN^-	0.0627	(1)	C_2H_2	−0.0159	(30)	n.a.	298
Cu^{2+}	0.1675	(8)	$HCrO_4^-$	0.0401	(1)	C_2H_4	0.0037	(15)	n.a.	298
Zn^{2+}	0.1537	(10)	HCO_3^-	0.0967	(2)	C_2H_6	0.0120	(55)	−0.601	273-348
Cd^{2+}	0.1869	(11)	$H_2PO_4^-$	0.0906	(8)	C_3H_8	0.0240	(17)	−0.702	286-345
Al^{3+}	0.2174	(10)	HSO_3^-	0.0549	(1)	$n\text{-}C_4H_{10}$	0.0297	(38)	−0.726	273-345
Cr^{3+}	0.0648	(2)	CO_3^{2-}	0.1423	(11)	H_2S	−0.0333	(15)	n.a.	298
Fe^{3+}	0.1161	(6)	HPO_4^{2-}	0.1499	(3)	SO_2	−0.0817	(36)	+0.275	283-363
La^{3+}	0.2297	(6)	SO_3^{2-}	0.1270	(3)	SF_6	0.0100	(10)	n.a.	298
Ce^{3+}	0.2406	(2)	SO_4^{2-}	0.1117	(111)					
Th^{4+}	0.2709	(1)	$S_2O_3^{2-}$	0.1149	(2)					
			PO_4^{3-}	0.2119	(3)					
			$[Fe(CN)_6]^{4-}$	0.3574	(1)					

*Exp. temperature range for the evaluation of the h_T parameter value.
**Number of encounters in the data set (in brackets).
†n.a. = not available.

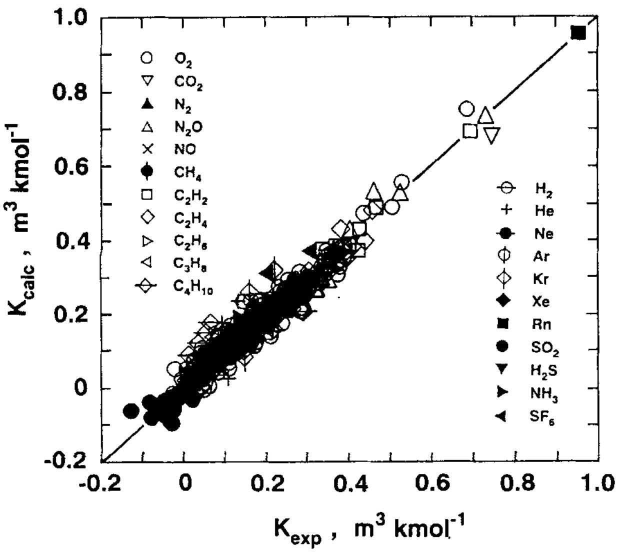

Figure 3. Parity plot for the suggested model (Eqs. 2–4) using the parameters in Table 1.

Sechenov constants is 0.026. The same value of the standard deviation was encountered by Hermann et al. (1995) when fitting Eq. 3 to experimental data at 298.15 K only. This shows that the temperature effect is adequately represented by Eq. 4. A parity plot is given in Figure 3.

The temperature effect could not be assessed for all gases and for others the full temperature range was not covered. Within a limited temperature frame, say 273 to 343 K, some extrapolation seems possible, that is, the h_T parameters may be applied outside the range covered experimentally for the respective gas. Some care is recommended where the listed h_i or h_G parameter is based on a single encounter of the ion or gas, respectively, in the data set (cf. bracketed numbers in Table 1).

It might be interesting to correlate the empirical parameter values with gas and ion properties, respectively. For example, the effect of ionic charge on the value of the ion-specific parameter appears to be linear rather than quadratic. However, theoretical interpretations are outside the scope of this strictly empirical study.

Application to mixed electrolyte solutions

As an example, the solubility of carbon dioxide at 298.15 K is estimated for a mixed electrolyte solution composed of 0.75 kmol/m^3 Na_2SO_4 and 1.5 kmol/m^3 HCl:

$$h_G = -0.0172 - 0.338\cdot 10^{-3}(298.15 - 298.15) = -0.0172$$

$$\begin{aligned} \log(c_{G,o}/c_G) &= 1.5(0.1143 - 0.0172) && (\mathrm{Na}^+) \\ &\quad + 0.75(0.1117 - 0.0172) && (\mathrm{SO_4}^{2-}) \\ &\quad + 1.5(0 - 0.0172) && (\mathrm{H}^+) \\ &\quad + 1.5(0.0318 - 0.0172) && (\mathrm{Cl}^-) \\ &= 0.2126 \end{aligned}$$

The gas solubility in pure water at the considered temperature could be looked up in the experimental data tabulated by Kertes (1979–90), calculated from Wilhelm et al. (1977) or obtained from other sources. Using the Bunsen coefficient of 0.754 as the $c_{G,o}$ value for carbon dioxide at 298.15 K (Schumpe et al., 1982), the Bunsen coefficient for the mixed salt solution is estimated as 0.462. This result compares well with the experimental value of 0.453 (Quicker et al., 1981).

Conclusions

Gas solubilities in aqueous salt solutions reported in the literature were used to evaluate 892 Sechenov constants for different gas/salt/temperature combinations in the range of 273 to 363 K. Approximately linear decrease of the Sechenov constant with temperature was observed in most cases; only for helium and sulfur dioxide, salting-out becomes stronger as the temperature is increased. A previously suggested empirical model for the salting-out of gases by electrolytes at constant temperature was extended to consider the temperature effect. The fitted parameter values allow to estimate the effects of 24 cations and 26 anions on the solubility of 22 gases with a standard deviation of 0.026 for the predicted Sechenov constants. The model applies also to mixed electrolyte solutions.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Max-Buchner Forschungsstiftung.

Notation

c_G = gas solubility in an electrolyte solution
c_i = concentration of ion i, kmol·m^{-3}
c_S = salt concentration, kmol·m^{-3}
$h_{G,o}$ = gas-specific parameter, m^3·kmol^{-1}
h_i = ion-specific parameter, m^3·kmol^{-1}
h_T = gas-specific parameter for the temperature effect, m^3·kmol^{-1}K^{-1}
K = Sechenov constant (Eq. 1), m^3·kmol^{-1}
T = temperature, K

Literature Cited

Danckwerts, P. V., *Gas-liquid Reactions*, McGraw-Hill, New York, p. 18 (1970).

Hermann, C., I. Dewes, and A. Schumpe, "The Estimation of Gas Solubilities in Salt Solutions," *Chem. Eng. Sci.*, **50**, 1673 (1995).

Kertes, A. S., ed., *Solubility Data Series*, Pergamon Press, Oxford (1979–90).

Markham, A. E., and K. A. Kobe, "The Solubility of Carbon Dioxide and Nitrous Oxide in Aqueous Salt Solutions," *J. Amer. Chem. Soc.*, **63**, 449 (1941).

Mishnina, T. A., O. I. Avdeeva, and T. K. Bozhovskaya, *Materialy Vses. Nauchn.-Issled. Geol. Inst.*, **46**, 93 (1961).

Mishnina, T. A., O. I. Avdeeva, and T. K. Bozhovskaya, *Inf. Sb., Vses. Nauchn.-Issled. Geol. Inst.*, **56**, 137 (1962).

Morrison, T. J., and F. Billet, "The Salting-Out of Non-Electrolytes: II," *J. Chem. Soc.*, 3819 (1952).

Onda, K., E. Sada, T. Kobayashi, S. Kito, and K. Ito, "Salting-Out Parameters of Gas Solubility in Aqueous Salt Solutions," *J. Chem. Eng. Japan*, **3**, 18 (1970).

Quicker, G., A. Schumpe, B. König, and W.-D. Deckwer, "Comparison of Measured and Calculated Oxygen Solubilities in Fermentation Media," *Biotechnol. Bioeng.*, **23**, 635 (1981).

Schumpe, A., G. Quicker, and W.-D. Deckwer, "Gas Solubilities in Microbial Culture Media," *Adv. Biochem. Eng.*, **24**, 1 (1982).

Schumpe, A., "The Estimation of Gas Solubilities in Salt Solutions," *Chem. Eng. Sci.*, **48**, 153 (1993).

Wilhelm, E., R. Battino, and R. J. Wilcock, "Low-Pressure Solubility of Gases in Liquid Water," *Chem. Rev.*, **77**, 219 (1977).

Manuscript received Mar. 20, 1995.