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Thermodynamics Works! Enthalpy and Heat Capacity Changes on Solution from Gas Solubility Data†

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Thermodynamic relationships connect many phenomena in somewhat surprising ways. This paper discusses how calorimetric information (enthalpy and heat capacity changes on solution) can be derived from data on the solubility of gases in liquids as a function of temperature. The primary examples come from the high-precision data on the solubility of a number of gases in water where there are calorimetric results on gas solubilities for comparison purposes.

Introduction

The many books on chemical thermodynamics are replete with equations connecting various physical phenomena. These equations give relationships between physical properties like pressure, temperature, volume, amounts of substance, concentration, and electromotive force and also between thermodynamic properties like the energy, entropy, enthalpy, and Gibbs functions (among others). The following may be considered to be the most remarkable equation in all of thermodynamics

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -RT \ln K = -zFE° \qquad (1)$$

The superzeros refer to standard state conditions. Recall that the Gibbs and enthalpy functions are not "fundamental" but are defined functions that have useful properties. $\Delta_r G°$ is the standard state change in the Gibbs function, in this paper for the solubility of a gas in water. In eq 1: R is the ideal gas constant; F is the Faraday constant; T is the absolute temperature; z is the charge number; K is a thermodynamic equilibrium constant; and $E°$ is the standard electrode potential. A solubility is effectively an equilibrium constant. Enthalpy and entropy changes are determined calorimetrically by measuring heat effects, and equilibrium constants are determined by measuring equilibrium compositions. The charge number is determined from the balanced chemical equation for the reaction, and the standard electrode potential is determined via cell potential measurements using high impedance devices or potentiometers.

What is remarkable about eq 1 is that it relates a convenience function (Gibbs energy change) to two calorimetrically determined functions ($\Delta_r H°$ and $\Delta_r S°$) using the absolute temperature, to the experimentally determined equilibrium constant (via measurements of equilibrium compositions), to a charge number (z), and to a measurement of a cell potential. Phenomenologically, these are quite different aspects of nature. The cell potentials of a few volts are somehow connected to determinations of temperature changes in calorimeters and also to the equilibria of solubilities. Conceptually, these are surprising connections, and it is only by the rigorous "magic" of thermodynamics that these connections can be appreciated and understood.

This paper illustrates to me the fascinating connection between calorimetry and solubility. To calculate the enthalpy and heat capacity at constant pressure changes on solution, solubility must be determined at several temperatures. The relevant equations are

$$(\partial(\Delta G°/T)/\partial T)_P = -(\Delta H°/T^2) \qquad (2)$$

$$(\partial \Delta H°/\partial T)_P = \Delta C_P° \qquad (3)$$

where we indicate standard state conditions to emphasize the connection to the equilibrium constant. The enthalpy change is derived from a first derivative of the solubility data as a function of temperature and the heat capacity change via a second derivative of the same solubility data. This means that the solubility data must be precise to obtain the enthalpy changes and highly precise to also obtain the heat capacity changes. There are few gas solubility data that meet these criteria. When enthalpy changes are derived from eq 2, they are called "van't Hoff" enthalpy changes.

Relevant Literature

To my knowledge, there are only three laboratories that have produced high-precision gas solubility data as a function of temperature. By high precision, I mean precisions greater than 0.1 %. Most gas solubility data in the literature are in the range (0.5 to 3) %. These three are Benson and co-workers, Battino and co-workers, and Cook, Hanson, and Alder.[1] The first two groups reported on many systems, and the last reported only on the solubility of hydrogen in organic solvents. Direct calorimetric determinations of the enthalpy change on solution of gases in liquids have been carried out by a limited number of researchers, primarily due to the very small heat effects involved. The enthalpy changes are generally of the order of about 1 $\text{kJ}\cdot\text{mol}^{-1}$. The difficulty is that the mole fraction solubility at one atmosphere partial pressure of gas is about 10^{-4} for solubilities in organic solvents and 10^{-5} for solubilities in water. These very small solubilities mean that the measured heat effects are correspondingly small, and temperature changes need to be determined in a precision of microkelvin with related energy changes of fractions of a joule. (Gases that chemically react with water such as NH_3, CO_2, and SO_2 are very soluble, and they are not considered here.) There were three early reports on direct calorimetric measurements.[2−4]

Alexander et al.[5] reported on the evaluation of thermodynamic functions from aqueous solubility measurements. They calcu-

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lated van't Hoff enthalpy changes on solution and compared them with the available literature values. Unfortunately, I believe they got carried away in their fitting of the data and used too many coefficients which resulted in erroneous values of $\Delta C_P°$. I was privileged as a Fulbright Scholar in 1979 to work with Stokes and Marsh to do the fourth set of measurements at the University of New England, and we reported[6] on the enthalpy change on solution of Ar and N_2 in CCl_4, c-C_6H_{12}, and C_6H_6 at 298.15 K and of CO_2, CH_4, C_2H_6, C_2H_4, and C_3H_8 in the same three solvents at (298.15 and 318.15) K. The early calorimetry papers[2−5] do not contain sufficiently precise data for illustrating the thesis of this paper.

The high-precision solubility data reported on by Battino and co-workers[6−11] were all done on an apparatus based on that of Benson and co-workers (briefly described in ref 12). Battino et al. measured the solubility of CH_4, C_2H_6, N_2, O_2, Ar, and CO in water over a roughly 50 °C range. In addition, in this paper, I am taking the liberty of using unpublished data for the solubility of C_2H_4 and C_3H_8 in water. Battino[12] published a review on the high-precision solubility of gases in water from about (273 to 333) K.

The high-precision work carried out by Benson and co-workers[13−19] on gas solubilities in water is also used herein.

The microcalorimeters developed by Gill and co-workers and Wadsö and co-workers (collaborating with each other) reported exceptionally precise data,[20−29] and their results are used in this paper. Biggerstaff et al.[30] directly measured the heat capacity of Ar in water from (306 to 578) K and reported an extrapolated value at 298.15 K.

Wilhelm[31] published a paper, somewhat similar to the present one, with an extensive literature survey, a description of the BK apparatus,[12] and a detailed presentation of the relevant thermodynamics for reducing gas solubility data to Henry's Law constants and enthalpy and heat capacity changes on solution.

Braibanti and co-workers[32−34] have developed a molecular thermodynamic model for the solubility of gases in water. They present various calculations of the enthalpy and heat capacity changes on solution and in their last paper[34] present a table comparing some van't Hoff and calorimetric values with their calculated ones. Maria et al.[35] have developed an apparatus based on a Tian-Calvet microcalorimeter for the measurement of the enthalpy of solution of gases in liquids but did not report any results pertinent to this paper.

Illustration

The direct calorimetric determination of the enthalpy change on solution was carried out by Gill and Wadsö and their co-workers in water for 21 gases. The van't Hoff enthalpy change on solution by Battino and Benson and their co-workers in water was determined for 12 gases. In addition, the review article on the solubility of gases in water by Wilhelm et al.[36] presented van't Hoff enthalpy changes on solution in water for many gases, and these results will also be used for comparison. Solubility temperature-dependent data yield enthalpy changes on solution via eq 2 (a first derivative) and heat capacity changes via eqs 2 and 3 (that is, via the second derivative of the solubility data as a function of temperature). Table 1 is a summary of these results at 298.15 K. Table 2 gives some results for the solubility of methane in water over a wide temperature range as an illustration of the temperature dependence of the enthalpy and heat capacity changes on solution from both solubility and calorimetric measurements. (I cannot be definitive about the uncertainties in the tables since this was not clear in the original papers, but I assume that the cited uncertainties are ± 1 standard deviation.)

Table 1. Comparison of van't Hoff and Calorimetry Determined Values for Gas Solubilities in Water at 298.15 K

	from solubility		from calorimetry	
	$-\Delta H°$	$\Delta C_P°$	$-\Delta H°$	$\Delta C_P°$
gas	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
He	0.55 ± 0.07[16]	118 ± 2[16]	0.65 ± 0.04[22]	135 ± 7[22]
	0.76 ± 0.20[36]		0.52 ± 0.04[24]	
Ne	3.83 ± 0.08[16]	149 ± 2[16]	3.64 ± 0.07[22]	145 ± 1[22]
	3.75 ± 0.14[36]		3.95 ± 0.09[24]	
Ar	11.97 ± 0.18[16]	186 ± 5[16]	12.01 ± 0.08[22]	200 ± 5[22]
	12.27 ± 0.12[36]	192[10]	11.94 ± 0.05[24]	189 ± 20[30]
	11.96[10]		12.0 ± 1.0[2]	
Kr	15.61 ± 0.06[16]	210 ± 3[16]	15.29 ± 0.06[22]	220 ± 4[22]
	15.70 ± 0.13[36]		15.28 ± 0.04[24]	
			15.8 ± 0.6[2]	
Xe	19.30 ± 0.08[16]	251 ± 4[16]	18.87 ± 0.12[22]	250 ± 9[22]
	18.42 ± 0.40[33]		19.10 ± 0.12[24]	279.8[b,39]
			17.2 ± 0.7[2]	
N_2	10.45 ± 0.04[9]	214 ± 2[9]		
O_2	11.97[11]	200[11]	12.056 ± 0.019[21]	205 ± 2[22]
	12.01[17]	196[17]	12.001 ± 0.05[23]	
CO	10.78[8]	215[8]		
CH_4	13.19 ± 0.04[7]	236.7 ± 3.0[7]	13.06 ± 0.15[22]	242 ± 6[22]
		207 ± 49[36]	13.18 ± 0.07[23]	217.5 ± 4.8[25]
			13.12 ± 0.07[26]	209.0 ± 2.9[26]
				247.6[d,40]
C_2H_6	19.50 ± 0.08[7]	272.1 ± 9.8[7]	19.30 ± 0.12[22]	317 ± 10[22]
		301 ± 37[36]	19.51 ± 0.12[23]	284 ± 10[25]
			19.43 ± 0.10[28]	272.6 ± 2.4[28]
C_2H_4	15.33 ± 0.07[36]	171 ± 54[36]	16.46 ± 0.07[23]	236.5 ± 5.4[25]
	16.40 ± 0.08[37]	288.6 ± 4.1[7]		263.4[c,40]
		239 ± 9.9[37]		
C_2H_2	14.79 ± 0.57[36]	178 ± 39[36]	14.62 ± 0.02[23]	153.8 ± 7.2[25]
C_3H_8	22.50 ± 1.2[36]	368 ± 70[36]	22.90 ± 0.08[22]	389 ± 20[22]
	23.41 ± 0.22[37]	370 ± 54[37]	23.27 ± 0.26[23]	332 ± 38[25]
			23.11 ± 0.13[28]	319.0 ± 3.1[28]
C_3H_6	28 ± 61[33]	−150 ± 1000[33]	21.64 ± 0.12[23]	278 ± 21[25]
c-C_3H_6	13.7 ± 9.2[33]	−420 ± 200[33]	23.26 ± 0.06[23]	303 ± 11[25]
n-C_4H_{10}	26.0 ± 2.5[36]	373 ± 160[36]	25.93 ± 0.08[22]	425 ± 17[22]
			25.92 ± 0.17[23]	390 ± 28[25]
			25.70 ± 0.15[27]	387 ± 9[27]
isobutane	22.5 ± 1.1[36]	−144 ± 71[36]	24.19 ± 0.25[23]	377 ± 20[25]
			23.97 ± 0.19[27]	360 ± 23[27]
$C(CH_3)_4$	27.8 ± 8.1[36]	520 ± 270[36]	25.11 ± 0.17[23]	486 ± 31[25]
1-butene[a]	53.27[36]		24.88 ± 0.11[23]	389 ± 28[25]
CCl_2F_2	23.5 ± 1.7[35]	197 ± 52[35]	26.13 ± 0.18[29]	315 ± 11[29]
$CClF_3$	17.2 ± 1.5[38]	375 ± 68[38]	21.24 ± 0.38[29]	278 ± 22[29]
$CBrF_3$			23.72 ± 0.21[29]	318 ± 17[29]
CF_4	15.06[36]	91[36]	15.77 ± 0.14[29]	
	27.7 ± 2.1[38]	638 ± 172[38]		

[a] The solubility datum is for 313.15 K. [b] Extrapolated value at 31 MPa. [c] Extrapolated value at 18 MPa. [d] Extrapolated value at 28 MPa.

Discussion

Scanning the results in Table 1 shows the remarkable correspondence between the van't Hoff and calorimetric enthalpy and heat capacity changes on solution. For the rare gases, there is correspondence within roughly the combined uncertainties of the Benson and co-workers results and those of Gill and Wadsö and co-workers. The only rare gas Battino and co-workers measured was argon, and the correspondence between both solubility groups and the calorimetry groups is outstanding. This is also the case for the heat capacity changes for argon and for most of the other rare gases.

There are no calorimetric results for the solubility of N_2 and CO in water. Battino and co-workers determined the solubilities of O_2, CH_4, C_2H_6, C_2H_4, and C_3H_8 in water, and these results can be compared with those of calorimetry. Again, for all these gases, the agreement with respect to the enthalpy change on solution is within the combined experimental uncertainties of both approaches. Correspondence for the heat capacity for all of these gases is also exceptional.

Table 2. van't Hoff and Calorimetry Data for Methane in Water at Various Temperatures[a]

	from solubility		from calorimetry	
	$-\Delta H°$	$\Delta C_P°$	$-\Delta H°$	$\Delta C_P°$
T/K	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
273.15	19.43 ± 0.19	262.7 ± 16.1	18.56 ± 0.08	226.9 ± 9.8
278.15	18.13 ± 0.12	257.5 ± 13.2	17.44 ± 0.05	223.3 ± 7.5
283.15	16.85 ± 0.06	252.3 ± 10.4	16.33 ± 0.05	219.7 ± 5.7
288.15	15.60 ± 0.04	247.1 ± 7.6	15.24 ± 0.06	216.1 ± 4.0
293.15	14.38 ± 0.04	241.9 ± 4.6	14.17 ± 0.07	212.5 ± 2.9
298.15	13.18 ± 0.04	236.7 ± 3.0	13.12 ± 0.07	209.0 ± 2.9
303.15	12.01 ± 0.05	231.5 ± 3.2	12.08 ± 0.07	205.4 ± 4.2
308.15	10.87 ± 0.04	226.3 ± 5.3	11.06 ± 0.07	201.8 ± 5.8
313.15	9.75 ± 0.04	221.0 ± 8.0	10.06 ± 0.08	198.2 ± 7.7
318.15	8.66 ± 0.07	215.8 ± 10.8	9.08 ± 0.10	194.6 ± 9.6
323.15	7.59 ± 0.13	210.6 ± 13.6	8.12 ± 0.14	191.0 ± 11.5

[a] Taken from Tables II and III in ref 26.

Where it is possible to compare results for the solubility of the halocarbons CCl_2F_2, $CClF_3$, and CF_4 with the values given by Scharlin and Battino,[38] the correspondence is quite good for the first two gases for the enthalpy change and poor for the heat capacity for the same two gases.

There are a number of cases where the only van't Hoff values available are those from the review article by Wilhelm et al.,[36] and although those values were the result of critical evaluations of the extant literature at the time, in general the correspondence with calorimetric results is poor. This is particularly the case for some of the heavier hydrocarbon gases. I can note in passing here that we gave up our attempts to do high-precision solubility measurements of butane in water due to inconsistent results, which we ended up attributing to adsorption effects of *n*-butane in our primarily glass apparatus.

To illustrate the correspondence between the two approaches as a function of temperature, Table 2 is given. In this table are presented results for the solubility of methane in water in the range (273.15 to 323.15) K. The agreement between the enthalpy values is almost perfect at 298.15 K, and the values drift apart above and below that temperature but are still within the combined uncertainties. The calorimetric heat capacities are always lower than the van't Hoff values, yet the differences (given that the van't Hoff values are the result of two differentiations) are surprisingly good. Figure 2 in Wilhelm[31] is a graph of the enthalpy of solution of methane in water from (273.15 to 353.15) K for the van't Hoff and calorimetric results. All of the calorimetry values are on or almost on the Rettich et al.[7] smoothed line for their data.

In conclusion, it is fair to state that the theme of this paper concerning thermodynamics works has been borne out by the illustrations. To me, it is conceptually remarkable, even astounding, that via the formalisms of "playing around" with thermodynamic equations it is possible to connect equilibrium solubilities with measurements of heat effects (calorimetry). We live in a surprising world!

Personal Note

I am honored to contribute this paper to this Festschrift recognizing the contributions of Professor R. H. Stokes on the occasion of his 90th birthday. I spent the last four months of 1979 working with him and K. N. Marsh at the University of New England. They modified one of their isothermal calorimeters so that I could measure the enthalpy change on solution of gases in liquids. With the assistance of their technical staff, I was able to do a series of measurements that resulted in a publication four months after I left—this was certainly the shortest time I ever experienced from start of research to publication! His thoughtfulness made for a most productive and memorable visit. Thank you, Robin.

Acknowledgment

The subject of this paper would not have been possible to write about without the research efforts of my colleagues Y. P. Handa, T. R. Rettich, and E. Wilhelm. Finally, I wish to acknowledge my debt to the late Scott E. Wood for his friendship, collaboration on many papers, and his mentoring of me in the field of thermodynamics. In fact, his son told me that Wood was editing a draft of a thermodynamics paper of mine on the last day of his life in his 97th year. Thank you, Scott.

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