

Interpretation of isotope effects on the solubility of gases

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Abstract Experimental results concerning the isotope effect on the solubility of gases are reviewed and the theory of the isotope effect on Henry's law constants is derived in terms of the statistical mechanical theory of condensed phase isotope effects. The performance of the method is demonstrated by detailed analysis of some of the available experimental data on solubility isotope effect.

Key words gas solubility • isotope effect • isotopic fractionation • Henry's law constant • partition function

Introduction

Whereas the differences in vapor pressure between isotopic substances (vapor pressure isotope effect) have received much attention, both theoretically and experimentally [17], relatively little is known about the isotope effect on the solubility of gases in liquids. This is connected with difficulties in the precise and accurate experimental determination of solubilities of gases and of the isotopic fractionation of gases dissolved in liquids.

The first investigations on the solubility isotope effect of gases were carried out in 1957 by Cook, Hanson and Alder [7], who determined the solubility of pure hydrogen and deuterium gas in eight nonpolar solvents from -25 to 35°C and found that deuterium is about $2.5 \pm 0.1\%$ more soluble than hydrogen. Isotope fractionation of natural gases during solution was first observed by Klots and Benson in 1963 [18] in studies of nitrogen and oxygen in water in the temperature range of 2–27°C. It was found that the heavier molecular species, $^{29}\text{N}_2$ and $^{34}\text{O}_2$, are more soluble in water than the respective lighter ones, $^{28}\text{N}_2$ and $^{32}\text{O}_2$, by $0.085 \pm 0.010\%$ and $0.080 \pm 0.015\%$, respectively at 0°C and both effects decreased to approximately 0.055% at 27°C. The precision and accuracy were considerably increased ($\pm 0.002\%$) by a method based on the direct mass spectrometric comparison of the isotopic ratio $^{34}\text{O}_2/^{32}\text{O}_2$ in the dissolved gas to that in the gas above the solution [1]. The largest 'normal isotope effect' (the isotope effect is called normal, if the heavier isotopic species is more soluble than the lighter one *vide infra*) was found for the solubilities of pure hydrogen and deuterium gases in water; the observed effect decreased from $8.6 \pm 0.5\%$ to $6.5 \pm 0.6\%$ between 5 and 30°C [20]. The first 'inverse isotope effect' (the lighter isotopic species is more soluble than the heavier one) on gas solubility was observed in 1970 in the study of isotopic fractionation between gaseous carbon dioxide and the equilibrated aqueous solution of the gas between 0 and

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60°C [23]. It was observed that $^{13}\text{C}^{16}\text{O}_2$ is slightly less soluble than $^{12}\text{C}^{16}\text{O}_2$ (by 0.012% at 0°C), while the oxygen isotopes exhibit a normal isotope effect ($^{12}\text{C}^{16}\text{O}^{18}\text{O}$ is about 0.08% more soluble than $^{12}\text{C}^{16}\text{O}_2$). The experimental data on the solubility isotope effect of gases in liquids available in the literature will be surveyed in the next section.

The purpose of this paper is to review briefly the early attempts to interpret the isotopic fractionation of gases during solution and then describe in more detail how one can understand the experimentally observed differences in the solubility between isotopic species within the framework of the statistical mechanical theory of condensed phase isotope effects.

Experimental data on the solubility isotope effect of gases

The equilibrium isotope fractionation factor (α) between the solution and the gas phase is defined as

$$(1) \quad \alpha = (N/N')_{sol} / (N/N')_{gas}$$

where N' and N are the number of molecules of the lighter and heavier isotopic species respectively, and the subscript *gas* denotes the gas while *sol* denotes the solution phase.

For dilute solutions of gases in which Henry's law is obeyed, α may be written as

$$(2) \quad \alpha = k'/k$$

where k' and k are the Henry's law constants for the lighter and heavier isotopic species, respectively. (Henry's law for a two-component system composed of a pure gas and liquid states that at constant temperature and at sufficiently low pressure the partial pressure of the gas in the vapor phase (p_{gas}) is proportional to the mole fraction of the gas in the solution (x), i.e. $p_{gas} = kx$, where k is the Henry's law constant.) Consequently, measurement of the isotopic fractionation factor yields the ratio of the Henry's law constants for the two isotopic species.

The solubility isotope effect is said to be normal if $\alpha > 1$, i.e. if the heavier isotopic species is more soluble than the lighter one, and inverse if $\alpha < 1$.

The experimental data available in the literature on the isotope effect on the solubility of gases are summarized in Table 1. Some remarks concerning the experimental data are in order. It was mentioned in [20] that Benson and Krause had carried out a series of isotopic fractionation measurements with rare gases (other than He) in water and found normal isotope effects the value of which decreased with increasing temperature. However, these results seem to have never been published, only the solubilities of the naturally occurring rare gases were reported [19].

The effect of pressure on the $^{12}\text{C}/^{13}\text{C}$ solubility isotope effect of methane in water was studied at 295 K up to a pressure of 40 MPa [14]. The isotope fractionation factor did not change between normal atmospheric pressure and 30 MPa, however, above 30 MPa a significant decrease in α was observed with increasing pressure. The influence of dis-

solved salts on the $^{12}\text{C}/^{13}\text{C}$ solubility isotope effect of methane in water was found to be negligible [15]. The effect of pressure on the H/D isotope effect between gaseous and dissolved methane in water was investigated by using deuterium enriched (5% D) methane samples [5]. The separation factor (1.0005 ± 0.0001 at ambient temperature and atmospheric pressure) was found to increase with increasing pressure and to decrease with increasing temperature and water salinity. The transfer of the results of this study to the system with natural isotopic abundance is not straightforward because the samples contain not just monodeuterated methane molecules.

Theoretical interpretation of solubility isotope effect of gases

One of the first interpretations concerning the isotope effects on the solubility of gases was proposed by Hillier and Walkley in 1963 [16]. These authors stated that the observed solubility differences between hydrogen and deuterium in a wide range of nonpolar solvents [7] may be a manifestation of quantum effects in dilute solutions.

The experimental data on isotope effects on Henry's law constants of hydrogen [20], oxygen [1] and helium [2] in water were interpreted in terms of a particle in a box model. In this model the free translations of the solute molecule in the gas phase become hindered in the aqueous phase, while the rotational and vibrational degrees of freedom of the molecule were assumed to be the same in the gaseous and dissolved states. From this analysis, in which the translational energy of the solute molecule in the dissolved state was treated in the zero-point energy approximation, the dimensions of the solvent cage surrounding the solute molecule in water could be inferred and in some cases physically unreasonable box dimensions were obtained (e.g. in the case of oxygen 2.5 Å). Bopp and Wolfsberg [6] pointed out the inadequacy and oversimplification of the above approach and the soundness of the criticism was acknowledged in a subsequent paper [3].

In order to interpret their experimental data on isotopic fractionation between gaseous CO_2 and an aqueous solution of the gas, Vogel, Grootes and Mook [23] have developed a theoretical expression on the assumption that the interaction between solute and solvent could be treated in the same manner as the interaction between molecules in a pure liquid. In this way the vapor-liquid data were used to predict the sense of the effects in the vapor-solute system in satisfactory agreement with experiment. Nevertheless, the entire calculation is of a very approximate nature and subject to refinement.

Since the isotope effect on the solubility of gases (see α defined in Eq. (1)) can be regarded as an isotope effect on the equilibrium of the atoms (molecules) between the solution phase and the gas phase [6], the statistical mechanical theory developed by Bigeleisen for the isotope effect on vapor-liquid equilibria [4] can be applied to the isotope effect on Henry's law constant. Thus one can write [10]

$$(3) \quad k'/k = f_{sol}/f_{gas}$$

Isotope	Solvent	Temperature range (°C)	Solubility difference (heavy – light) (%) ^a	Reference
³ He/ ⁴ He	water ^b	0 – 60	1.817 – 1.320	2
H ₂ /D ₂	water	5 – 30	8.6 – 6.5	20
H ₂ /D ₂	nonpolar solvents	-25 – 35	≈2.5	7
H ₂ /D ₂	argon	87, 100, 120 (K)	21.3, 20.2, 18.5	24
¹⁴ N ₂ / ¹⁵ N ¹⁴ N	water	2 – 27	0.08 – 0.055	18
¹⁶ O ₂ / ¹⁸ O ¹⁶ O	water	2 – 27	0.08 – 0.055	18
¹⁶ O ₂ / ¹⁸ O ¹⁶ O	water	0 – 60	0.085 – 0.055	1
¹² C ¹⁶ O ₂ / ¹³ C ¹⁶ O ₂	water	0 – 60	-0.118 – -0.093	23
¹² C ¹⁶ O ₂ / ¹² C ¹⁶ O ¹⁸ O	water	0	0.08	23
H ₂ ³² S/H ₂ ³⁴ S	water	0 – 80	0.107(0°C), 0.080(20°C)	12
H ₂ ³² S/H ₂ ³⁴ S	water	11, 20, 30	0.217, 0.155, 0.110	21
¹² CH ₄ / ¹³ CH ₄ ^c	water	20 – 80	0.062 – 0.033	13
CH ₄ /CD ₄	water	12 – 52	-1.6 ^d	9
¹² C ₂ H ₆ / ¹³ C ₂ H ₆	water	13, 32, 80	0.048, 0.041, 0.040	11

Table 1. Experimental data on the isotope effect on solubility of gases in liquids.

^a The values are given at the lowest and highest temperatures.

^b The isotope fractionation was also determined in heavy water, seawater, methanol and ethanol.

^c The effect of pressure and salt on the solubility isotope effect was also studied (see text).

^d No significant trend with temperature was observed.

where f is the so-called reduced isotopic partition function ratio (quantum mechanical partition function divided by the classical partition function) and the subscripts *sol* and *gas* refer to the solution and gas phase, respectively.

In the case of an ideal gas, the molecules are freely rotating and translating therefore for the $3n-6$ vibrational modes (n is the number of atoms in the molecule, $3n-6$ is the number of internal degrees of freedom) f_{gas} can be written in the harmonic oscillator approximation as [17]

$$(4) \quad f_{gas} = \prod_i^{3n-6} \frac{u_i}{u_i'} \exp\left(\frac{u_i' - u_i}{2}\right) \left(\frac{1 - \exp(-u_i')}{1 - \exp(-u_i)} \right) x f_{nerot}$$

where $u_i = hc\nu_i/kT$ (ν_i is the harmonic frequency of mode i in cm^{-1}) and f_{nerot} is the contribution to the reduced partition function ratio arising from non-classical rotation in the gas phase.

In the solution phase the reduced partition function ratio for the solute molecule (f_{sol}) will be calculated within the framework of a simplified cell model in which the solute molecule has $3n$ degrees of freedom, of these $3n-6$ are similar to the vibrational modes of the gas-phase molecule. The other six external degrees of freedom correspond to the gas-phase translations and rotations which have become bound (hindered) in the condensed phase. In this approximation

$$(5) \quad f_{sol} = \prod_i^{3n} \frac{u_i}{u_i'} \exp\left(\frac{u_i' - u_i}{2}\right) \left(\frac{1 - \exp(-u_i')}{1 - \exp(-u_i)} \right)$$

The most common approximation, which can also be applied to the calculation of the solubility isotope effect, makes use of the fact that very often the $3n$ molecular frequencies happen to fall neatly into two groups [17]. The first group contains the low translational and rotational frequencies (ν_{ext}) of the solute molecule in the solution phase, which are treated in the first-order quantum correction (first term on the right hand side of Eq. (6)). The second group contains the high frequencies, usually the internal vibrational frequencies, for which $u_i = hc\nu_i/kT \gg 1$, these may be treated in the so-called zero-point energy approximation (second term on the right hand side of Eq. (6))

$$(6) \quad \ln \alpha = \ln k' / k = \ln f_{sol} / f_{gas} \approx \frac{1}{24} \left(\frac{hc}{kT} \right)^2 \left[\sum_{ext} (\nu_{ext}^2 - \nu_{ext}^2) - \frac{1}{2} \frac{hc}{kT} \left\{ \sum_{int} [(\nu_{gas} - \nu_{sol}) - (\nu_{gas} - \nu_{sol})] \right\} \right]$$

Equation (6) makes it easier to understand the contributions from the different molecular motions to the solubility isotope effect. One can see that the hindered translations and rotations will always work in the direction of a normal isotope effect ($\nu' > \nu$). The frequencies of the internal vibrations shift in most cases toward lower frequencies (red shift) when the molecule passes from the gas phase to the solution phase and this leads in the direction of an inverse isotope effect.

In order to evaluate the solubility isotope effect one has to know (a) the hindered translational and rotational frequencies of the solute molecule in the solution phase and (b) the internal vibrational frequencies of the solute molecule (at least of one of the isotopic species) in the gas and solution phase.

In the following, the application of Equations (3)–(6) to the interpretation of experimentally observed isotope effects on the solubility of gases will be demonstrated on some selected systems.

In the case of rare gases only the three hindered translations contribute to the isotope effect, consequently it is always normal ($\alpha > 1$), i.e. the heavier isotopic species is more soluble than the lighter one. This conclusion is corroborated by the experimental data on the ³He/⁴He isotope fractionation during the dissolution of helium gas in water [2].

Dang, Bopp and Wolfsberg [10] have calculated the hindered translational frequency of ⁴He atoms dissolved in liquid water by carrying out molecular dynamics (MD) simu-

Table 2. Contributions to the solubility isotope effect of methane in water^a.

Motion	CH ₄ /CD ₄	¹² CH ₄ / ¹³ CH ₄
Hindered translation	+	+
Hindered rotation	+	0
Non-classical rotation	+	0
Symmetric stretching vibration (1) ^b	-	0
Symmetric bending vibration (2)	-	0
Asymmetric stretching vibration (3)	-	-
Asymmetric deformation vibration (3)	-	-

^a Normal isotope effect: +, inverse isotope effect: -.

^b The number in parenthesis gives the degeneracy of the vibration.

lation at 295 K and then calculated α using this frequency. The agreement between calculation ($\alpha=1.034$) and experiment ($\alpha=1.016$) can be considered satisfactory, if one takes into account the approximate nature of the helium-water interaction potential employed in the MD simulation. By the same method, a value of 1.0017 was obtained for α of $^{36}\text{Ar}/^{40}\text{Ar}$, however no experimental data are available for comparison.

The least squares fits of the isotopic fractionation factor for helium dissolved in water to different functions gave the best fit in the case of the three-term equation $\ln\alpha = A/T^2 + B/T + C$ [2]. Since in the harmonic oscillator approximation for the translational degrees of freedom the temperature dependence $\ln\alpha \propto T^{-2}$ (see Eq. (6)) is expected, the above fact clearly indicates that anharmonic oscillators must be used to describe the real frequencies. Taubmann and Witschel [22] have carried out a detailed study of different effective potentials in which the dissolved helium atom moves in the liquid. They suggested that a spherical quadratic-quartic anharmonic model potential is necessary to describe the experimental data sufficiently.

In the case of diatomic molecules the calculation of the isotope effect on the Henry's law constants requires the knowledge of the triply degenerate hindered translational, doubly degenerate rotational frequencies of the solute molecule in the solution phase and the frequency shift of the stretching vibration when the molecule passes from the gas phase to the solution. These frequencies were calculated for $^{14}\text{N}_2$ in liquid water by MD simulation at 295 K and the agreement between the calculated ($\alpha=1.00093$) and experimental ($\alpha=1.00071$) isotope effect values is quite good [10]. The isotope effect is normal, all three contributions are non-negligible, although the rotational and vibrational contributions cancel each other.

Vogel, Grootes and Mook [23] have observed an inverse $^{12}\text{C}/^{13}\text{C}$ isotope effect for the solubility of CO_2 in water. Since the isotope substitution takes place in the center of the molecule, the two hindered rotations and the symmetric CO stretching vibration do not contribute to the $^{12}\text{C}/^{13}\text{C}$ isotope effect, while the contribution from the two degenerate bending vibrations is negligibly small. It follows that the negative vibrational contribution arising from the frequency shift of the asymmetric CO stretching vibration when the CO_2 molecule dissolves in water must outweigh the positive hindered translational contribution.

Deuterated methane was observed [9] to be less soluble in water than methane (on average by 1.6% around room temperature), while the solubility of $^{13}\text{CH}_4$ is higher than that of $^{12}\text{CH}_4$ (e.g. at 20°C by 0.06%) [13]. A preliminary interpretation of the experimental data was carried out [8] using the available spectroscopic data. The detailed analysis (see Table 2) indicated that the $^{12}\text{C}/^{13}\text{C}$ solubility isotope effect is determined by the hindered translational motions of the methane molecules in the aqueous solution and by the frequency shifts of the asymmetric vibrations of the methane molecule during solution. In the case of the H/D isotope effect there are also significant contributions from the hindered rotations and symmetric vibrations. The methane molecule can be considered as a light molecule. Consequently, at room temperature a correction term

accounting for the non-classical rotation of the methane molecule in the vapor phase must be included into the calculations (this term can be readily evaluated from the known moments of inertia of CH_4 and CD_4). Molecular dynamics simulations and IR spectroscopic measurements are in progress to determine the hindered translational and rotational frequencies of methane molecules in water and the frequencies of the asymmetric vibrations of the methane molecule dissolved in water, respectively.

Conclusions

It has been demonstrated by the theoretical analysis of some of the high-precision data on the isotope effect on the solubility of gases that the isotope effect can be well understood in terms of the statistical mechanical theory of condensed phase isotope effects. The experimental solubility isotope effect data can be quantitatively described using hindered translational and rotational frequencies of the solute molecule in the solution phase and the frequency shifts of the internal vibrations of the molecule on transferring the molecule from the gas phase into the solution phase. One can expect that the frequencies required by the isotope effect calculations will be available for more systems in the future with the widespread use of molecular dynamic simulations and with the availability of spectroscopic instruments capable of detecting very low intensity peaks in the solutions of gases.

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