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Solubility phenomena related to CO_2 capture and storage*

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Abstract: Capturing CO_2 emissions from energy production and storing it under the ground is a potential CO_2 mitigation strategy that currently receives much attention. Both CO_2 capture and CO_2 storage are solubility problems. This paper reviews some important solubility aspects of CO_2 capture and storage that are often overlooked. Until very recently, there was not a single CO_2 solubility relationship that was both applicable in a wide temperature range and thermodynamically consistent with the enthalpy of solution of CO_2. Furthermore, very often the relationship used for the first acidity constant of carbonic acid as a function of temperature is inconsistent with the relationship used for the solubility constant (or Henry constant) of CO_2. The removal of CO_2 from a gas stream with amine solutions is usually viewed as a chemical reaction, which leads to the practice of heating to remove the CO_2 from the solvent. However, viewing this process as a solubility phenomenon suggests the practice of using vacuum to remove the CO_2 from the solvent, a potentially more efficient approach.

Keywords: calcite; chemical equilibrium; CO_2; solubility; solution chemistry.

INTRODUCTION

The mixing ratio of CO_2 in the atmosphere has increased from 270 to 390 ppm since pre-industrial times. As a consequence, the global temperature has increased by about 0.8 °C in the last century. It is anticipated that a doubling of the CO_2 concentration will lead to a global temperature increase of 2.1–4.4 °C [1].

The impact of CO_2 on climate is not a new area of study. The first study of the climate's sensitivity to CO_2 concentrations was published in 1896 by Arrhenius [2]. However, the research has taken on a new urgency since the 1980s, when the warming began to exceed the natural climate variability.

As the main greenhouse gas, CO_2 is the primary target for greenhouse gas emission reductions. However, due to its link with energy production, deep CO_2 emission reductions are difficult to achieve, and thus the capture and storage of CO_2 has become an area of intense study.

The capture of CO_2 from power plant flue gases is possible with a well-established technology, amine scrubbing. It is used, for instance, to separate CO_2 from hydrogen in the ammonia synthesis process. Some industrial experience with the underground storage of CO_2 is available from enhanced oil recovery, where CO_2 or other compounds are injected in an oil field to increase the pressure and the mobility of the oil in the reservoir.

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Solubility and related equilibrium phenomena are at the heart of both CO_2 capture and storage, and our understanding of these processes can be improved by considering CO_2 solubility more explicitly. The objective of this paper is to highlight the solubility and related equilibrium aspects of CO_2 capture and storage.

HOW WELL DO WE UNDERSTAND CO_2 SOLUBILITY IN WATER?

There are hundreds of CO_2 solubility measurements in the literature. They were summarized in Vol. 62 of the Solubility Data Series [3]. Mathematically, they can be represented by the solubility constant and by the Henry constant [4]. Applied to the solubility of CO_2, the solubility constant is defined as

$$K_S = [\gamma(CO_2)m(CO_2)/m^\circ]/[f(CO_2)/f^\circ] \quad (1)$$

where $\gamma(CO_2)$ is the activity coefficient of CO_2 in the aqueous phase, $m(CO_2)$ is molality of CO_2 in the aqueous phase, $f(CO_2)$ is fugacity of CO_2 in the gas phase, m° (= 1 mol kg^{-1}) is the standard molality, and f° (= 1 bar) is the standard fugacity. The solubility constant is unitless. The Henry constant is defined as

$$k_H = \lim[f(CO_2)/x(CO_2)]_{x(CO_2)\to 0} \quad (2)$$

where $x(CO_2)$ is the mole fraction of CO_2 in the liquid phase. k_H has units Pa (or bar = 10^5 Pa). In eqs. 1–2, it is assumed that all dissolved CO_2 is in the unhydrated form. Hence, the variables $m(CO_2)$ and $x(CO_2)$ implicitly include the hydrated form H_2CO_3(aq) as well. The relationship between K_S and k_H is

$$K_S = 55.508f^\circ/k_H \quad (3)$$

Empirical equations for K_S or k_H were derived by Harned and Davis [5], Wilhelm et al. [6], Plummer and Busenberg [7], Carroll et al. [8], Crovetto [9], Rumpf and Maurer [10], Fernández-Prini et al. [11], De Visscher and Vanderdeelen [12], and De Visscher et al. [13]. The correlation of Stumm and Morgan [14] that had been referred to in an earlier analysis [12] turned out to be identical to the correlation of Plummer and Busenberg [7]. These relationships correspond well with each other, to within 5 % up to 100 °C, and with larger deviations (up to 30 %) at higher temperatures. However, around 0 °C and the critical point of water, the slopes of the equations are highly divergent, indicating a poor thermodynamic consistency between the equations. For a relationship describing the temperature dependence of the Henry constant or the solubility constant of CO_2, its slope must be consistent with the enthalpy of solution of CO_2 to within experimental error. The standard enthalpy of solution of CO_2, $\Delta_{sol}H^\circ$, can be calculated from the *CODATA Key Values for Thermodynamics* [15], and is found to be –19.748 kJ mol^{-1}. The uncertainty of this value is the uncertainty of the heat of solution of CO_2 measured by Berg and Vanderzee [16,17], and was found to be 0.167 kJ mol^{-1}.

The enthalpies of solution of CO_2 in water, predicted by the different relationships for the solubility constant or the Henry constant of CO_2 are shown in Fig. 1. Of the two relationships of Crovetto [9], only the low-temperature relationship was tested. The relationship of De Visscher and Vanderdeelen [12] was not tested because it was forced to be consistent with CODATA.

Of the eight relationships, only four are consistent with the thermodynamic data. In fact, the relationship of De Visscher et al. (2012 part 1) was developed because of this lack of consistency, as all the thermodynamically consistent equations had a limited temperature range of applicability (<100 °C). In fact, there is a tendency of deterioration in the thermodynamic consistency over time, probably due to the need for wider temperature ranges, which trumped the need for thermodynamic consistency. Crovetto [9] tried to avoid this issue by defining a low-temperature (0–80 °C) and a high-temperature (100–374 °C) relationship, but the two relationships do not join smoothly, creating a slight internal inconsistency around 100 °C.

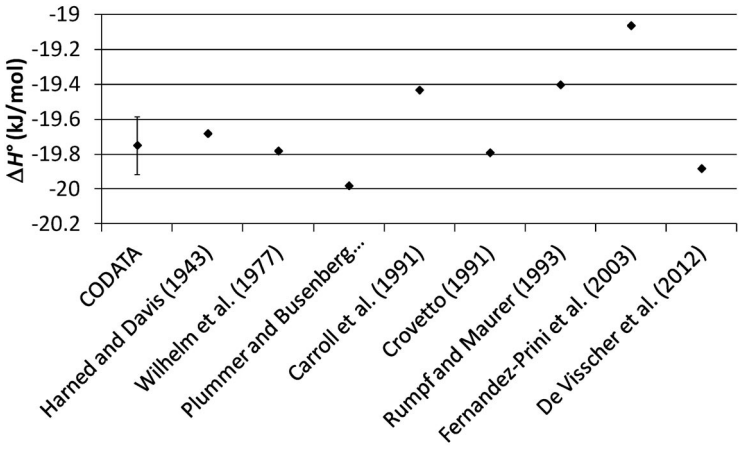

Fig. 1 Enthalpy of solution of CO_2 calculated from CODATA thermodynamic values and from various semi-empirical equations.

It is interesting to consider the relationship of Fernández-Prini et al. [11], because it had the widest range of applicability and the worst thermodynamic consistency

$$\ln(k_H/p_{1v}) = A/T_r + B\theta^{0.355}/T_r + CT_r^{-0.41}\exp(\theta) \quad (4)$$

where p_{1v} is the vapor pressure of water, T_r is the reduced temperature (= T/T_c with T_c the critical temperature, 647.096 K), and $\theta = 1 - T_r$. The advantage of this equation is that it emulates the effect of solvent density on the equilibrium. However, to arrive at internationally accepted correlations, both thermodynamic consistency and a wide temperature range of applicability should be observed. To that effect, De Visscher et al. [13] extended eq. 4 as follows:

$$\ln(k_H/p_{1v}) = A/T_r + B\theta^{0.355}/T_r + CT_r^{-0.41}\exp(\theta) + D \quad (5)$$

They found $A = -9.14122$, $B = 2.81920$, $C = 11.28516$, and $D = -0.80660$. This equation is valid from 0 °C to the critical point of water, and is thermodynamically consistent with the enthalpy of solution of CO_2 in water to within experimental uncertainty. Equation 5 also removes the small effect of CO_2 dissociation in the CO_2 solubility experiments (reaction 7), an effect that was ignored in most studies, introducing a slight inconsistency in carbonate equilibrium models. For p_{1v}, the correlation of Wagner and Pruß [18] was used

$$\ln(p_{1v}/p_c) = (T_c/T)(a_1\theta + a_2\theta^{1.5} + a_3\theta^3 + a_4\theta^{3.5} + a_5\theta^4 + a_6\theta^{7.5}) \quad (6)$$

where p_c = critical pressure (220.64 bar), $a_1 = -7.85951783$, $a_2 = 1.84408259$, $a_3 = -11.7866497$, $a_4 = 22.6807411$, $a_5 = -15.9618719$, and $a_6 = 1.80122502$.

HOW WELL DO WE UNDERSTAND THE ACIDITY OF CO_2?

The acid–base reactions of dissolved CO_2 can be described as follows:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \quad (7)$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \quad (8)$$

with equilibrium constants K_1 and K_2, respectively. One of the most frequently cited sources of correlations for K_1 and K_2 is Plummer and Busenberg [7]. However, this study overlooks an important consistency issue. On p. 1015, the authors state: "In defining K_1 between 0 and 50 °C we have relied on

the careful EMF measurements of Harned and Davis (1943) (...).” Two pages earlier, on the solubility of CO_2, they stated: “One of the most frequently cited sources of CO_2-water solubility data (Harned and Davis, 1943) was judged less reliable (...). For this reason we have not included the CO_2-solubility data of Harned and Davis (1943) in our final analysis.” However, upon closer inspection of the electromotive force measurements of Harned and Davis [5], it is found that these experiments measure the equilibrium constant of the following reaction:

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{9}$$

which has equilibrium constant $K_S K_1$. Hence, to derive K_1 from the EMF data of Harned and Davis [5], the result must be divided by K_S to obtain K_1. Hence, if K_S is “less accurate”, then this translates into less accurate values of K_1. In retrospect, the K_S data of Harned and Davis (1943) are among the best in the literature. Nevertheless, it is useful to recalculate K_1 whenever a new correlation for K_S is used. De Visscher et al. [13] recommended the following, which is consistent with eq. 5:

$$\ln K_1 = A + B/(T/\mathrm{K}) + C \lg(T/\mathrm{K}) + \mathrm{D}(T/\mathrm{K}) + E/(T/\mathrm{K})^2 \tag{10}$$

with $A = -441.490479$, $B = 26901.0527$, $C = 157.2016907$, $D = -0.07219967$, and $E = -2003878.4$. The equation is valid at $p = p_{1v}$ and temperatures ranging from 0 to 300 °C. Duan and Li [19] presented a pressure correction for this equation. An earlier pressure correction of Li and Duan [20] contains errors, and should not be used.

For K_2 the consistency problem does not occur as this property is evaluated without a gas phase [21].

HOW DOES LIMESTONE AFFECT CO_2 SOLUBILITY?

Known as Iceland spar, chalk, limestone, marble, and scale, calcium carbonate in the calcite form is ubiquitous in the environment. Its solubility is closely linked with the solubility of CO_2 because of the common carbonate and bicarbonate ions. The dissolution reaction of calcite is as follows:

$$CaCO_3(cr) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \tag{11}$$

The protonation of the dissolved carbonate consumes protons, stimulating the dissociation of carbonic acid, enhancing the solubility of CO_2. On the other hand, the acidity of carbonic acid promotes the dissolution of $CaCO_3$. Consequently, the solubility of calcite is an important factor in the fate of CO_2 in the atmosphere, and can be of consequence in the proposed practice of storing CO_2 in underground aquifers.

The solubility of calcite, as well as other alkaline earth carbonates, is the subject of Vol. 95 of the Solubility Data Series [13,22]. For the solubility constant of calcite, the following equation was put forward:

$$\ln K_s = A + B/(T/\mathrm{K}) + C \lg(T/\mathrm{K}) + \mathrm{D}(T/\mathrm{K}) + E/(T/\mathrm{K})^2 \tag{12}$$

where $A = -1345.16079$, $B = 74633.752$, $C = 486.880004$, $D = -0.223388933$, and $E = 4600214.42$. In the development of this equation, the interaction between the ions $Ca^{2+}(aq)$ and $HCO_3^-(aq)$ was described with the Pitzer formalism [23–28], with parameters based on Pitzer et al. [29] and He and Morse [30]. In the analysis, calcite, aragonite, and vaterite solubility were analyzed simultaneously, using various thermodynamic data [31–36] to ensure thermodynamic consistency.

The link between the solubility of calcite and the solubility of CO_2 can be seen based on the following reaction:

$$CaCO_3(cr) + CO_2(g) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq) \tag{13}$$

For each calcite molecule that dissolves, one molecule of CO_2 dissolves as well. A simulation model was developed that included all the significant reactions in the aqueous solubility of CO_2 and $CaCO_3$. Based on the model, the solubility of CO_2 in calcite suspensions was calculated and compared with the solubility of CO_2 in pure water. The result is shown at 25 °C in Fig. 2. From Fig. 2 it is clear that the solubilizing effect of limestone is very pronounced in atmospheric conditions (a factor 28 increase at 380 ppm and 1 bar), whereas the effect is limited at elevated concentrations (a factor 1.27 increase for pure CO_2 at 1 bar), and elevated pressures (a factor 1.03 at 64 bar). Similarly, the presence of sandstone minerals can have a solubilizing effect, with the formation of $CaCO_3$. An example is feldspar

$$CaAl_2Si_2O_8(cr) + CO_2(g) + 2H_2O(l) \rightleftharpoons CaCO_3(cr) + Al_2Si_2O_5(OH)_4 \quad (14)$$

An overview of similar reactions is given by Lackner et al. [37].

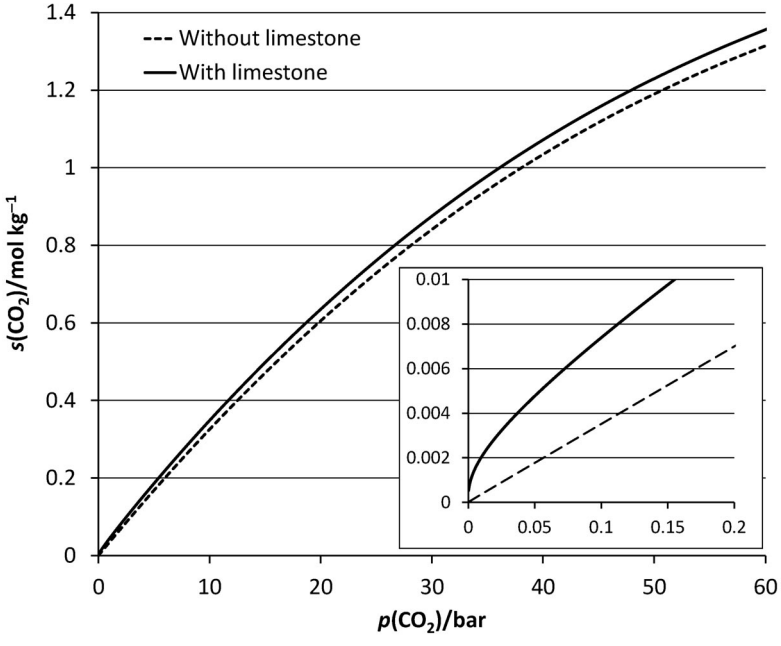

Fig. 2 Solubility of CO_2 in pure water and in limestone suspensions at 25 °C-model predictions.

CO_2 CAPTURE AS A SOLUBILITY PROCESS

Absorption in aqueous ethanolamine solutions is a commonly used technique to remove CO_2 from a process gas stream. The interaction between the CO_2 and the ethanolamine (e.g., diethanolamine, DEA) is an acid–base reaction. This reaction is exothermic and reversible. Hence, increasing the temperature reverses the reaction. Therefore, regeneration of the solvent is accomplished by heating the CO_2-rich solution. However, most of the energy is spent heating the solvent (>90 % of the solution when the gas stream contains 10 % CO_2), which makes the process very energy intensive. This is a significant hurdle to the practical application of amine absorption in CO_2 storage, because of the size of the gas flows. Furthermore, to achieve the deep CO_2 emission reductions that are necessary to ward off dangerous anthropogenic climate change, leaner gas streams will need to be treated. The absorption process can be optimized for leaner gas streams, but it is essentially a process with an energy consumption inversely

proportional to the CO_2 partial pressure, which rules out its application to waste gas streams much leaner than 10 % CO_2, unless solvents with better CO_2 solubilities can be found.

This picture of amine absorption changes drastically when it is viewed as a solubility phenomenon. The solubility of CO_2 in a solvent depends on the temperature, the CO_2 partial pressure, and the type of solvent used. It follows that applying vacuum offers an alternative pathway of solvent regeneration in an amine absorption process. Indeed, running the regeneration step under vacuum is known to reduce the energy requirement of an amine process, but processes using this feature still rely mostly on heat to regenerate solvent, and the game-changing nature of this alternative is not fully appreciated.

The reason why vacuum is a potential game changer in amine absorption is a thermodynamic one. The minimum work required to separate CO_2 from a gas stream is the Gibbs free energy of mixing, which is also the Gibbs free energy of compression in the case of an ideal gas mixture [38]

$$w = RT \ln(p_2/p_1) \tag{15}$$

where p_1 and p_2 are initial and final CO_2 partial pressures. In practice, p_1 is the equilibrium partial pressure of CO_2 in the solvent after regeneration (e.g., 0.01 bar in the case of an ideal process removing CO_2 from a gas stream at 1 bar containing 10 % CO_2 with 90 % efficiency). It follows that compression is the thermodynamically cheapest way to concentrate a gas. It also follows that the energy consumption of CO_2 capture should be inversely proportional to the logarithm of the CO_2 partial pressure, and there is no thermodynamic reason to rule out carbon capture at CO_2 partial pressures lower than 10 %, or even as low as ambient CO_2 partial pressures. For instance, eq. 14 predicts a minimum energy requirement of 22.8 kJ mol^{-1} to remove 90 % CO_2 from a gas stream containing 10 % CO_2 at 1 bar and 25 °C, and to compress it to 100 bar in a hypothetical ideal gas case. To remove 50 % CO_2 from a gas stream containing 400 ppm CO_2 at 1 bar and compress it to 100 bar would require 32.5 kJ mol^{-1}, an increase of less than 50 % in the energy requirement. In comparison, the current state of the art in amine technology projects an energy consumption of 59 kJ mol^{-1} for a large-scale CO_2 capture process from a power plant flue gas [39]. In some cases, the advantage of freely choosing the optimal site for atmospheric CO_2 capture and storage could outweigh the increased energy cost [40].

It is not feasible to modify an amine absorption unit in its current form for regeneration by vacuum alone (i.e., without heating the solvent) because too much energy would be required to compress the water vapor evaporating in the desorption stage. Process simulations with VMGSim (Virtual Materials Group, Inc., Calgary, AB, Canada) indicate that this problem can be overcome with a staged desorption approach. This involves desorbing a portion of the CO_2 with a less deep vacuum that leads to less water evaporation, and a staged recompression of the CO_2 desorbed at the deepest vacuum that avoids complete recompression of the water evaporated at this stage.

Current efforts to develop a practical approach to capture CO_2 from ambient air focus on thermal cycles like the one based on the reaction [41]

$$CaO(cr) + CO_2(g) \rightleftharpoons CaCO_3(cr) \tag{16}$$

This cycle requires heating the calcium carbonate to temperatures on the order of 900 °C and consuming an excessive amount of energy for that reason. A titanate cycle is thought to reduce the energy requirement [42], but still requires heating to similar temperatures.

The replacement of an amine solution with a sorbent could solve the water vapor evaporation problem if sorbents with a sufficient selectivity to CO_2 can be found. Some zeolites offer a feasible solution in dry air, but not in humid air [43]. Other sorbents are reviewed by Goeppert et al. [44]. Most studies consider heating (temperature swing adsorption, TSA) as the main desorption mechanism [45], or a combination of heating and vacuum (temperature vacuum swing adsorption, TVSA) [43,46], whereas fewer studies have considered vacuum [47,48] as the main desorption mechanism.

CONCLUSION

By evaluating the thermodynamic consistency of the solubility of CO_2 and the first acidity constant of carbonic acid, it was possible to point out flaws in earlier attempts to generate correlations for the equilibrium constant. More recent correlations that do not show these flaws were pointed out. Based on calculations with a recently published model, it was shown that limestone increases the solubility of CO_2 by about 3 % in representative CO_2 storage conditions. Based on a thermodynamic consideration, it is argued that more efforts should be made to develop vacuum-based CO_2 capturing schemes.

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