Macroscopic Thermodynamics of Interfaces at Water Pore Scales: Effects on Water-Rock Interactions and Mass Transfer

Lionel Mercury

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Macroscopic thermodynamics of interfaces at the water pore scales: effects on water-rock interactions and mass transfer

Lionel Mercury[a,b,c]∗

[a]Université d'Orléans, ISTO UMR 7327, 45071 Orléans, France
[b]CNRS/INSU, ISTO UMR 7327, 45071 Orléans, France
[c]BRGM, ISTO UMR 7327, BP 36009, 45060 Orléans, France

Abstract

The possible role of liquid-air and solid-liquid interfacial curvature on the water-rock mass transfers in natural setting is here studied by macroscopic thermodynamics that includes Young-Laplace interphase pressure gradient. Capillary water in non-saturated soils (liquid-air concave curvature toward air), and curved solid as a function of pore sizes (solid-liquid concave curvature towards infilling solution) exemplify what can be expected in terms of solubility. Gases solubility in capillary water is increasing with curvature, promoting the gas uptake and so moving chemical equilibria in solutions (e.g., redox and/or acido-basic) accordingly. Applied to solid solubility, the macroscopic thermodynamics of interfaces treatment highlights the versatility offered by crystalline shaping with respect to the capillary degree (if any) of the surrounding aqueous solution. Additionally, the solid curvature associated with decreasing pore sizes makes the solid less soluble in the infilling bulk solution.

1. Introduction

Interfaces attract much attention of the geochemistry community because they are the true location where solid-liquid or liquid-gases interact, depending on the local thermodynamic potential. Many efforts were and are undertaken to describe the physical and physic-chemical properties of interfaces down to the atomic-scale, in terms of structure (e.g., review by Brown et al. [1]) and/or chemical fluxes (e.g., [2]).

Macroscopic thermodynamics calculate the driving force existing in one extended system using the chemical potential for those phase transitions that arise at constant (T,P). Meanwhile, it does not appear to be the relevant tool to deal with the atomically heterogeneous interfaces. Yet, interface has got one feature that can be addressed in continuum terms: its curvature that directly links to phase pressure owing

to the Young-Laplace equation (YLE) and the interphase surface tension (e.g., [3]). Originally declined for liquid-gas interfaces, YLE can be extended to liquid-solid equilibrium situations and allows taking into account the interfacial curvature into chemical potential and so reaction driving force (e.g., [4-5]). The present contribution develops the different thermodynamic sketches, and evokes the natural settings in which they should be relevant.

2. Liquid-air interfacial curvature

Capillary water in non-saturated porous system display liquid-air interface concave toward air, while water droplets experience an opposite convex shape of their liquid-air interfaces. Indeed, capillary water is largely encountered in natural settings, in soils (featuring most of the immobile water) and trees (sap ascent) mainly, and water nano/micro-droplets are common in clouds and fogs. In all these cases, the driving force to curve a liquid with respect to the ambient pressure is the partial pressure of vapor in air (Kelvin law). A capillary meniscus is driven by a lower relative humidity (RH hereafter) than saturation's, while cloud droplets imply RH conditions above saturation's: liquid-air curvature is then air humidity-dependent. The true difference between droplet and meniscus is that the former closes on itself and then can stand as such, while the latter needs a support to sustain its curvature without collapsing: only a pore/channel network can host capillary water. The properties of curved-shape liquids are easily worked out by simple thermodynamics, as follows:

$$\mu_{CURVED} - \mu^{\circ}_{REF} = V^{\circ}_{phase} \ x \ (P_{phase} - 1) \tag{1}$$

with μ_{CURVED} and μ°_{REF} are the chemical potentials of, respectively, the curved and the reference phase, V°_{phase} is the molar volume of the wetting phase (water), assumed or not constant with curvature, P is the wetting phase internal pressure.

Water phase pressure can be determined from RH values (Kelvin law), from capillary sizes (Young-Laplace law), or from lifetime of capillary water when metastable (nucleation theory) [6]. Capillary water becomes metastable whenever hosted in pore/channel with interior larger than the meniscus locations, typically an ink-bottle shape, frequently evoked in soil physics (e.g. [6-7]).
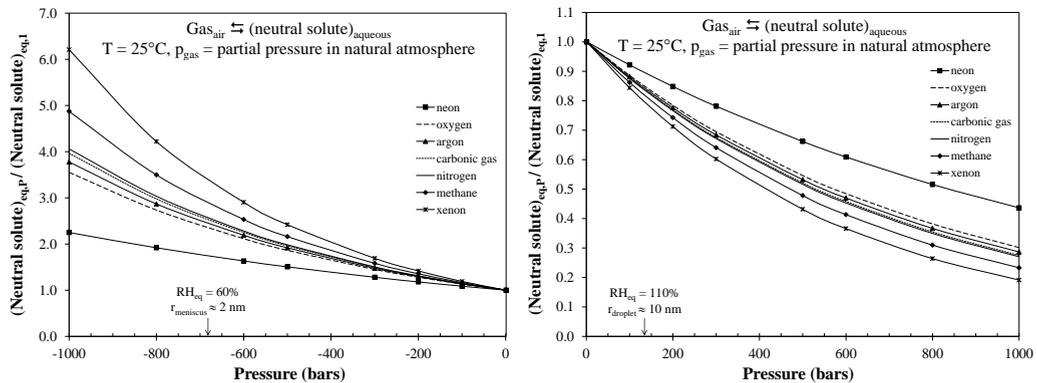
Fig. 1. Gases solubility ratio between capillary and bulk water and (a) concave-curved capillary water; (b) convex-curved droplet.

The whole dataset of capillary thermodynamic properties can be calculated (e.g., [8]), and so the solvent properties of capillary water with respect to gases and solids (e.g. [3,8-10]). At first sight, gases and solids have nothing to do with the capillary state. For instance, gas pressures stay constant in the

atmosphere even while contacting a capillary meniscus or a fog/cloud water droplet. The reaction driving force only includes the role of liquid-air curvature embedded into the liquid Young-Laplace pressure:

$$d\Delta_R G_{cap} = \int_{P_{ref}=0.1}^{P} (V_{water} + V_{solutes})dP \qquad (2)$$

In this typically anisobaric case, capillary water is pumping in the gases, while the water droplet has the reverse behaviour with respect to the bulk (Fig. 1). Capillary water appears a better solvent for gases, favouring for instance the embolism resistance in trees (e.g., [11]) and oxidation reactions (e.g., [10]). It is also a good CO_2 sink, especially in arid and semi-arid zones wherein the capillarity magnitude becomes large and the petrophysical properties of soils are relevant.

3. Liquid-solid interfacial curvature

Solid curvature is related to external shape. YLE has been early used to define the natural geometrical features of many crystals, by the so-called Wulff's construction (e.g, [4]). Using YLE for crystal-solution equilibria means that the chemical potential of solids is curvature-dependent. If they are curved concavely to their native shape, their chemical potential is negatively affected by the PdV term, and the reverse for those solids convexically curved. As a whole, the pressures of liquid and interacting solids can be equal (isobaric scheme), or different (anisobaric scheme), by a value controlled by the pressure difference across liquid-solid interface. A simple example of the anisobaric configuration takes place in porous media when measuring a decreasing melting point of liquid water as a function of pore radius (Gibbs-Thompson equation). In this case, the solid and the solution pressures are different because their mutual interface can change according to the YLE. Equation (2) becomes (generic reaction: cristal X + H_2O = cristal Y + cation + anion):

$$-RTd\Delta_R G_P = \int_{P_r}^{P_1}(V_{Cat^+} + V_{An^-} - V_{H_2O})dP + \int_{P_r}^{P_2} V_{Y_{cristal}} dP - \int_{P_r}^{P_3} V_{X_{cristal}} dP \qquad (3)$$
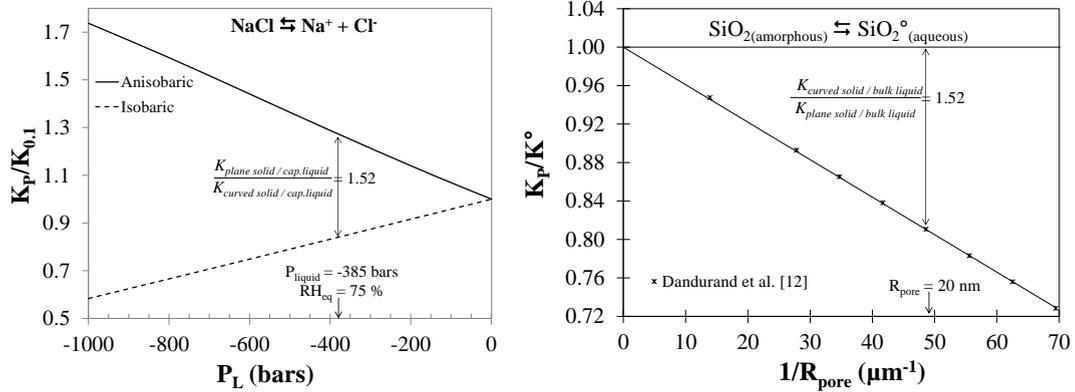

Fig. 2. Isobaric and anisobaric contexts illustrated for (a) NaCl solubility as a function of capillary pressure; (b) amorphous silica solubility as a function of pore radius (compared to experiments from [12]).

Equation (3) makes clear that any combination of liquid and solid pressures is possible, even having the pressures of the two crystals be different (e.g., [8]). The calculation leads to conclude that the solids can be more or less soluble in capillary water (Fig. 2a), depending on their own behaviour and shaping,

and that a decreasing pore size in saturated system is accompanied with a decreasing solubility matching well experimental data (Fig. 2b). The effect is clearly expressed for pore sizes smaller than 0.1 μm.

As a consequence, water-rock interactions in non-saturated zone should consider the crystalline habit of the solids. It is clear that a solution saturated with respect to the normal crystal ("anisobaric case") is supersaturated with respect to the curved solid (Fig. 2a), favouring such precipitation and a slightly less concentrated capillary solution (e.g., [13]). Meanwhile, pores implies that the host solid is curved concave to the infilling solution (saturated zone), leading to decrease the solubility threshold and promoting unexpected phase transition along a flowline (Fig. 2b).

4. Interfaces without curvatures

Figures 1 and 2 illustrate the versatility of the thermodynamic treatment to involve the interfacial curvature into the calculation of the equilibrium constants. Solubility of gases and solids are thus changed, and unexpected driving forces are possible, for instance by turning normal into curved solids (Fig. 2a, and [13]). An additional extension of the present reasoning can be done toward the weathering by adsorption thin films. It is well known that they have the same chemical potential than the mother water reservoir (capillary cluster, saturated zone). It is less known that they are chemically active, even restricted to high thinness, one monolayer or so (e.g., [14-15]). Using the same thermodynamic treatment, it seems possible to expect a strong influence of adsorbed water on the mass transfer at the field scale.

References

[1] Brown Jr G.E., Henrich V.E., Casey W.H., Clark D.L., Eggleston C., Felmy A., Goodman D.W., Grätzel M., Maciel G., et al. Metal oxides surfaces and their interactions with aqueous solutions and microbial organisms. Chem. Rev. 1999;99:77-174.

[2] Hellmann R., Penisson J.-M., Hervig R. L., Thomassin J.-H., Abrioux M.-F. An EFTEM/HRTEM high-resolution study of the near surface of labradorite feldspar altered at acid pH. Phys Chem Minerals 2003;30:192–197.

[3] Mercury L. and Tardy Y. Negative pressure of stretched liquid water. Geochim.Cosmochim. Acta 2001;65:3391-3408.

[4] Defay R., Prigogine I., and Bellemans A. *Surface tension and adsorption*. Longmans, Green & Co, London, 1966.

[5] Sanfeld A. and Steinchen A. Surface energy, stress, capillary-elastic pressure and equilibrium constant in nanoparticles. Surf. Science 2000;463:157-173.

[6] Bouzid M., Mercury L., Lassin, A. et Matray J.-M. Salt precipitation and trapped liquid cavitation in micrometric capillary tubes. J. Colloid Interf. Sci. 2011;360:768-776.

[7] Pettenati M., Mercury L., and Azaroual M. Capillary geochemistry in non-saturated zone of soils. Water content and geochemical signatures. Applied Geochem. 2008;23:3799-3818.

[8] Mercury L., Azaroual M., Zeyen H., and Tardy Y. Thermodynamic properties of solutions in metastable systems under negative or positive pressures. Geochim. Cosmochim. Acta 2003;67:1769–1785.

[9] Mercury L., Pinti D. L., and Zeyen H. The effect of the negative pressure of capillary water on atmospheric noble gas solubility in ground water and palaeotemperature reconstruction. Earth & Planetary Sci. Lett. 2004;223:147–161.

[10] Lassin A., Azaroual M., and Mercury L. Geochemistry of unsaturated soil systems: aqueous speciation and solubility of minerals and gases in capillary solutions. Geochim.Cosmochim. Acta 2005;69:5187-5201.

[11] Tyree M.T. and Zimmermann M.H. *Xylem Structure and the Ascent of Sap*. Springer Series in Wood Science (T.E Tindell Ed.), Springer Verlag, 2nd edition, 2002.

[12] Dandurand J.-L., Mizele J., Schott J., Bourgeat F., Valles V., and Tardy Y. Premiers résultats sur la solubilité de la silice amorphe dans les pores de petite taille. Sci. Géol. Bull. 1982;35:71-79.

[13] Bouzid M., Mercury L., Lassin A., Matray J.-M. and Azaroual M. In-pore tensile stress by drying-induced capillary bridges inside porous materials. J. Colloid Interf. Sci. 2011;355:498-506.

[14] Hausner D.B., Reder, R.J., and Strongin D.R. Humidity-induced restructuring of the calcite surface and the effect of divalent heavy metals. J. Colloid. Interf. Sci. 2007;305:101–110.

[15] Richard T., Mercury L., Massault M. et Michelot J.-L. Experimental study of D/H isotopic fractionation factor of water adsorbed on porous silica tube. Geochim. Cosmochim. Acta 2007;71:1159-1169.