

01C The Chemical Potential

The Generality of Chemical Potential

•Cross-cutting

The chemical potential is a cross-cutting parameter which applies to chemistry, materials science, electrochemistry, mechanical problems, etc. etc.

•It is species specific: an example, H₂O

-H₂O is a species;

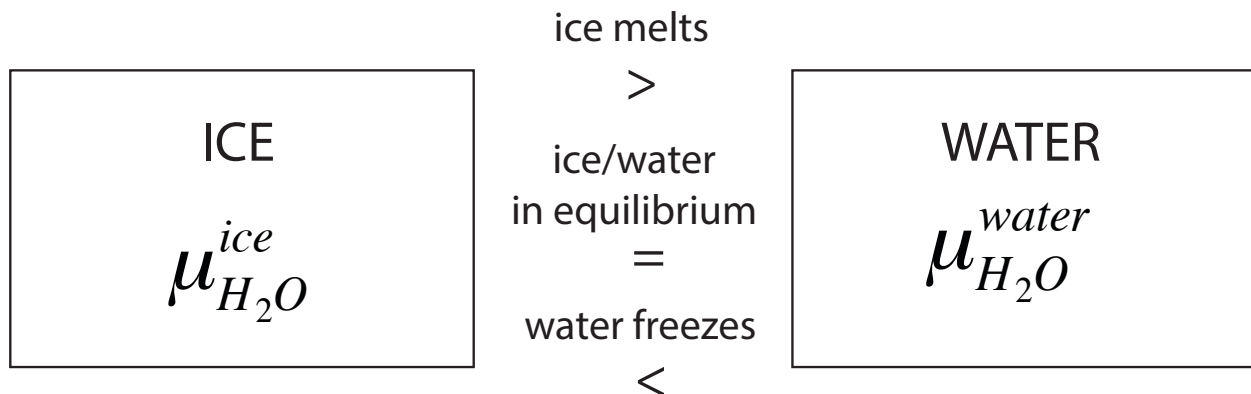
-H₂O can exist in different forms, such as water, vapor and ice.

-In each of these forms we can speak of the chemical potential of the H₂O molecule

Nomenclature: the symbol for chemical potential is μ_{H_2O} . We can write the chemical potential in each of these phases as

$$\mu_{H_2O}^{water}, \mu_{H_2O}^{vapor}, \mu_{H_2O}^{ice}$$

•The difference in the chemical potential between two states for example



(i) The chemical potentials of H₂O are equal in ice and water at the melting point where the two phases are in equilibrium

(ii) The phase wants to transform from one to the other in order to equalize the chemical potential, and reach equilibrium.

(iii) As the chemical potentials seek to equalize there is a give and take with the environment. The difference in the chemical potential is the amount of work the system can do on the environment (if the chemical potential decreases), or that the environment can do on the system (the chemical potential increases)

In the above example when ice melts (the chemical potential difference decreases) then the latent heat of melting is released to the environment.

•Other Examples

Electrical work as in batteries

Chemical potential of Li is higher at the anode than at the cathode. This difference in the chemical potential is the work available to the environment when a Li species migrates from the anode (higher chemical potential) to the cathode (lower chemical potential).

This work is watts or Joules per second. The time enters into the equation because the Li is transported across the cell as a certain rate (the kinetics).

The above example illustrates the role of thermodynamics (chemical potential) and kinetics (the rate of mass transport).

The above concept can be written in a general way as follows

$$\text{the current} = (\text{driving force}) * (\text{the transport kinetics usually controlled by diffusion}) \quad (1)$$

The driving force is given by the **difference in the potential** at the anode and the cathode

$$\Delta V$$

The Units

•Energy has units of Joules, Power has units of Watts or J sec^{-1} .

•Since the chemical potential defines the energy level of a given species in a given state.. it also has units of energy but since it is species specific it is

chemical potential has units of energy per mole, or energy per atom (obtained through the Avogadro's number).

Energy in Electrical Scenarios

Volts do not have units of energy. However when an electron (or a unit charge) is transferred from one potential state to another work is done by the environment or on the environment. The work done to transport one electron between a voltage different of ΔV is derived in electrostatics (by the force on an electron multiplied by the displacement) and is given by

$$e\Delta V, \text{ or, } eV$$

eV has units of Joules with the following conversion

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

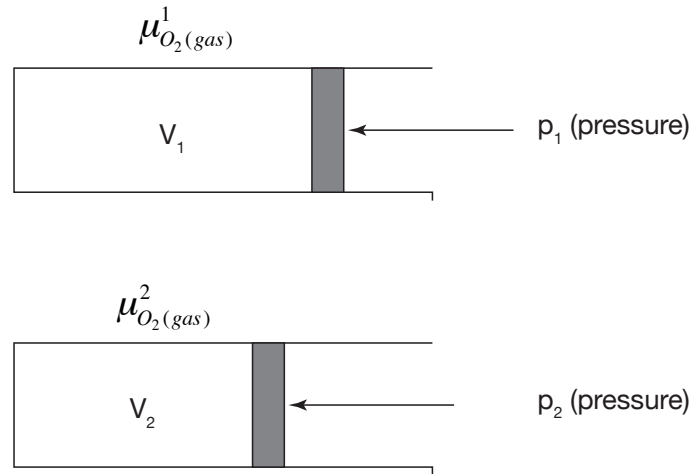
Sometime the electrical energy is written as work done per mole of electrons in which case the work done is $F\Delta V$, where F is the Faraday constant or the charge in one mole of electrons.

$$F = 96,485 \text{ Coulombs per mole.}$$

(HW: calculate the charge on one electron in Coulombs).

$$\mu_{\text{Li}}^{\text{anode}} - \mu_{\text{Li}}^{\text{cathode}} = eV$$

The Chemical Potential of a gas as a function of its pressure



As discussed above

$$\mu_{p_{O_2}}^{(2)} - \mu_{p_{O_2}}^{(1)} = - \int_{V_1}^{V_2} p dV, \text{ minus sign since the environment does work on the system.}$$

$$PV = RT$$

$$\mu_{p_{O_2}}^{(2)} - \mu_{p_{O_2}}^{(1)} = - \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_1}{V_2} = RT \ln \frac{p_2}{p_1} \quad (2)$$

Note that pressure also represents the volumetric concentration of the species.

Later we shall see that the chemical potential of a species can always be expressed in the following way,

$$\mu_X = \mu_X^\circ + RT \ln(a_X) \quad (3)$$

where a_X is called the activity. The pressure in the gas above represents its activity in the initial and the final state.

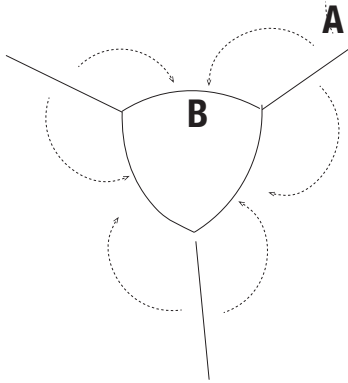
μ_X° is the chemical potential of that species in a standard or a reference state.

We shall use Eq. (2) in the study of electrochemical reactions and also in reduction-oxidation reactions.

The Chemical Potential for Mechanical and Sintering problems

The mechanism of sintering we have discussed is related to the transport of atoms from the grain boundaries into the adjacent pores.

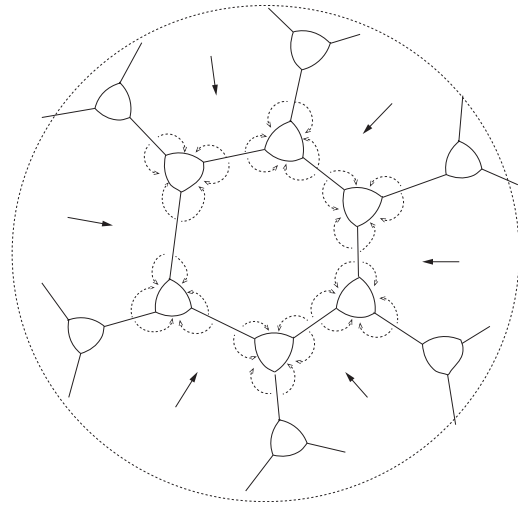
We also derived the driving force of sintering as being the force exerted on a surface from curvature.



$$p_{SX}^B = \frac{2\gamma_S}{r}$$

where p_{SX} is the sintering pressure, r is the radius of curvature of the surfaces in the pore, and γ_S is the surface energy of the free surfaces of the pore.

The above mechanism of sintering is shown schematically on the right. The mass transport is driven by a difference between the chemical potential of the atoms (the species) at the grain boundary and at the pore surface, that is from A to B as shown below



(4)

Therefore the driving force for sintering is given by

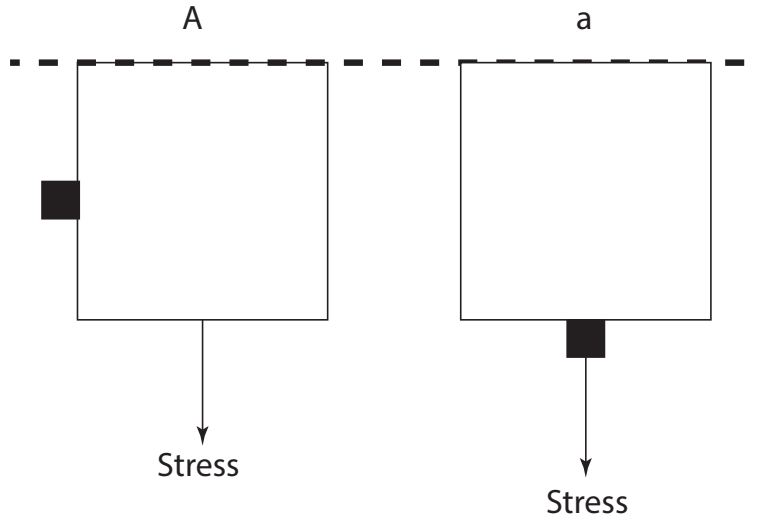
$$\Delta\mu_{AB} = \Delta\mu_A - \Delta\mu_B \quad (2)$$

Now if there is no pressure applied to accelerate the sintering rate, the pressure at site A is small (we shall consider a free body diagram to make an estimate of it).

At site B the curvature of the surfaces produces a negative stress on the surface. this is the driving force for the sintering process, and as derived before it is given by

$$p_{SX} = \frac{2\gamma_S}{r} \quad (3)$$

where p_{SX} is the sintering pressure, r is the radius of curvature of the surfaces in the pore, and γ_S is the surface energy of the free surfaces of the pore. The next question is how mechanical forces can induce a chemical potential.



$$\mu_x^A - \mu_x^B = \sigma \Omega_x$$

where Ω_x is the species volume of the atom or molecule shown in black above. Here

$$\sigma^B = \frac{2\gamma_s}{r} \quad (4)$$

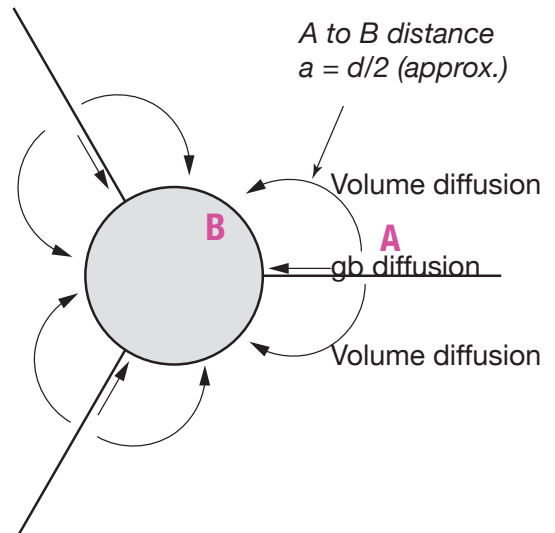
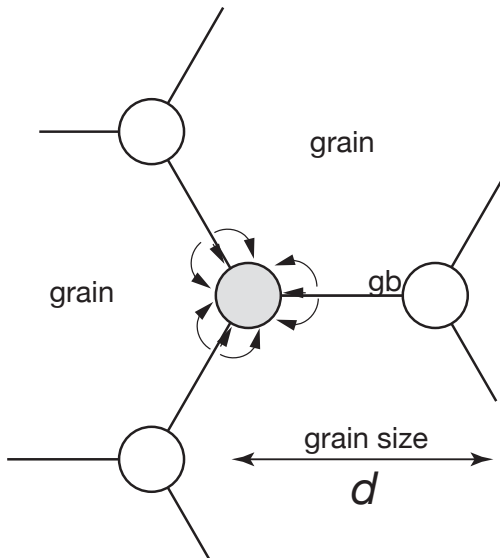
Omega is the volume of one atom visualized as a cube.

Driving force for transport is the gradient of the chemical potential.

Approximate gradient of the driving force

$$\text{Driving Force} = \frac{d\Delta\mu_{SX}^{AB}}{dx} = \frac{\Delta\mu_{SX}^{AB}}{d/2}$$

where d is the size of the particles. The gradient lies between points A and B in the figure just below



Now, the chemical potential at B is given by Eq. (3) so that

$$\mu_{SX}^B = \frac{2\gamma_s}{r} \Omega_{SX} \quad (4)$$

Remember that the subscripts refer to the species, that is SX in the present instance, while the superscripts refer to the state of the species.

We ask what would be the chemical potential at site A? It is not zero but we shall assume it to be so. It is finite because imagine drawing a free body diagram that intersects the pores and the grain boundaries. The tensile force at pore surfaces exerted by the surface tension must now be balanced by a compressive force across the grain boundaries. However the latter will be much smaller than the first since the effective cross sectional area of the pore is smaller, perhaps much smaller than the cross sectional area of the grain boundaries. This difference becomes ever greater as the pore sinters and grows smaller. While the problem can be analyzed with rigor it is better to assume a simple form in order that the result can reflect physical meanings.

Therefore we now have the full equation for the driving force for diffusion of matter that will fill the pore,

$$Driving\ Force = \frac{2}{d} (\Delta\mu_{SX}^B - \Delta\mu_{SX}^A) \approx \frac{4\gamma_s \Omega_{SX}}{dr} \quad (5)$$

Let us check the units

- the driving force has units of Newtons
- γ_s has units of $J\ m^{-2}$
- Ω_{SX} has units of m^3
- r and d have units of m , the product being m^2

Therefore the RHS has the units

$$\frac{J}{m^2} \cdot m^3 \cdot \frac{1}{m^2} = \frac{J}{m}, \text{ that is the units of force.}$$

The next topic in sintering is the develop an equation for mass transport driven by the driving force as in Eq. (5)

