INTERLUDE

Interphase Mass Transfer – see “Interlude Handout”
Complete Problems 1 & 2 (page 12)

At equilibrium a species will distribute (or “partition”) between two phases.

Examples:

1. oxygen (species) will partition between air (gas phase) and water (liquid phase).
2. benzene (species) will partition between ground water (liquid phase) and soil (solid phase).

Equilibria are quantified by specific "distribution laws".

An example of a distribution law is given by Henry's Law, which is used to calculate the liquid phase concentration of a gas (i.e., gas solubility):

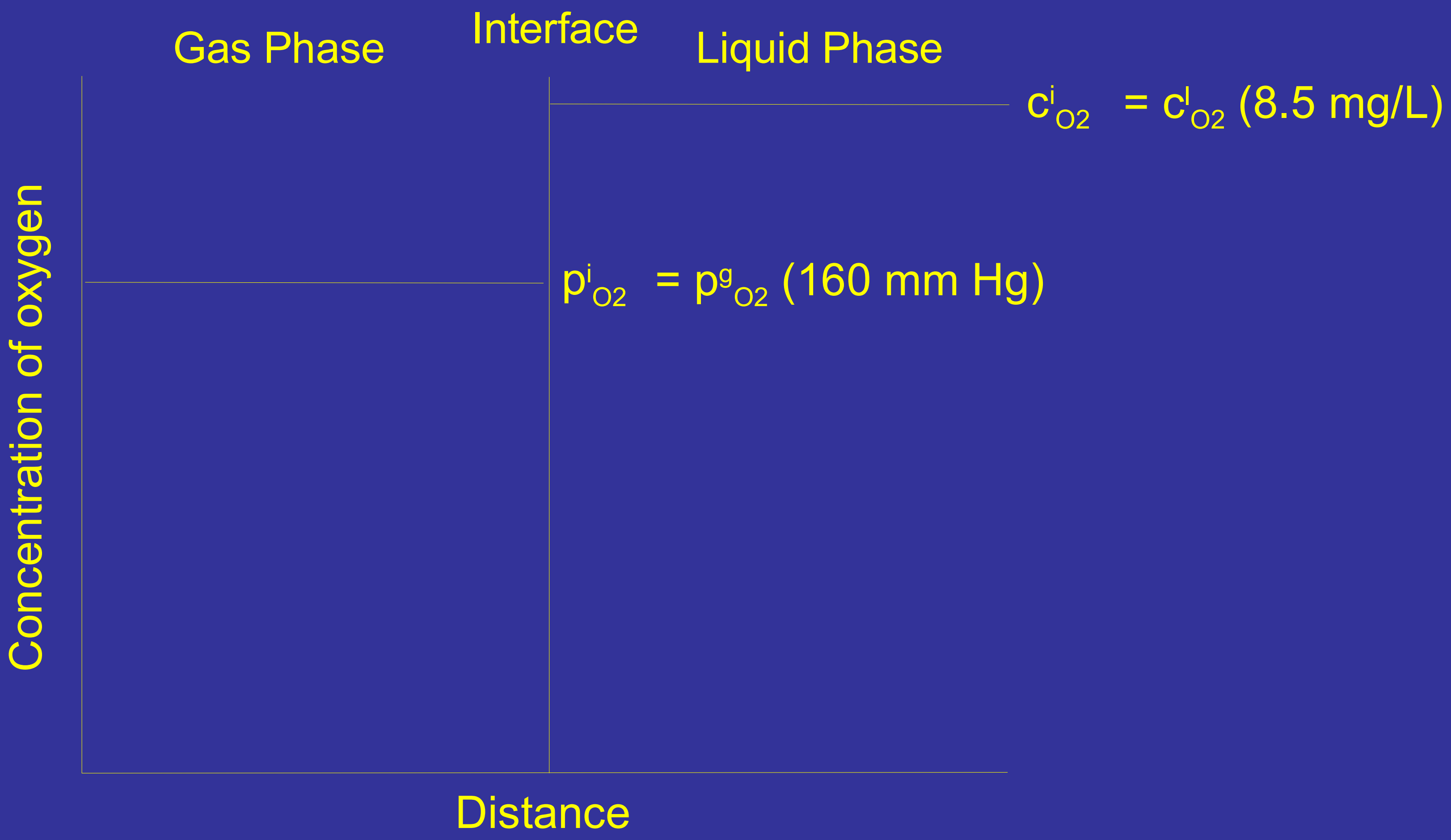
$$p_{O2} = x_{O2}H_{O2}$$

If liquid is water, and gas is rather insoluble in liquid (like oxygen):

$$p_{O2} \approx c_{O2}H_{O2}M_{H2O}/(c_{H2O}M_{O2})$$

see Question 1 (page 2) for an example calculation.

At equilibrium:



Gas Phase

Interface

Liquid Phase

$c^{i}_{O2} = c^{l}_{O2}$ (8.5 mg/L)

$p^{i}_{O2} = p^{g}_{O2}$ (160 mm Hg)

Concentration of oxygen

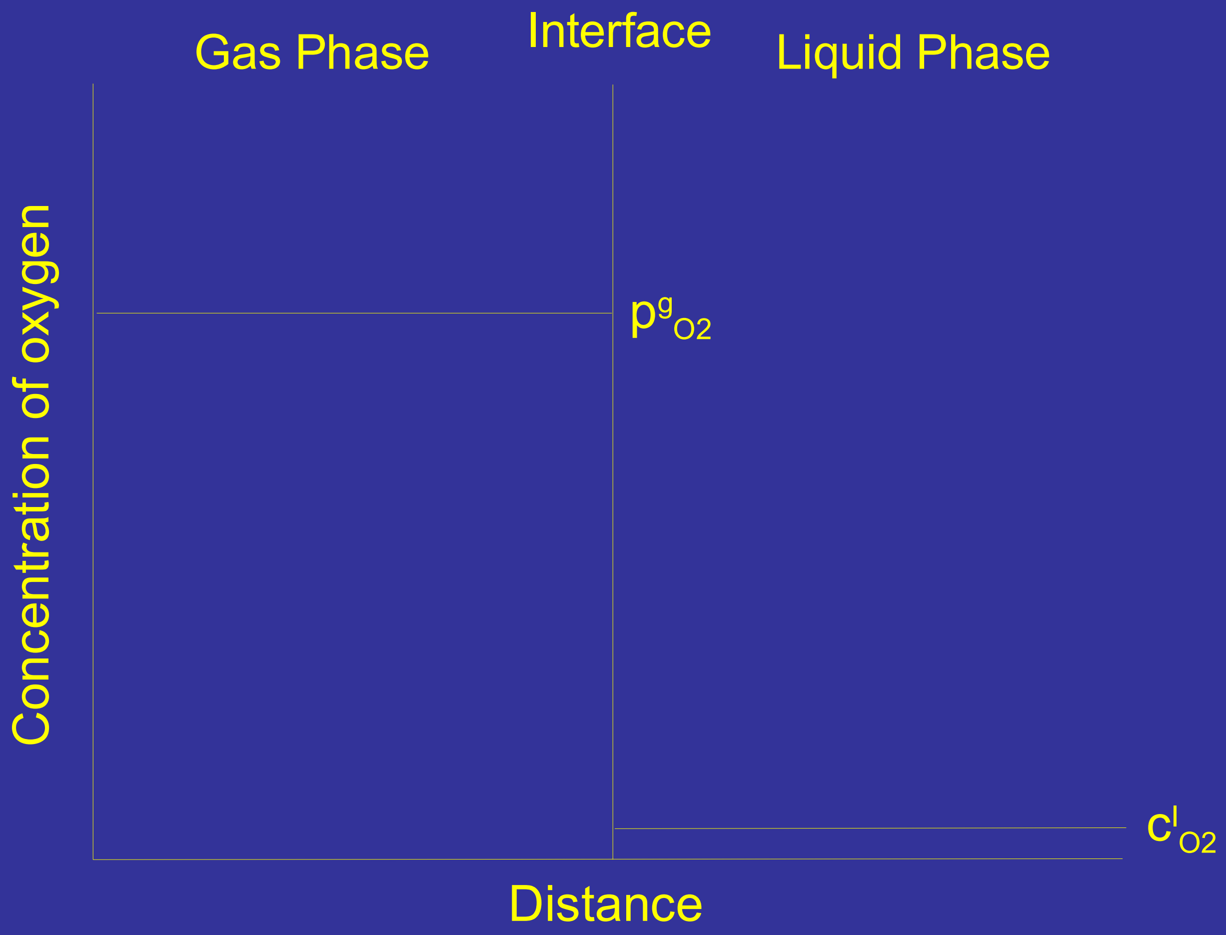
Distance

Consider now the physical situation:

Two phases are suddenly brought into contact in which concentrations of the species are not in equilibrium.

Let us contemplate this situation using the specific example of a gas containing oxygen at a concentration of p^g_{O2} and a liquid containing oxygen at a concentration of c^l_{O2}, such that the species oxygen will be transferring from the gas to the liquid.

Not at equilibrium:

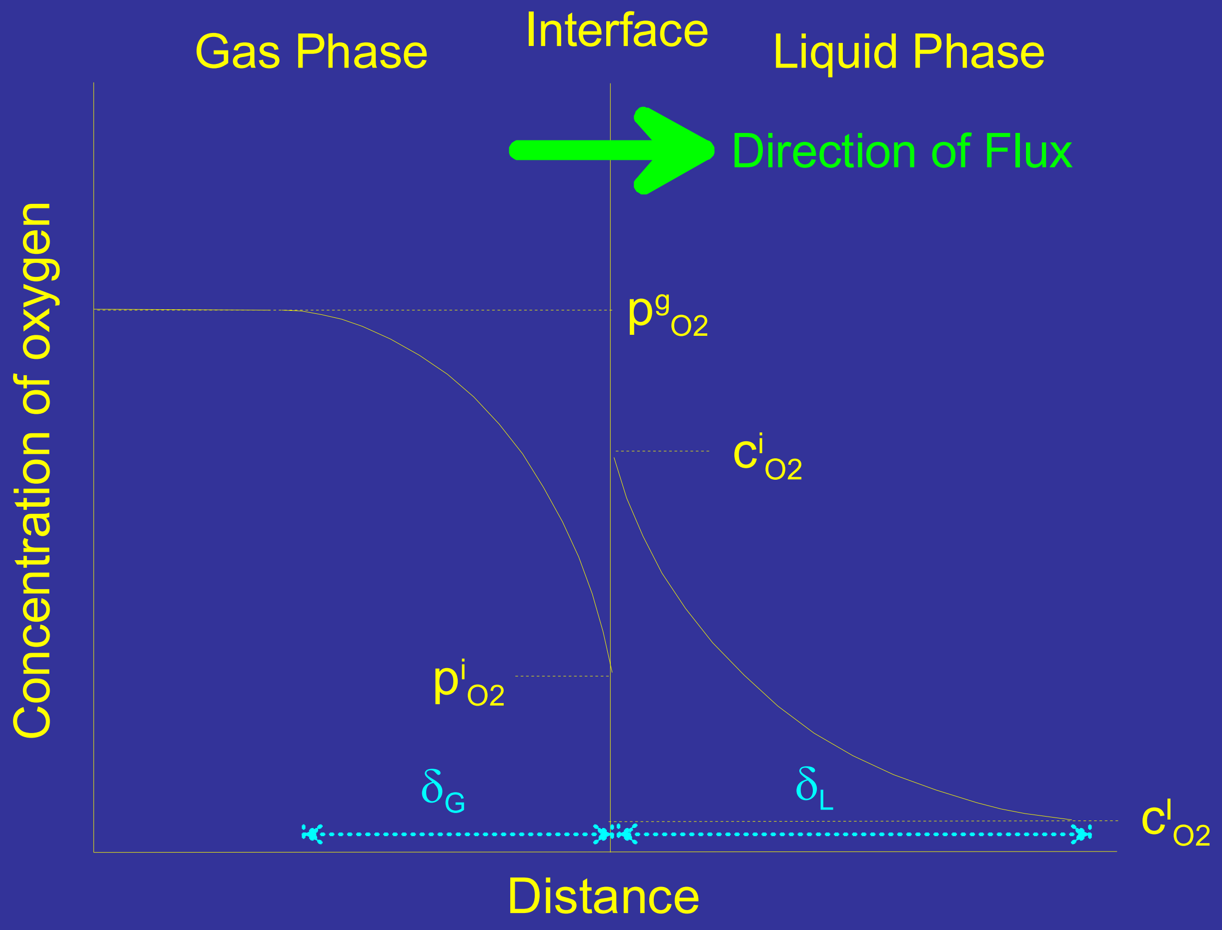


What happens?

Two-resistance theory proposes that rate of diffusion across a microscopic interface is instantaneous, and that therefore equilibrium at the interface “locally” will be achieved immediately (“local equilibrium”).

However, in either bulk solution (distant from the interface) the concentration will not have changed. Thus, a concentration gradient will develop in each phase.

Moving towards equilibrium:



How do we predict the flux?

Flux $\propto$ Concentration Gradient

However, we don't have values for film thicknesses (δ_G, δ_L)

Flux $\propto$ Concentration Difference

So, we can write a proportionality in either phase:

Flux (Gas Phase) $\propto$ $(p^g_{O2} - p^i_{O2})$

Flux (Liquid Phase) $\propto$ $(c^i_{O2} - c^l_{O2})$

Note also that if system is at steady-state:

Flux (Phase I) = Flux (Phase II) = Φ_{O2}

For each phase we will *define* a proportionality constant called a mass transfer coefficient such that:

$$\boxed{\begin{array}{l}\Phi_{O2} = k_G(p^g_{O2} - p^i_{O2}) \\ \Phi_{O2} = k_L(c^i_{O2} - c^l_{O2})\end{array}}$$

I.3

I.4

$(p^g_{O2} - p^i_{O2})$ is the "gas phase driving force" for mass transfer

$(c^i_{O2} - c^l_{O2})$ is the "liquid phase driving force" for mass transfer

$$\boxed{\begin{aligned}\Phi_{O2} &= k_G(p^g_{O2} - p^i_{O2}) \\ \Phi_{O2} &= k_L(c^i_{O2} - c^l_{O2})\end{aligned}}$$

Good News:

1. k_L depends only on liquid phase, while k_G depends only on gas phase.
2. Knowing properties of that one phase (e.g., viscosity, density, velocity) allows us to calculate k_L, k_G empirically.

(Really) Bad News:

1. We don’t know values for interface concentrations.

We would really like to have a mass transfer coefficient which is related to the total, overall driving force…

We'd like to have something like $\Phi_{O2} \propto (p^g_{O2} - c^l_{O2})$!

The problem with $(p^g_{O2} - c^l_{O2})$ is that these two concentrations are in different phases (one in terms of pressure and the other in terms of liquid concentration). We cannot compare the two concentrations directly.

However, we can relate the gas phase concentration (p^g_{O2}) to the liquid phase concentration that *would theoretically be in equilbrium* with that concentration (c^*_{O2}). So, instead of the overall driving force being (p^g_{O2} – c^l_{O2}), it is ($c^*_{O2} - c^l_{O2}$). We define an overall mass transfer coefficient K_L as:

$$\boxed{\Phi_{O2} = K_L(c^*_{O2} - c^l_{O2})} \qquad \text{I.6}$$

Remember, c^*_{O2} is in equilibrium with p^g_{O2}. If the equilibrium relationship is linear, then

$$p^g_{O2} = m_{O2}c^*_{O2} \qquad \text{I.9}$$

Similarly, we can relate the liquid phase concentration (c^l_{O2}) to the gas phase concentration that would theorectically be in equilbrium with that concentration (p^*_{O2}). In this case, we define an overall mass transfer coefficient K_G as:

$$\boxed{\Phi_{O2} = K_G(p^g_{O2} - p^*_{O2})} \qquad \text{I.5}$$

In this case, p^*_{O2} is in equilibrium with c^l_{O2}. If the equilibrium relationship is linear, then

$$p^*_{O2} = m_{O2}c^l_{O2} \qquad \text{I.8}$$

$$\boxed{\begin{aligned}\Phi_{O2} &= K_G(p^g_{O2} - p^*_{O2}) \\ \Phi_{O2} &= K_L(c^*_{O2} - c^l_{O2})\end{aligned}}$$

K_G – overall mass transfer coefficient in terms of gas phase driving force

K_L – overall mass transfer coefficient in terms of liquid phase driving force

Good News:

1. The concentrations at the interface do not appear in the equations.

Bad News:

1. K_G and K_L depend on properties of both phases (strictly, but we often make a simplification!)

Derive relationship between K_L and k_G, k_L:

$$c^*_{O2} - c^l_{O2} = (c^*_{O2} - c^i_{O2}) + (c^i_{O2} - c^l_{O2})$$

Divide each term by Φ_{O2}

$$\frac{c^*_{O2} - c^l_{O2}}{\Phi_{O2}} = \frac{(c^*_{O2} - c^i_{O2})}{\Phi_{O2}} + \frac{(c^i_{O2} - c^l_{O2})}{\Phi_{O2}}$$

Note that $p^g_{O2} = m_{O2}c^*_{O2}$ and $p^i_{O2} = m_{O2}c^i_{O2}$

$$\frac{c^*_{O2} - c^l_{O2}}{\Phi_{O2}} = \frac{(p^g_{O2} - p^i_{O2})}{m\Phi_{O2}} + \frac{(c^i_{O2} - c^l_{O2})}{\Phi_{O2}}$$

$$\frac{c^{*}_{O2} - c^{l}_{O2}}{\Phi_{O2}} = \frac{(p^{g}_{O2} - p^{i}_{O2})}{m\Phi_{O2}} + \frac{(c^{i}_{O2} - c^{l}_{O2})}{\Phi_{O2}}$$

From the definitions of mass transfer coefficients…

$$\boxed{\frac{1}{K_L} = \frac{1}{mk_G} + \frac{1}{k_L}}$$

Similarly…

$$\boxed{\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L}}$$

Consider two extreme cases:

1) gas is very soluble in liquid (NH_3 in H_2O)

m is very small

$$\frac{1}{K_G} = \frac{1}{k_G} + \xcancel{\frac{m}{k_L}}$$

$$K_G \approx k_G$$

We can use gas phase properties to calculate an overall mass transfer coefficient

2) gas is very insoluble in liquid (O_2 in H_2O)

m is very large

$$\frac{1}{K_L} = \cancel{\frac{1}{mk_G}} + \frac{1}{k_L}$$

$$K_L \approx k_L$$

We can use liquid phase properties to calculate an overall mass transfer coefficient

Two mass transfer expressions

$$\Phi_{NH3} = K_G(p^g_{NH3} - p^*_{NH3})$$

$$\Phi_{O2} = K_L(c^*_{O2} - c^l_{O2})$$

can be “simplified” to yield:

$$\Phi_{NH3} = k_G(p^g_{NH3} - p^*_{NH3})$$

$$\Phi_{O2} = k_L(c^*_{O2} - c^l_{O2})$$

Note, we can’t write:

$$\Phi_{O2} = k_G(p^g_{O2} - p^*_{O2})$$

$$\Phi_{NH3} = k_G(p^g_{NH3} - p^*_{NH3})$$

$$\Phi_{O2} = k_L(c^*_{O2} - c^l_{O2})$$

(Only) Good News:

1. k_L depends only on liquid phase, while k_G depends only on gas phase.
2. Knowing properties of that one phase (e.g., viscosity, density, velocity) allows us to calculate k_L, k_G empirically.
3. We can calculate all the concentrations, in particular p^*_{O2} and c^*_{O2}.