

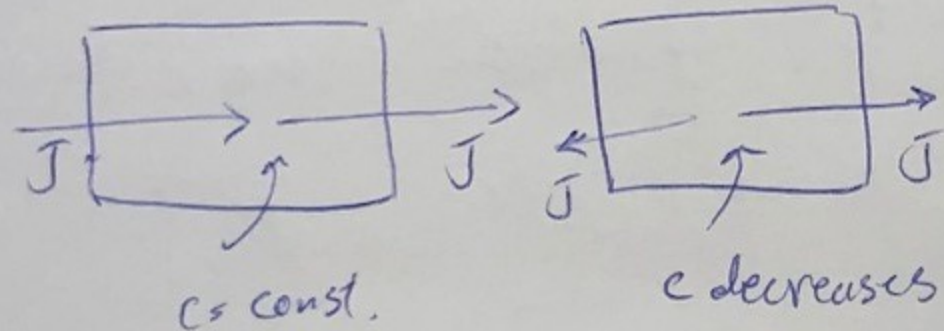
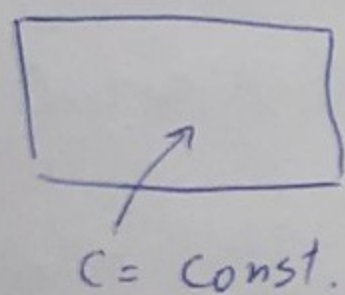
L36: review

\* combine all the "driving forces", e.g.  
concentration ( $RT \ln c(x)$ ), pressure ( $v_i P(x)$ ),  
electric potential ( $q_i V_e(x)$ ), etc.  
to get  $\mu_{g_i}(x)$  for the system of interest

$$* \bar{J} = -u c \frac{d\mu_{g_i}}{dx}; \text{ either } \bar{J} = 0^{\text{net}} \text{ (steady state)}$$

$$\text{or use } \frac{\partial c}{\partial t} = -\frac{\partial \bar{J}}{\partial x} \Rightarrow \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( u c \frac{d\mu_{g_i}}{dx} \right)$$

to obtain  $c(t)$ .



~~Review~~

Today: equation for integrated flux  
is steady-state ( $\bar{J}$  constant). Applications  
- Le Châtelier  
- transition state theory

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start with

$$\bar{J} = -u c \frac{d\mu_{g_i}}{dx}; \text{ integrate this eq. under constant flux condition}$$

$$\mu_{g_i} = \mu^0 + RT \ln c(x); \text{ solve for concentration}$$

$$\hookrightarrow c = e^{\frac{\mu_{g_i} - \mu^0}{RT}}; \text{ plug into } \bar{J}$$

$$\Rightarrow \bar{J} = -u e^{\frac{\mu_{g_i} - \mu^0}{RT}} \frac{d\mu_{g_i}}{dx}; \text{ we assume constant temperature next}$$

$$\Rightarrow \bar{J} = -RT u e^{\frac{\mu_{g_i} - \mu^0}{RT}} \frac{d(\mu_{g_i}/RT)}{dx}$$

$$\Rightarrow J = \frac{e^{\frac{\mu^0}{RT}}}{RTu} dx' - e^{\frac{\mu_g}{RT}} d\left(\frac{\mu_{gi}}{RT}\right)$$

$J$  is const so independent of  $x$

integrate

over  $x'$   
from 0 to  $x$

$$J = - \frac{\int_0^x e^{\frac{\mu_{gi}}{RT}} d\left(\frac{\mu_{gi}}{RT}\right)}{\int_0^x \frac{e^{\frac{\mu^0(x')}{RT}}}{RTu}} > 0$$

$$= \frac{e^{\frac{\mu_{gi}(x)}{RT}} - e^{\frac{\mu_{gi}(x=0)}{RT}}}{\int_0^x \frac{e^{\frac{\mu^0(x')}{RT}}}{RTu(x')}} > 0$$

because  
one of the  
terms in integral  $> 0$

⇓

As a consequence:

$$\mu_{gi}(x) > \mu_{gi}(0) \Leftrightarrow J < 0$$

$$\mu_{gi}(x) < \mu_{gi}(0) \Leftrightarrow J > 0$$

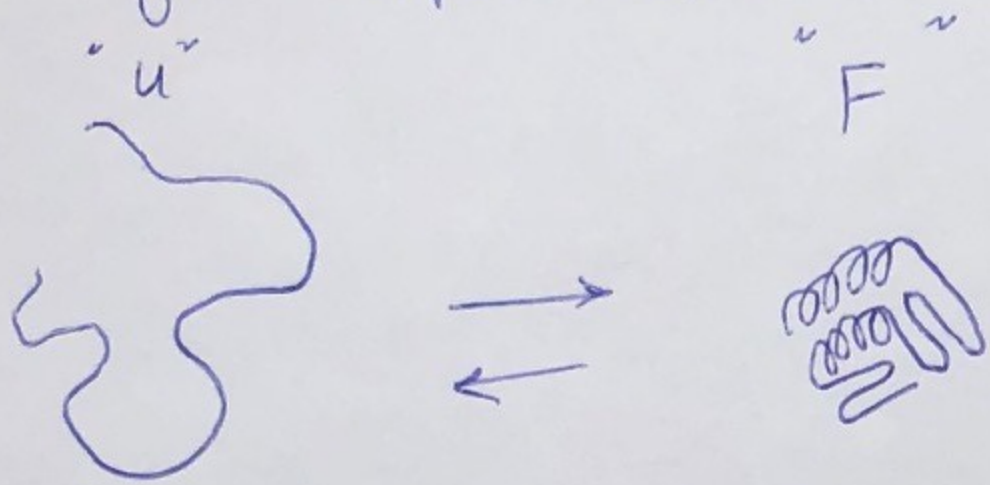
$$\mu_{gi}(x) = \mu_{gi}(0) \Leftrightarrow J = 0$$

1) Particles flow to lower values of  $\mu$  when the system is taken out of equilibrium

2) The  $RT \ln(x)$  term in  $\mu_g$  increases where  $\mu$  is lower & vice versa

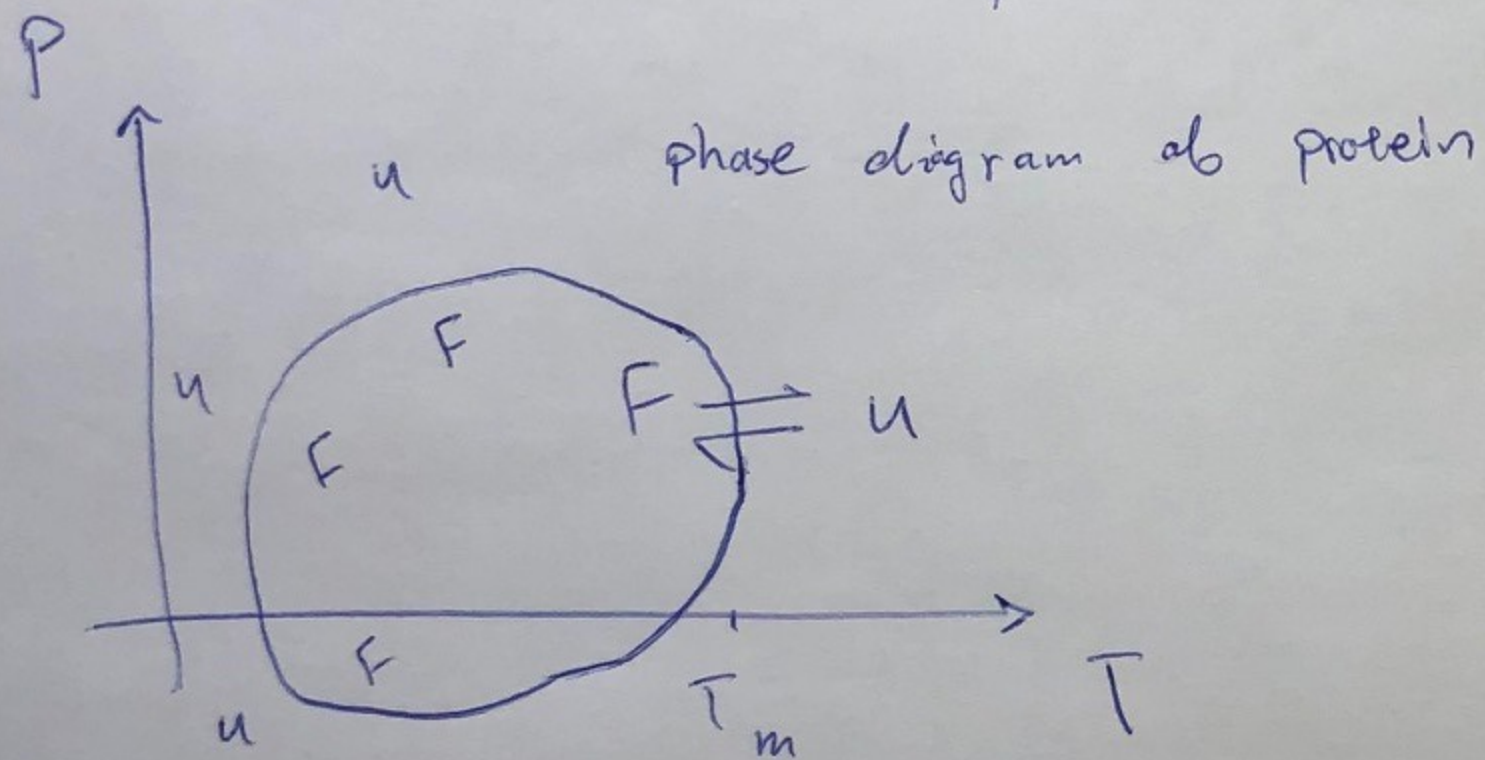
Summary: when a system experiences a difference in chemical potential, the flux will be in the direction to equalize the chemical potential until  $\mu(x) = \mu(0)$  and equilibrium is restored: Le Chatelier's Principle

Thought experiment:



$$W_u \gg W_F$$

$$S_u > S_F$$



\* note that at high pressure, proteins become unfolded because the molar volume of unfolded is smaller:

$$v_u < v_F \Rightarrow \text{high pressure: } M_u < M_F$$

the reason to  $v_u < v_F$  is that packing in the folded state is not perfect so there is "void" inside the protein, whereas unfolded proteins are covered by solvent and there is no empty space.

\* why does protein unfold at low temperature?

the short answer: entropy of water decreases faster than the increase in entropy of the protein chain.

water's entropy decreases upon unfolding of protein because of formation of "water cage" or "clathrates"

around hydrophobic residues that would have been otherwise in the protein core.

