Lecture 4.2

Phase Transfer and Equilibria

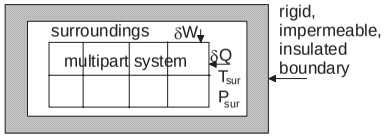
O'Connell & Haile
Chapter 7.1-7.3

Topics:

- Extrema of properties at equilibrium for constrained changes of state
- Interfacial transfers between phases gives driving forces & equilibrium
- Criteria for equilibrium

CLOSED, NONREACTING SYSTEMS

Equations derived for changes of systems with multiple parts in terms of surroundings T_{sur}, P_{sur}



$$\sum_{k=parts} \boldsymbol{d}(N_k \boldsymbol{u}_k) + \boldsymbol{P}_{sur} \sum_{k=parts} \boldsymbol{d}(N_k \boldsymbol{v}_k) - T_{sur} \sum_{k=parts} d(N_k s_k) \le \boldsymbol{0} \qquad \textbf{(7.1.11)}$$

$$N\Delta \boldsymbol{u} + N\boldsymbol{P}_{sur}\Delta \boldsymbol{v} - N\boldsymbol{T}_{sur}\Delta \boldsymbol{s} \le \boldsymbol{0} \qquad \textbf{(7.1.12)}$$

Cases of isolated & adiabatic systems

$$\sum_{k=parts} d(N_k s_k)_{U,V} \ge 0 \le NT_{sur}\Delta s \qquad \textbf{(7.1.14)}$$

Means spontaneous changes constrained to constant (*U*,*V*) go to maximum *S*

Spontaneous changes from removing internal restraint

Can compute Δs for some easy cases (7.1.3, 7.1.6)

For spontaneous cases when $\Delta T = \Delta v = 0$
(7.1.12) is $\Rightarrow \sum_{k=parts} \Delta(N_k a_k)_{T,V} \le 0$ **(7.1.35)**

Equivalent to $\Rightarrow \sum_{k=parts} \sum_{i=1}^{C} \overline{G}_{ki} dN_{ki} \le 0$ **(7.1.48)**

∴ Spontaneous changes at <u>fixed</u> *T*,*V* decrease *A* to minimum

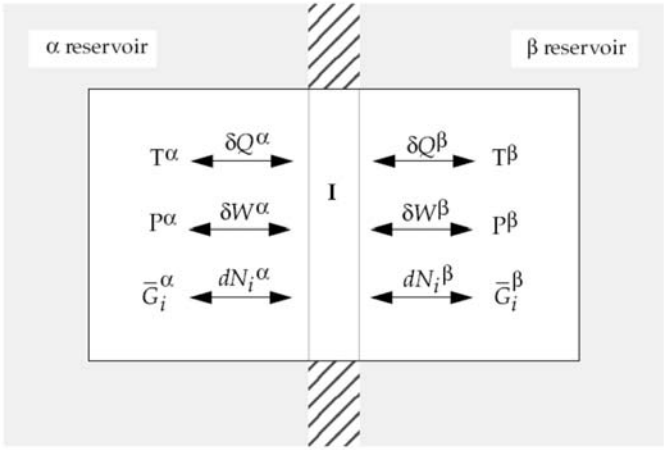
For spontaneous cases when $\Delta T = \Delta P = 0$
(7.1.12) is $\sum_{k=parts} \Delta(N_k g_k) \le 0$ **(7.1.39)**

$\Rightarrow \sum_{k=parts} \sum_{i=1}^{C} \overline{G}_{ki} dN_{ki} \le 0$ **(7.1.48)**

∴ Spontaneous changes at <u>fixed</u> *T*,*P* decrease *G* to minimum

OPEN NONREACTING SYSTEMS

Stuff Equations on interface of 2 phases in closed box ignoring accumulation, MB



MB $dN_i^{\alpha} + dN_i^{\beta} = -dN_i^{I} = 0$ **(7.2.4)**

EB $d(h^{\alpha}N^{\alpha}) + \delta Q^{\alpha} + \delta W^{\alpha} + d(h^{\beta}N^{\beta}) + \delta Q^{\beta} + \delta W^{\beta} = 0$ **(7.2.6)**

NB $d(s^{\alpha}N^{\alpha}) + \frac{\delta Q^{\alpha}}{T^{\alpha}} + d(s^{\beta}N^{\beta}) + \frac{\delta Q^{\beta}}{T^{\beta}} + dS_{gen}^{I} = 0$ **(7.2.7)**

Eliminating δQ^{α}, *etc.* → *always true* for phase transfers

$$\delta Q^{\beta}\left(\frac{T^{\alpha}}{T^{\beta}} - 1\right) - (\delta W^{\alpha} + \delta W^{\beta}) - \sum_{k=\alpha}^{\beta}[d(h^k N^k) - T^{\alpha} d(s^k N^k)] \geq 0 \quad \textbf{(7.2.9)}$$

When interface open to mass transfer,

$$dN_i^{\alpha} = -dN_i^{\beta}$$

$$\delta Q^{\beta}\left(\frac{T^{\alpha}}{T^{\beta}} - 1\right) - (\delta W^{\alpha} + \delta W^{\beta}) - \sum_{i=1}^{C}\left[\bar{G}_i^{\alpha} - \left(\bar{H}_i^{\beta} - T^{\alpha}\bar{S}_i^{\beta}\right)\right] dN_i^{\alpha} \geq 0 \quad \textbf{(7.2.13)}$$

Cases of *spontaneous* changes

Heat flows from high to low *T* (workfree, no mass transfer)

$$\delta Q^{\beta}\left(\frac{T^{\alpha}}{T^{\beta}} - 1\right) \geq 0 \Rightarrow T^{\alpha} > T^{\beta} \text{ for } \delta Q^{\beta} > 0$$

***PV* Work "flows" from high to low *P* (isothermal, no mass transfer)**

$$-\delta W^{\beta} - \delta W^{\alpha} = P^{\beta} dV^{\beta} + P^{\alpha} dV^{\alpha} = (P^{\beta} - P^{\alpha}) dV^{\beta} \geq 0$$
$$\Rightarrow P^{\beta} > P^{\alpha} \text{ for } \delta V^{\beta} > 0$$

Uncoupled mass transfers (each term in sum independent) flow from high to low $\bar{G}_i$ or f_i (isothermal, workfree)

$$-(\bar{G}_i^{\alpha} - \bar{G}_i^{\beta}) dN_i^{\alpha} \geq 0 \Rightarrow \bar{G}_i^{\beta} > \bar{G}_i^{\alpha} \text{ for } dN_i^{\alpha} > 0 \quad \textbf{(7.2.31)}$$
$$f_i^{\beta} > f_i^{\alpha} \text{ for } dN_i^{\alpha} > 0 \sim \textbf{(7.2.32)}$$

For multicomponent coupled transfers, must use full summation

$$-\sum_{i=1}^{C}(\bar{G}_i^{\alpha} - \bar{G}_i^{\beta}) dN_i^{\alpha} \geq 0 \leq RT \sum_{i=1}^{C} \ln \frac{f_i^{\alpha}}{f_i^{\beta}} \quad \textbf{(7.2.33)}$$

SOME CONSEQUENCES

Limits on irreversible processes

Heat & Work effects & connections

(for $\delta W^{\alpha} < 0$)

$$|\delta W^{\alpha}| > \delta W^{\beta} > 0 \Rightarrow \delta Q^{\alpha} > |\delta Q^{\beta}| > 0$$

Differences = lost work for <u>both</u> in, out

Always converted into heat

Phase Equilibrium (nonreacting systems)

Replace $\geq$ with = ;

get (7.3.5, 7.3.7, 7.3.11, 7.3.12)

$$\Rightarrow T^{\alpha} = T^{\beta}, P^{\alpha} = P^{\beta}, \overline{G}_i^{\alpha} = \overline{G}_i^{\beta},\ f_i^{\alpha} = f_i^{\beta}$$

Note: though single & multicomponent diffusion directions can differ for real coupled transfers, "equilibrium" transfers only in same direction

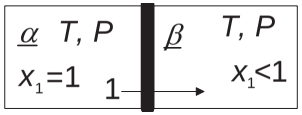
Note: Work could be done for spontaneous diffusion of *i* from α to β

$$w_i^{\alpha \to \beta} = -\overline{G}_i^{\alpha} + \overline{G}_i^{\beta} < 0$$

Equality of $\overline{G}_i$ criterion is the same as achieving minimum *G* where $(dG)_{T,P} = 0$ (Sec. 7.3.6)

OSMOTIC EQUILIBRIUM

Solvent(1) & solution(solvent 1/solute2) with membrane that passes only solvent (semipermeable)



Nonequilibrium observation:

$$P^{\alpha} = P^{\beta} \equiv P,\ T^{\alpha} = T^{\beta} \equiv T,\ x_1 < 1,$$

solution (β) diluted by solvent component (1) leaving pure phase (α), & going through membrane to solution

$$\Rightarrow \overline{G}_{pure\ i}^{\alpha}(T,P) > \overline{G}_i^{\beta}(T,P,x_1),\ \ f_{pure\ i}^{\alpha} > f_i^{\beta}$$

At equilibrium:

$$\overline{G}_{pure\ i}^{\alpha}(T,P) = \overline{G}_i^{\beta}(T,P,x_1),\ f_{pure\ i}^{\alpha} = f_i^{\beta}$$

How change conditions to $\overline{G}_i^{\alpha} = \overline{G}_i^{\beta}; f_{pure\ i}^{\alpha} = f_i^{\beta}$

Can a) raise $\overline{G}_i^{\beta}$, f_i^{β} or b) lower $\overline{G}_{pure\ i}^{\alpha}$, $f_{pure\ i}^{\alpha}$

b) impossible with $T^{\alpha} = T^{\beta}$; a) OK if increase P^{β}

Phases are liquids $\Rightarrow \left.\frac{\partial \ln f_i^{\beta}}{\partial P}\right|_{T,\{x\}} = \frac{\overline{V}_i^{\beta}}{RT} > 0$

At equilibrium,

1. FFF#5 with $P_1^o = P^{\alpha},\ f_1^o = f_{pure\ 1}$, for same fugacity of solvent (1) in α & β

$$f_{pure\ 1}(T,P^{\alpha}) = x_1^{\beta}\gamma_1^{\beta}[T,P^{\alpha},x_1;\ f_{pure\ 1}^{o}]\, f_{pure\ 1}(T) \exp\left[\int_{P^{\alpha}}^{P^{\beta}} \frac{\overline{V}_1^{\beta}}{RT}\, d\pi\right]$$

2. FFF#3 with $P_1^o = P^\alpha$, $f_1^o = f_{pure\,1}$ for same fugacity of solvent (1) in α & β

$$f_{pure\,1}(T, P^\alpha) = x_1^\beta \gamma_1^\beta (T, P^\beta, x_1;\ f_{pure\,1}^o)\, f_{pure\,1}(T)\ \exp\left[\int_{P^\alpha}^{P^\beta} \frac{v_{pure\,1}}{RT}\, d\pi\right]$$

Design: Find P^β from $\quad x_1^\beta, \gamma_1^\beta, P^\alpha, T, \overline{V}_1^\beta / v_{pure\,1}$

Analysis: Find $(x_1^\beta \gamma_1^\beta)$ from $P^\beta, P^\alpha, T, \overline{V}_1^\beta / v_{pure\,1}$

Experiment: Find x_1^β from

$$\gamma_1^\beta, P^\beta, P^\alpha, T, \overline{V}_1^\beta / v_{pure\,1}$$

Modeling: Find γ_1^β from

$$x_1, P^\beta, P^\alpha, T, \overline{V}_1^\beta \text{ or } v_{pure\,1}$$

Approximations

$v_{pure\,1} \neq f(P)$, define $\Pi = P^\beta - P^\alpha$ **gives simplified**

$$x_1^\beta \gamma_1^\beta \approx \exp\left[\frac{-\Pi v_{pure\,1}}{RT}\right]$$