Lectures 12

Applications of Thermodynamics II.

O'Connell & Haile
Chapter 12.3-12.5

Topics:

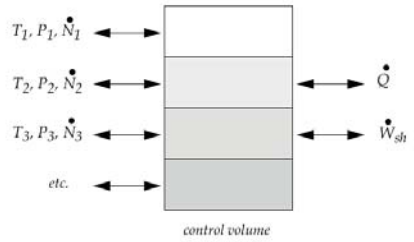
- Independent variables for steady flow processes
- Heat effects in steady-flow processes
  - Enthalpy-concentration diagrams
  - Flash separators, Absorbers, Chemical reactors
- Respones of selected properties
  - Standard state fugacities, Reactor yield

Independent Variables in Steady-Flow Processes

Mass & energy stuff equations
($\mathscr{C}$+1 total equations, variables)
no accumulation, no reaction $\Rightarrow$
Amounts of $\mathscr{C}$ components *i* through inports α, outports β

$$0 = \sum_{\alpha} \dot{N}_{\alpha i} - \sum_{\beta} \dot{N}_{\beta i}$$

$$0 = \sum \dot{Q} + \sum \dot{W} + \sum_{\alpha} \dot{N}_{\alpha i} \overline{H}_{\alpha i} - \sum_{\alpha} \dot{N}_{\beta i} \overline{H}_{\beta i}$$



To change state, $\mathscr{V}_{ex} = N_p(\mathscr{C} + 2) + 2 - \mathscr{S}_{ex}$

Identify state, $\mathscr{P}$ phases in equilibrium

$\mathscr{F}_{ex} = (N_p - \mathscr{P})(\mathscr{C}+2) + 3 - \mathscr{S}_{ex}$ Equilibrium (12.3.8)

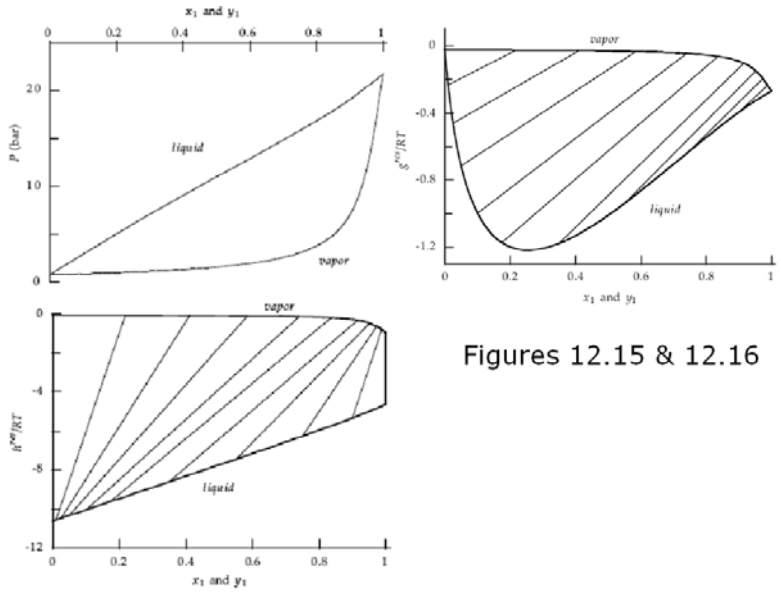
$\mathscr{F}_{ex} = N_p(\mathscr{C}+2) - (\mathscr{C}-1) - \mathscr{S}_{ex}$ Nonequilibrium (12.3.9)

Example (Sec.12.3.3)

HEAT EFFECTS IN STEADY FLOW SYSTEMS (12.4)

Describes energy balance in real cases of reactions & separations, needed in $\mathscr{F}$ ' adiabatic problems

P-x, h^{res}-*x*, g^{res}-*x* diagrams (Fig. 12.15 & 16)



Figures 12.15 & 12.16

Flash calculations (used for any 2-phase system) get *q* from phase enthalpies, *e.g.*, Eq. 12.4.11 for $T_l = T_v$

$$q \equiv \frac{Q}{N_f} = Vh_v^{res}(1-V)h_l^{res} - h_f^{res} + \Delta h^{ig}$$

Adiabatic vapor phase amount, *V*, via (12.4.14)

$$V = \frac{h_f^{res}(T_f,P_f,\{z\}) - h_l^{res}(T,P_l,\{x\}) - \Delta h^{ig}}{h_v^{res}(T,P_v,\{y\}) - h_l^{res}(T,P_l,\{x\})}$$

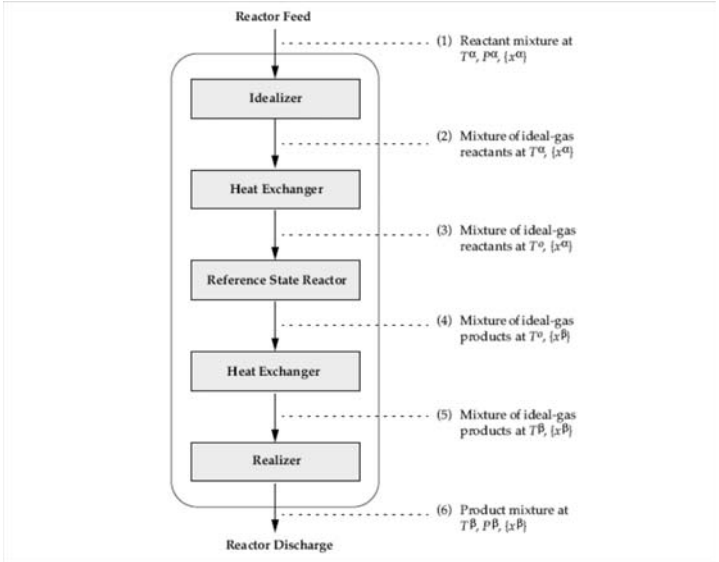
Example case (Sect. 12.4.3)

Use for gas absorbers when amount absorbed (& heat) significant

Note adiabatic & isothermal operation different

For reactors, how use tabulated $\Delta h_j^o(T^o)$?

Invent process with reference state reactor (Fig.12.18)



Property responses to changes of state

SS fugacities $f_i^o = \phi_i^s(T)P_i^s(T),\ H_i(T)$

Lewis-Randall Pure Saturated Standard State

Extrapolation OK up to $T/T_c \sim 1.2$

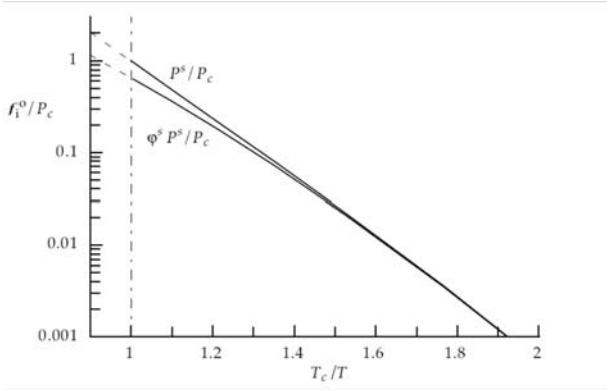


Figure 12.19

Henry's Law Standard State

Note maxima; can cause convergence problems for cases solving for *T*

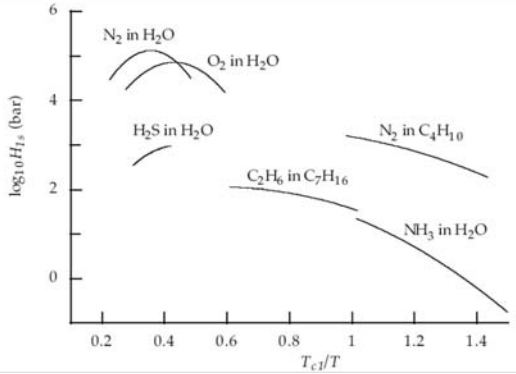


Figure 12.20

Extent of reaction response to *T*, *P*, N_{in}

Increased ξ_{eq} means greater product yield

$$\left.\frac{\partial \xi_{eq}}{\partial T}\right)_P \propto \frac{\Delta h^o}{RT^2} \qquad \left.\frac{\partial \xi_{eq}}{\partial P}\right)_T \propto \frac{-\sum \nu_{ij}}{P} = \frac{-\sigma}{P} \qquad \left.\frac{\partial \xi_{eq}}{\partial N_{inert}}\right)_{T,P} \propto \frac{\sigma}{N}$$