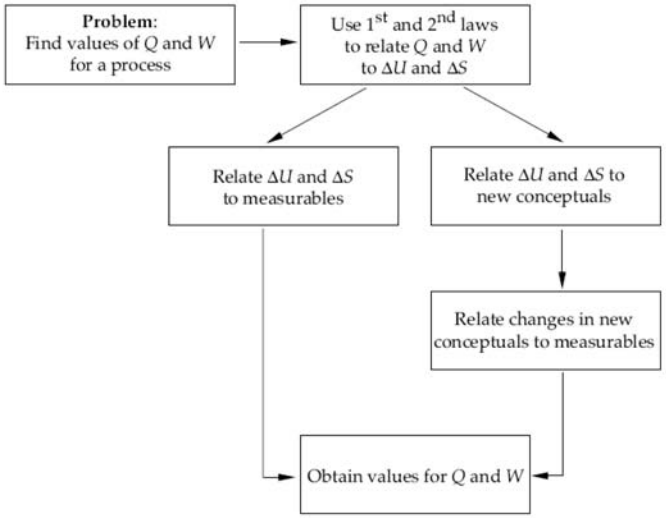
Lecture 2.2
Property Relations

O'Connell & Haile
Chapter 3

Topics:

- Routes to Properties
- States, Fundamental Equations

ROUTES TO ENGINEERING QUANTITIES
Figure 3.1



SPECIFYING SINGLE-PHASE THERMODYNAMIC STATES & CHANGES

Systems require specific numbers of specifications (independent variables) with the rest to be solved for (dependent)

Consider application to 1-phase systems

$\mathcal{V}_{max}$ = # available (orthogonal) interactions

Open systems, boundary work & heat, no E_k, E_p; often $\mathcal{V}_{max} = \mathcal{C}+2$: $\mathcal{C}$ components, heat, Pv work

For $\mathcal{S}_{ext}$ external constraints on system,

$\mathcal{V} = \mathcal{V}_{max} - \mathcal{S}_{ext}$ often $\mathcal{V} = \mathcal{C}+2-\mathcal{S}_{ext}$

Closed system $\mathcal{S}_{ext}=\mathcal{C}$, $\mathcal{V}_{ext}=2 \Rightarrow$ Duhem's Theorem

To change system state, change $\mathcal{V}$ variable values; other variables follow

Note: Fully *identify* extensive state when set constraints & equilibrium occurs,

independent variables

$\mathcal{F}_{ex} = \mathcal{V}_{max}$ - Constraints

Constraints: boundary, $\mathcal{S}_{ext}$; internal, $\mathcal{S}$

Intensive states from $\mathcal{F} = \mathcal{F}_{ex}-1$ usually $= \mathcal{C}+1-\mathcal{S}$

("degrees of freedom" for single phase)

Be sure to get all internal constraints of multiphase systems!

Careful selecting variables even after correct #

State often not unique in nonmonotonic variables (*e.g.*, water density with T)

Avoid redundant property pairs (v & ρ)

FUNDAMENTAL EQUATIONS

Closed system change of state specified by *dU*

$$dU = \delta Q_{irr} + \delta W_{irr} = \delta Q_{rev} + \delta W_{rev} = TdS - PdV$$

$$\Rightarrow U = U(S,V) \text{ and, since } dU = \left.\frac{\partial U}{\partial S}\right|_V dS + \left.\frac{\partial U}{\partial V}\right|_S dV$$

$$\Rightarrow T = \left.\frac{\partial U}{\partial S}\right|_V \quad \& \quad -P = \left.\frac{\partial U}{\partial V}\right|_S$$

"Fundamental" eq.; note, $U = U(S,P)$ incomplete

Other conceptuals via Legendre Transforms

$$H \equiv U - (-PV) = U + PV$$

$$\Rightarrow dH = TdS + VdP \Rightarrow H(S,P)$$

$$A \equiv U - (TS) \Rightarrow dA = -SdT - PdV \Rightarrow A(T,V)$$

$$G \equiv H - TS \Rightarrow dG = -SdT + VdP \Rightarrow G(T,P)$$

$$dA_T = -PdV = \delta W_{T\,rev} \qquad dH_P = TdS = \delta Q_{P\,rev}$$

Open systems (varying composition)

$$U = U(S,V,\{N\})$$

$$dU = \left.\frac{\partial U}{\partial S}\right|_{V,\{N\}} dS + \left.\frac{\partial U}{\partial V}\right|_{S,\{N\}} dV + \sum_{i=1}^{C} \left.\frac{\partial U}{\partial N_i}\right|_{S,V,N_{j\neq i}} dN_i$$

$$dU = TdS - PdV + \sum_{i=1}^{C} \left.\frac{\partial U}{\partial N_i}\right|_{S,V,N_{j\neq i}} dN_i$$

$H(S,P,\{N\})$, **etc.**

$$dH = TdS + VdP + \sum_{i=1}^{C} \left.\frac{\partial H}{\partial N_i}\right|_{S,P,N_{j\neq i}} dN_i$$

$$dG = -SdT + VdP + \sum_{i=1}^{C} \left.\frac{\partial G}{\partial N_i}\right|_{T,P,N_{j\neq i}} dN_i$$

$$\Rightarrow \left.\frac{\partial U}{\partial N_i}\right|_{S,V,N_{j\neq i}} = \left.\frac{\partial H}{\partial N_i}\right|_{S,P,N_{j\neq i}} = \left.\frac{\partial A}{\partial N_i}\right|_{T,V,N_{j\neq i}} = \left.\frac{\partial G}{\partial N_i}\right|_{T,P,N_{j\neq i}} \equiv \overline{G}_i(T,P,\{x\})$$

Note integrated forms in 3.2.3

RESPONSE FUNCTIONS

Example: How to get "the response of *U* to a change in *V* at constant *T*"

Straightforward by integrating *dU* in Eq. 3.2.3

But partial derivative best to work with

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$ **Note: nearly optimal - Class II**

Get Class I from *rhs* by Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

Table 3.1 has most useful response functions
Look for maximum # measurables in derivative, including variable(s) being held constant
Remember: goal is to get *integrable* form to connect measurables to conceptual differences

Closed System Response to *T* Change

"Mechanical" $\gamma_V = \left(\frac{\partial P}{\partial T}\right)_v \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial \ln V}{\partial T}\right)_P$

"Thermal"

$$C_v \equiv \left(\frac{\partial U}{\partial T}\right)_V \equiv \lim_{\Delta T \to 0}\left(\frac{\delta Q_{rev}}{\Delta T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_P \equiv \lim_{\Delta T \to 0}\left(\frac{\delta Q_{rev}}{\Delta T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

Heat capacities connect 1st & 2nd Law Properties!

Also, $\left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial A}{\partial T}\right)_V = -S$ **Not useful except EoS models**

Gibbs-Helmholtz relations more useful, since get *H* from experiment

$$\left(\frac{\partial (G/T)}{\partial T}\right)_P = -\frac{H}{T^2} \text{ or } \left(\frac{\partial (G/T)}{\partial (1/T)}\right)_P = H$$

$$\left(\frac{\partial (A/T)}{\partial T}\right)_V = -\frac{U}{T^2} \text{ or } \left(\frac{\partial (A/T)}{\partial (1/T)}\right)_V = U$$

See 3.3.2 for use in difference of *G* / *T* for *T* change

Closed System Response to *P* Change

"Compressibilities" $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_T = \frac{\partial \ln \rho}{\partial P}\Big)_T > 0$

(density, $\rho \equiv \frac{N}{V}$ **)** $\kappa_S = -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_S = \frac{\partial \ln \rho}{\partial P}\Big)_s > 0$

More - $\alpha = \gamma_V \kappa_T$ **from triple product rule**

Also, mechanical related to thermal!

$\frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_v}$; $C_p - C_v = \frac{TV\alpha^2}{\kappa_T} = TV\gamma_v^2 \kappa_T$

For ideal gas = *R*

For incompressible fluid = 0

Finally, $\frac{\partial G}{\partial P}\Big)_T = V$ **and** $\frac{\partial S}{\partial P}\Big)_T = -\frac{\partial V}{\partial T}\Big)_P = -V\alpha$

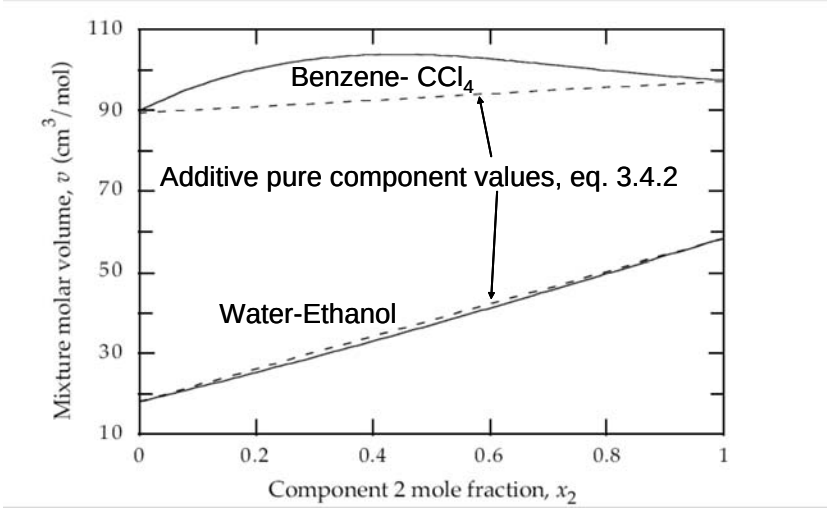
$\frac{\partial A}{\partial V}\Big)_T = -P$ **and** $\frac{\partial S}{\partial V}\Big)_T = \frac{\partial P}{\partial T}\Big)_v = \gamma_V$

Table 3.2: Response magnitudes of gases, liquids

Property	Air	Saturated Liquid Water
Molecular weight	29	18
Temperature, T (K)	300	293.15
Pressure, P (bar)	1	0.023
Density, ρ (g/cm^3)	0.0012	1
Isobaric heat capacity, c_p (J/mol K)	29	75.3
Isometric heat capacity, c_v (J/mol K)	21	74.8
Volume expansivity, α (K^{-1})	0.0033	21.(10^{-5})
Thermal pressure coefficient, γ_v (bar/K)	0.0033	4.6
Isothermal compressibility, κ_T (bar^{-1})	1	45.9(10^{-6})
Adiabatic compressibility, κ_s (bar^{-1})	0.72	45.6(10^{-6})

Closed System Response to N_i Change

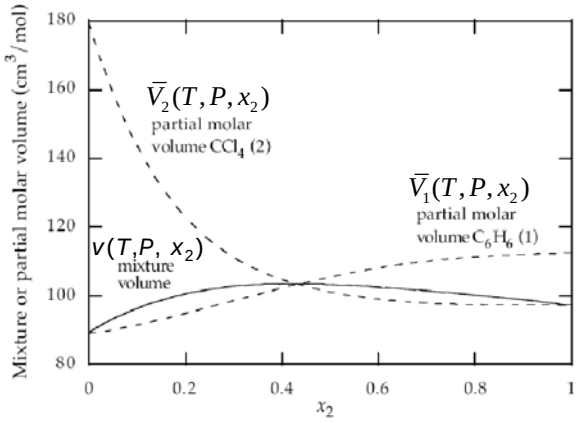
Not normally linear addition of pure values



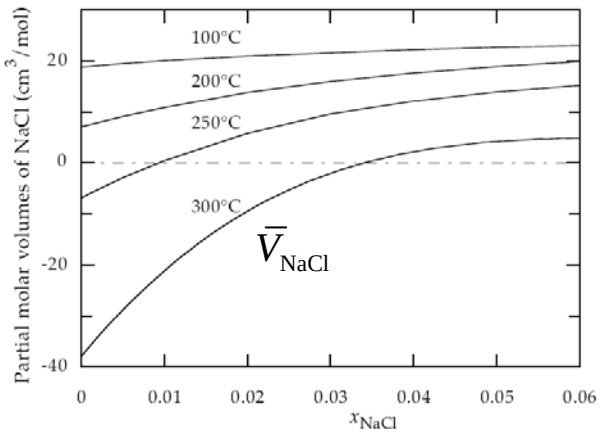
Use partial molar property, $\overline{F}_i = \frac{\partial F}{\partial N_i}\Big)_{T,P,N_{j\neq i}}$

Case: volume, $F \equiv V = Nv \Rightarrow \overline{F}_i = \overline{V}_i$

For binary (only N_2 varying)



Note: *Derivative*, so any sign possible!
e.g., salt in water



Section 3.4.1 + Appendix A.8 gives

a. Summing partial molar properties(intensive) gives solution property value

$$F(T,P,\{N\}) = \sum_{i=1}^{C} N_i \bar{F}_i(T,P,\{x\}) \qquad \textbf{(3.4.4)}$$

b. Math operations on properties are linear, so decorations consistent

$$U = TS - PV + G \Rightarrow \bar{U}_i = T\bar{S}_i - P\bar{V}_i + \bar{G}_i$$

and *e.g.*, $\left(\frac{\partial G}{\partial P}\right)_{T,\{N\}} = V \Rightarrow \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,\{x\}} = \bar{V}_i$**, etc.**

APPENDIX A-8

Gibbs-Duhem Equations: *F* for Multivariables,

Some Homogeneous: $\{\lambda n\} \equiv (\lambda n_1, \lambda n_2, ...)$ **;**
***e.g.*, {λn} = *V*, *U*, *H*, *S*, . . .**
Some Not: {*Y*} ; *e.g.*, *T*, *P*, . . .

Then $\boldsymbol{F}(\{\lambda n\},\{Y\}) = \lambda F(\{n\},\{Y\})$

$\Rightarrow \quad \boldsymbol{F} = \sum_i \bar{F}_i N_i$ **with** $\bar{F}_i \equiv \left(\frac{\partial \boldsymbol{F}}{\partial N_i}\right)_{\{Y\},N_{j\neq i}}$

Plus $-\sum_i N_i d\bar{F}_i + \sum_j \left(\frac{\partial \boldsymbol{F}}{\partial Y_j}\right)_{\{N\},Y_{k\neq j}} dY_j = 0$

Here $\{Y\} = \{T,P\}$**;** $\boldsymbol{F}(\{\boldsymbol{N}\},\{T,P\}) = N\boldsymbol{F}(\{\boldsymbol{x}\},\{T,P\})$

so: $\sum_i N_i d\bar{F}_i - \left(\frac{\partial \boldsymbol{F}}{\partial T}\right)_{P,\{\boldsymbol{N}\}} dT - \left(\frac{\partial \boldsymbol{F}}{\partial P}\right)_{T,\{\boldsymbol{N}\}} dP = 0$

Example:

$\boldsymbol{F} = N\nu;\ \lambda = N;\{n\} = (x_1, x_2, ...);\ \{Y\} = (T,P);$

Then $\bar{F}_i = \bar{V}_i(\{x\},\{T,P\}) \quad \boldsymbol{V} = \sum_i N_i \bar{V}_i$

& $-\sum_i N_i d\bar{V}_i + \left(\frac{\partial \boldsymbol{V}}{\partial T}\right)_{\{N\},P} dT + \left(\frac{\partial \boldsymbol{V}}{\partial P}\right)_{\{N\},T} dP = 0$

For $\mathcal{C}$+2 variables $\{\bar{V}\}, T, P$ **only $\mathcal{C}$+1 independent**
Extra relation is Gibbs-Duhem Equation
Must use it, but not very convenient!

Note: don't use $\bar{V}_i \equiv \left(\frac{\partial v}{\partial x_i}\right)_{T,P,x_{j\neq i}}$**:** $x_{j\neq i}$ **not constant**

Implications for variations of $\overline{U}_i, \overline{S}_i, \overline{V}_i, \overline{G}_i$, etc.

e.g., **if $\overline{F}_i$ increases for 1 component (*i* = 1),**

$\overline{F}_j$ must decrease for at least 1 other component (*j* ≠ 1) at constant *T, P*.

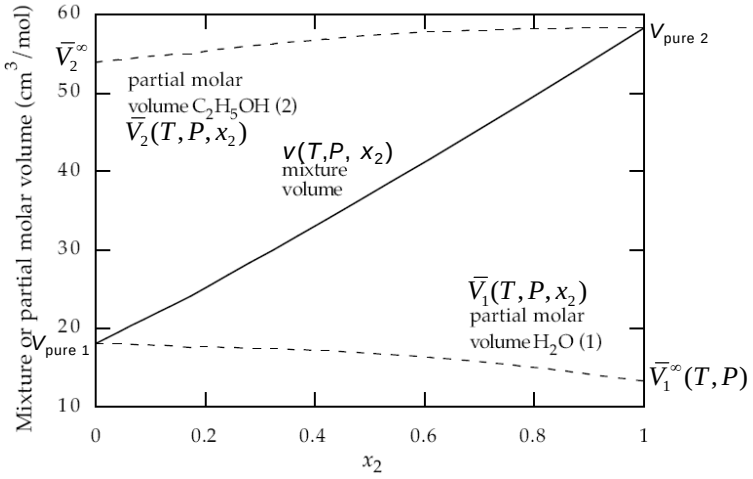
For, *e.g.*, *F* = *G*, in binary, either opposite signs

$$x_1 d\overline{G}_1 = -x_2 d\overline{G}_2 \quad \textbf{(}T,P\textbf{ fixed)}$$

or same sign with large enough *T* / *P* variation

$$x_1 d\overline{G}_1 + x_2 d\overline{G}_2 = -s dT + v dP$$

Partial molar volumes in binaries
Note slopes have opposite signs



CONCEPTUAL / MEASURABLE RELATIONS

Rearrange fundamental equations to integrate

Examples $\boldsymbol{H}(\boldsymbol{S}, P, \{N\}) \Rightarrow \boldsymbol{H}(T, P, \{N\})$

$$\boldsymbol{dH} = \left.\frac{\partial \boldsymbol{H}}{\partial T}\right|_{P,\mathbf{N}} dT + \left.\frac{\partial \boldsymbol{H}}{\partial P}\right|_{T,\mathbf{N}} dP + \sum_{i=1}^{C} \left.\frac{\partial \boldsymbol{H}}{\partial N_i}\right|_{T,P,N_{j\neq i}} dN_i$$

$$= C_p dT + (\boldsymbol{V} - T\boldsymbol{V}\alpha) dP + \sum_{i=1}^{C} \overline{H}_i dN_i$$

$$\boldsymbol{dS} = \frac{C_p}{T} dT - \boldsymbol{V}\alpha dP + \sum_{i=1}^{C} \overline{S}_i dN_i$$

$$\boldsymbol{dU} = C_v dT + (T\gamma_v - P)\boldsymbol{dV} + \sum_{i=1}^{C} (\overline{H}_i - T\gamma_v \overline{V}_i) dN_i$$

$$\boldsymbol{dS} = \frac{C_v}{T} dT + \gamma_v \boldsymbol{dV} + \sum_{i=1}^{C} (\overline{S}_i - \gamma_v \overline{V}_i) dN_i$$

MOLAR STUFF EQUATIONS

Always True Differentials **- Use Exterior View**

Mass / Nonreacting Moles - MB (Conserved) (3.6.2)

$$dN_{si} = \sum_{\alpha=\text{in ports}} dN_{\alpha i} - \sum_{\beta=\text{out ports}} dN_{\beta i} \qquad i = 1, \ldots, C$$

Energy - EB (Conserved) - no KE, PE, (3.6.7)

$$\sum_i \overline{U}_{si} dN_{si} + \left(\frac{\partial U}{\partial T}\right)_{PN} dT + \left(\frac{\partial U}{\partial P}\right)_{TN} dP =$$

$$\sum_{i=1}^{C} \left\{ \sum_{\alpha=\text{in ports}} \overline{H}_{\alpha i} dN_{\alpha i} - \sum_{\text{out ports}} \overline{H}_{\beta i} dN_{\beta i} \right\}$$

$$+ \sum_{\text{heat flows}} \delta(Q_{ext})_f + \delta W_{boundary} + \delta W_{shaft}$$

Entropy - NB (Generated) - (3.6.10)

$$\sum_i \bar{S}_{si} dN_{si} + \left(\frac{\partial S}{\partial T}\right)_{PN} dT + \left(\frac{\partial S}{\partial P}\right)_{TN} dP = \sum_{i=1}^{C} \left\{ \sum_{\alpha=\text{in ports}} \bar{S}_{\alpha i} dN_i - \sum_{\beta=\text{out ports}} \bar{S}_{\beta i} dN_{\beta i} \right\} + \sum_{\text{heat flows}} \delta\left(\frac{Q_{ext}}{T_{ext}}\right)_f + dS_{gen}$$

DIFFERENT VARIABLES IN PROBLEMS ON pp. 102-4

Get $\mathcal{V}$ & $\mathcal{F}_{ex}$ from similar analysis to Section 3.1

$$\mathcal{V}_{max} = N_p (\mathcal{C} + 2) + 2 \qquad \mathcal{V} = \mathcal{V}_{max} - \mathcal{S}_{ext}$$

For real systems, $N_{ports} \geq 2$, $\mathcal{C} \geq 1$, $\mathcal{S}_{ext} \geq 0$

Also, $\mathcal{F}_{ex} = \mathcal{V} - \mathcal{S}$; <u>usually</u> $\mathcal{F}_{ex} = N_p (\mathcal{C}+2)-(\mathcal{C}-1)-\mathcal{S}_{ext}$

Ex. 3.6.3: 2 pure streams in heat exchanger
Note difference of case 1, where *Q* desired, & case 2 where *Q* not needed

HEAT & WORK IN OPEN SYSTEMS

***Q* appears in both EB & NB - Use NB *<u>only</u>* if interested in Q_{rev} (then *S* conserved) in (3.7.2)**

$$\frac{\delta Q_{rev}}{T_{ext}} = \sum_i \bar{S}_{sys\,i} dN_{sys\,i} + \left(\frac{\partial S}{\partial T}\right)_{PN} dT + \left(\frac{\partial S}{\partial P}\right)_{TN} dP - \sum_{\alpha=in} \sum_i \bar{S}_{\alpha i} dN_{\alpha i} + \sum_{\beta=out} \sum_i \bar{S}_{\beta i} dN_{\beta i}$$

***W* appears only in EB -**
Substitute *Q* from NB into EB (3.7.10)

$$\delta W_t = \sum_i \left(\bar{U}_{si} - T_{ext}\bar{S}_{si}\right) dN_{si} - \sum_\alpha \sum_i \left(\bar{H}_{\alpha i} - T_{ext}\bar{S}_{\alpha i}\right) dN_{\alpha i} + \sum_\beta \sum_i \left(\bar{H}_{\beta i} - T_{ext}\bar{S}_{\beta i}\right) dN_{\beta i} + T_{ext}\delta S_{gen}$$

Chapter summary shows isomorphisms & patterns of thermodynamics & calculus.