

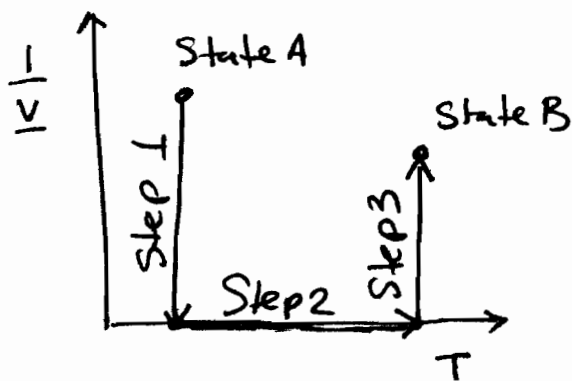
Fundamental Equations from Data

Given C_p^{IG}, C_v^{IG} } → obtain $\underline{u}, \underline{A}, \underline{G}, \underline{S}, \dots$

P, V, T EOS

Most practical equations of state are pressure-explicit:

$P = P(\underline{v}, T)$ → integrations in \underline{v} easier



$\frac{1}{\underline{v}} \rightarrow 0$ is Ideal Gas State

Start with $\Delta \underline{u} = \underline{u}_B - \underline{u}_A$

Step 1 const. T , change in \underline{v}

$$d\underline{u} = T d\underline{s} - P d\underline{v} \Rightarrow \left. \frac{\partial \underline{u}}{\partial \underline{v}} \right|_T = T \left. \frac{\partial \underline{s}}{\partial \underline{v}} \right|_T - P = T \left. \frac{\partial P}{\partial T} \right|_{\underline{v}} - P$$

$$\Rightarrow \Delta \underline{u}_1 = \int_{\underline{v}_A}^{\infty} \left[T \left. \frac{\partial P}{\partial T} \right|_{\underline{v}} - P \right] d\underline{v}$$

Maxwell's on
 $d\underline{A} = -\underline{s} dT - P d\underline{v}$

Step 2 $T_A \rightarrow T_B$ $\left. \frac{\partial \underline{u}}{\partial T} \right|_{\underline{v}} = C_v \Rightarrow \Delta \underline{u}_2 = \int_{T_A}^{T_B} C_v^{IG} dT$

Step 3: Same as 1, $\Delta \underline{u}_3 = \int_{\infty}^{\underline{v}_B} \left[T \left. \frac{\partial P}{\partial T} \right|_{\underline{v}} - P \right] d\underline{v}$

$$\Delta \underline{u} = \underline{u}_B - \underline{u}_A = \Delta \underline{u}_1 + \Delta \underline{u}_2 + \Delta \underline{u}_3$$

Now, need $\Delta \underline{s} = \underline{s}_B - \underline{s}_A$

$$\left. \frac{\partial \underline{s}}{\partial \underline{v}} \right|_T = \left. \frac{\partial P}{\partial T} \right|_{\underline{v}} \quad (\text{above})$$

$$T \left. \frac{\partial \underline{s}}{\partial T} \right|_{\underline{v}} = C_v$$

$$\therefore \Delta \underline{S} = \int_{\underline{V}_A}^{\infty} \left. \frac{\partial P}{\partial T} \right|_{\underline{V}} d\underline{V} \Big|_{T=T_A} + \int_{T_A}^{T_B} \frac{C_{V,IG}}{T} dT + \int_{\infty}^{\underline{V}_B} \left. \frac{\partial P}{\partial T} \right|_{\underline{V}} d\underline{V} \Big|_{T_B}$$

For ideal gases, $\left. \frac{\partial P}{\partial T} \right|_{\underline{V}} = \frac{R}{\underline{V}}$, $\int \frac{d\underline{V}}{\underline{V}} = \ln \underline{V} \rightarrow \infty$ as $\underline{V} \rightarrow \infty$

but... 1st + 3rd terms of $\Delta \underline{S}$ are equal & opposite so that $\Delta \underline{S}$ does not diverge.

Given $\Delta \underline{U}$, $\Delta \underline{S}$, other thermo. functions are:

$$\Delta \underline{H} = \Delta(\underline{U} + P\underline{V}) = \Delta \underline{U} + \Delta(P\underline{V})$$

↳ from Eos

$$\Delta \underline{A} = \Delta \underline{U} - \Delta(T\underline{S})$$

↳ need \underline{S} ref. value

$$\Delta \underline{G} = \Delta \underline{H} - \Delta(T\underline{S})$$

Fugacity

Ideal-gas chemical potential μ diverges as $P \rightarrow 0$ or $\underline{V} \rightarrow \infty$:

$$d\underline{G} = d\mu = -S dT + \underline{V} dP \quad \left. \frac{\partial \mu}{\partial P} \right|_T = \underline{V} = \frac{RT}{P}$$

$$\mu^{IG}(T, P) - \mu^{IG}(T, P^0) = \int_{P^0}^P \frac{RT}{P} dP = RT \ln \frac{P}{P^0}$$

$$\text{as } P \rightarrow 0 \quad \mu^{IG}(T, P) \rightarrow -\infty$$

To get a handle on μ for low P , we define a transformed chemical potential, f :

$$RT \ln \frac{f}{f^\circ} = \mu(T, P) - \mu^\circ(T, P^\circ)$$

we usually set the reference fugacity f° to be 1 bar at $P=1$ bar and write a dimensionally inconsistent relationship:

$$\boxed{RT \ln f = \mu(T, P) - \mu^\circ(T, P^\circ)} \quad \text{Convenient definition of } f$$

For ideal gases, $\boxed{f = P}$ (if $f^\circ = P^\circ$)

Fugacity coefficient $\phi = f/P$

Fugacity is not a pressure; it ^{measures} chemical potentials.

Pressure dependence of f

$$\left. \frac{\partial \mu}{\partial P} \right|_T = \underline{V} \Rightarrow RT \left. \frac{\partial \ln f}{\partial P} \right|_T = \underline{V} \Rightarrow$$

$$RT \ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} \underline{V} dP$$

if \underline{V} is indep. of P (as it is for liquids and solids at moderate pressures; incompressible)

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$$\ln f_2 = \ln f_1 + \frac{(P_2 - P_1)V}{RT} \Rightarrow f_2 = f_1 \exp\left(\frac{V \Delta P}{RT}\right)$$

"Poynting" correction

Example 7.2: change of f for H_2O @ 300K

$$f(P=100 \text{ bar}) / f(P=1 \text{ bar}) = 1.07$$

$$f(P=1000 \text{ bar}) / f(P=1 \text{ bar}) = 2.04$$

How do we obtain f ?

$$h_I = h_{II} \Rightarrow f_I = f_{II} \quad \text{for low vapor pressures, } f_{II} \approx p^{\text{sat}}$$

$$\Rightarrow f(\text{Liquid or solid at } p^{\text{sat}}) = p^{\text{sat}}$$

Pop Quiz: estimate f for H_2O @ 20°C

For systems described by pressure-explicit

$$\text{EoS: } \ln \frac{f}{P} = \ln \phi = z - 1 - \ln z + \frac{1}{RT} \int_{\infty}^V \left(\frac{RT}{V} - P \right) dV$$

Temperature dependence

$$\left. \frac{\partial h}{\partial T} \right|_P = -S \quad \text{no good} \quad \left. \frac{\partial (h/T)}{\partial T} \right|_P = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2}$$

$$= -\frac{H}{T^2} \Rightarrow \boxed{\frac{\partial \ln f}{\partial T} = -\frac{H-H^0}{RT^2}} \quad \text{compare to Clausius-Clapeyron}$$