

Phase Equilibria

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2:30 PM

Review

$$Q(N, V, T) = \frac{q_{\text{trans}}^N}{N!} = \frac{1}{N!} \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3N}{2}} V^N$$

internal energy $U = \frac{3}{2} RT$

pressure (new!):

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N, T}$$

$$\ln Q = \ln [V^N \dots] = N \ln V + \dots$$

$$P = k_B T \frac{N}{V}$$

$$PV = Nk_B T = nN_A k_B T$$

atomically:

$$PV = nRT \quad \text{ideal gas law}$$

↳ molar form $PV = RT$

this holds for polyatomic ideal gases

↳ add terms to Q , but no V dependence,

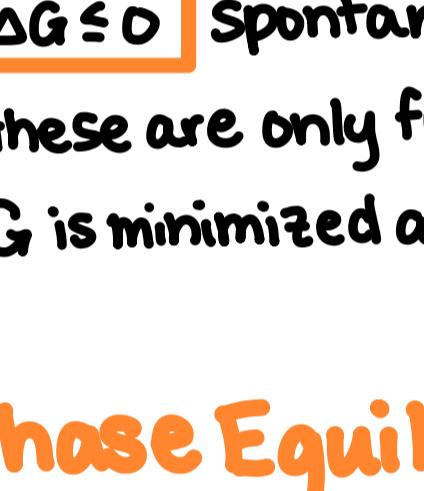
so $\frac{\partial \ln Q}{\partial V} \Big|_{N, T}$ is the same

primer: enthalpy and Gibbs energy

useful properties for processes:

$$\left. \begin{array}{l} \text{@ const. } P : H = U + PV \\ \text{@ const. } T, P : G = H - TS \end{array} \right\}$$

$$\left. \begin{array}{l} \text{@ const. } T, P : G = H - TS \end{array} \right\}$$



1st law:

$$\Delta U = Q + W - P\Delta V$$

$$Q = \Delta U + P\Delta V$$

$$Q = \Delta(U + PV)$$

$$Q = \Delta H \quad \text{isobaric}$$

2nd law:

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T \quad \Delta S_{\text{surr}} = \frac{-Q}{T} = -\frac{\Delta H_{\text{sys}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S - \frac{\Delta H}{T} \geq 0$$

$$\Delta(TS - H) \geq 0$$

$$\Delta G \leq 0 \quad \text{spontaneity}$$

these are only for isobaric + isothermal

G is minimized at equilibrium

Phase Equilibria

phase: region of homogeneous properties

phase equilibrium: stable coexistence of phases

in any proportions



$$\alpha = H_2O(s)$$

$$\beta = H_2O(l)$$

phase boundaries are diathermal, movable, open!

$$\text{thermal eq. } T^\alpha = T^\beta$$

$$\Rightarrow \text{mechanical eq. } P^\alpha = P^\beta$$

$$\text{chemical eq. } \mu_i^\alpha = \mu_i^\beta \Rightarrow g_i^\alpha = g_i^\beta \quad (\text{pure species only})$$

$$\text{recall: } \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq i}$$

$$\text{pure species } i: G = n_i g_i$$

Gibbs Phase Rule

nonreactive system contains m chemical species and π -phases

$$\text{"degrees of freedom": } F = m - \pi + 2$$

↳ # of intensive properties

to constrain system

ex: pure species ($m=1$)

$$F = 3 - \pi$$

$$\rightarrow \pi = 1: F = 2$$

e.g. liquid H_2O , specify T, P

$$\rightarrow \pi = 2: F = 1$$

e.g. liquid H_2O + steam, specify P/T

$$\rightarrow \pi = 3: F = 0$$

this is triple point

Phase Diagram

H_2O :

isobaric, $P = 101325 \text{ Pa}$

$\Delta_{\text{fusion}} = \text{latent heat}$

$\Delta_{\text{vapor}} = \text{latent heat}$

$\Delta_{\text{isobaric}} = \text{sensible heat}$

$= \int_{T_1}^{T_2} C_p dT$

$\Delta_{\text{isobaric}} = \text{sensible heat}$

$= \int_{T_1}^{T_2}$