

Rotational Partition Function

$$q_{\text{rot}}(T) = \sum_J (2J+1) e^{-\beta \bar{B} J(J+1)} \quad \bar{B} = \frac{h^2}{2I}$$

$\bar{B}/h$ - rotational temperature Θ_r

- Sum cannot be evaluated analytically, but if the temperature is large enough, then it can be converted to an integral

$$q_{\text{rot}}(T) = \int_0^\infty (2J+1) e^{-\beta \bar{B} J(J+1)} dJ$$

$$\Rightarrow v = J(J+1)$$

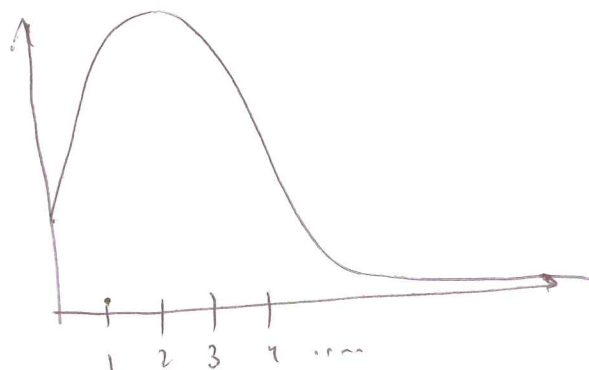
$$dv = (2J+1) dJ$$

$$= \int_0^\infty e^{-\beta \bar{B} v} dv = \frac{e^{-\beta \bar{B} v}}{-\beta \bar{B}} \Big|_0^\infty = \frac{1}{\beta \bar{B}} = \frac{T}{\Theta_r}$$

- for low temperatures, or for molecules with large $\bar{B}$, Θ_r , one can sum directly

- $\frac{N_J}{N}$ - fraction of molecules in the rotational state J

$$\frac{N_J}{N} = \frac{(2J+1) e^{-\beta \bar{B} J(J+1)}}{\sum_{J=0}^\infty (2J+1) e^{-\beta \bar{B} J(J+1)}}$$



$$Q_{\text{rot}}(T) = \sum_J (2J+1) e^{-\beta J(J+1)} \Rightarrow \text{valid for} \\ \text{diatomic but heteronuclear molecules}$$

if homonuclear: need to consider nuclear spin and symmetry of wavefunction

- example: H_2 - each nucleus has spin $-\frac{1}{2}$
- two spin $-\frac{1}{2}$ particles give



$$\underbrace{\frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2)}_{\text{symmetric (triplet)}}, \underbrace{\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)}_{\text{anti-symmetric (singlet)}}$$

- nuclear spin couples to angular momentum, since

rotation by π corresponds to an exchange of particles



- for simplicity assume our H_2 is a molecule on a plane $\Rightarrow$ rotation described by one angle ϕ and one quantum number m

wavefunctions: $\frac{e^{im\phi}}{\sqrt{2\pi}}$

- overall wavefunction must be antisymmetric, since H_2 consists of fermions $\rightarrow$ rotation by π must change sign of wavefunction

overall wavefunction: $\psi(\phi)\psi_{\text{spin}}$

$$\psi(\phi) = \frac{e^{im\phi}}{\sqrt{2\pi}}$$

ψ_{spin} is either of the triplet/singlet states from above

Overall wavefn. can be antisymmetric in two ways

$$\Psi = \Psi_{sp} \Psi_{spin}$$

1.) Ψ_{sp} is symmetric / Ψ_{spin} is antisymmetric

2.) Ψ_{sp} is antisymmetric / Ψ_{spin} is symmetric

1.) $\Psi_{sp} = \frac{e^{im\phi}}{\sqrt{2\pi}}$ with $m = 0, \pm 2, \pm 4, \dots \Rightarrow$ even

$$\Psi_{spin} = \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 - \alpha_2 \beta_1) \text{ --- Singlet state}$$

2.) $\Psi_{sp} = \frac{e^{im\phi}}{\sqrt{2\pi}}$ with $m = \pm 1, \pm 3, \dots \Rightarrow$ odd

$$\Psi_{spin} = \frac{1}{\sqrt{2}} (\alpha_1 \alpha_2 + \alpha_2 \alpha_1) \beta_1 \beta_2$$

- however, degeneracies of different spin states ~~are~~ depend on symmetry

- in this case we have $\omega_{odd} g_{odd} + \omega_{even} g_{even}$

$$g_{rot}(I) = \omega_{odd} - 3 \text{ (triplet)}, \omega_{even} - 1 \text{ (singlet)}$$

- in general it holds that J states are symmetric if J is even, antisymmetric if J is odd

- nuclear spin degeneracy rules: for spin I

~~Integral spin (e.g. deuteron)~~

$I(2I+1)$ - anti-symmetric nuclear spin functions

$(I+1)(2I+1)$ - symmetric nuclear spin functions

~~half integral spin~~

if nuclei have half-integral spin (H_2)

antisymmetric nuclear spin functions couple with even-J

symmetric nuclear spin functions couple with odd-J

if nuclei have integral spin (example D_2)

the overall wavefunction must be symmetric

$\psi_{sp}(\alpha)$ maintains sign upon rotation by π

$$\Rightarrow \psi_{sp}(\alpha) = \psi(\alpha) \psi_{spin}$$

if $\psi(\alpha)$ is even - symmetric

if ψ_{sp} is a symmetric combination

overall ψ will be symmetric

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antisymmetric wavefunctions couple with ~~symmetric~~ ^{anti-symmetric} spin functions

symmetric wavefunctions couple with ~~anti-symmetric~~ ^{symmetric} spin functions

example: D_2 (integral spin)

$$q_{rot, nucl}(\tau) = (I+1)(2I+1) \sum_{J \text{ even}} (2J+1) e^{-\beta B J(J+1)} \\ + I(2I+1) \sum_{J \text{ odd}} (2J+1) e^{-\beta B J(J+1)}$$

example: H_2 (half integer spin)

$$q_{rot, nucl}(\tau) = I(2I+1) \sum_{J \text{ even}} e^{-\beta B J(J+1)} \\ + (I+1)(2I+1) \sum_{J \text{ odd}} e^{-\beta B J(J+1)}$$

Chemical Equilibrium

①

consider gas phase chemical reaction



ν 's - stoichiometric coefficients

$$+ \nu_C \Delta N_C + \nu_D \Delta N_D = 0$$

define $\Delta N \Rightarrow \Delta N_A = \nu_A \Delta N, \Delta N_B = \nu_B \Delta N, \dots$

Helmholtz free energy:

$$dA = -SdT - pdV + \sum_j \mu_j dN_j \quad dN_j = \nu_j dN$$

if reaction vessel is at constant T and V

$$dA = \sum_j \mu_j dN_j = \left[\sum_j \mu_j \nu_j \right] dN$$

at equilibrium: free energy must be a minimum

$$dA = 0 \Rightarrow \sum_j \mu_j \nu_j = 0$$

$$\mu_A \nu_A + \mu_B \nu_B - \mu_C \nu_C - \mu_D \nu_D = 0$$

connection with statistical mechanics

$$Q(N_A, N_B, N_C, N_D, V, T) = Q_A(N_A, V, T) Q_B(N_B, V, T) Q_C(N_C, V, T) Q_D(N_D, V, T)$$

$$= \frac{q_A(V, T)^{N_A}}{N_A!} \frac{q_B(V, T)^{N_B}}{N_B!} \frac{q_C(V, T)^{N_C}}{N_C!} \frac{q_D(V, T)^{N_D}}{N_D!}$$

$$\mu_A = -kT \left(\frac{\partial \ln Q}{\partial N_A} \right)_{N_j, V, T} = -kT \ln \frac{q_A(V, T)}{N_A}$$

$$\begin{aligned} \text{obtained from: } \frac{\partial \ln \frac{q_A(V, T)^{N_A}}{N_A!}}{\partial N_A} &= \frac{\partial}{\partial N_A} [N_A \ln q_A - N_A \ln N_A + N_A] \\ &= \ln q_A - \ln N_A - 1 + 1 \\ &= \ln \frac{q_A}{N_A} \end{aligned}$$

$$\nu_A \mu_A + \nu_B \mu_B - \nu_C \mu_C - \nu_D \mu_D = 0$$

②

$$-kT \nu_A \ln \frac{q_A}{N_A} - \nu_B kT \ln \frac{q_B}{N_B} + \nu_C kT \ln \frac{q_C}{N_C} + \nu_D kT \ln \frac{q_D}{N_D} = 0$$

$$\ln \frac{\left(\frac{q_C}{N_C}\right)^{\nu_C} \left(\frac{q_D}{N_D}\right)^{\nu_D}}{\left(\frac{q_A}{N_A}\right)^{\nu_A} \left(\frac{q_B}{N_B}\right)^{\nu_B}} = 0$$

$$\Rightarrow \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}}$$

$$g = \frac{N}{V}$$

multiplies by $\frac{V_A^{\nu_A} V_B^{\nu_B}}{V_C^{\nu_C} V_D^{\nu_D}}$

$$\frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} = \frac{g_C^{\nu_C} g_D^{\nu_D}}{g_A^{\nu_A} g_B^{\nu_B}}$$

$$= \frac{(q_C/V)^{\nu_C} (q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}} = \frac{g_C^{\nu_C} g_D^{\nu_D}}{g_A^{\nu_A} g_B^{\nu_B}}$$

Since for an ideal gas $q = V f(T)$ q/V is a function of T only

$$K_c(T) = \frac{(q_C/V)^{\nu_C} (q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}}$$

$K_c(T)$ - equilibrium constant in terms of partition function

Example:

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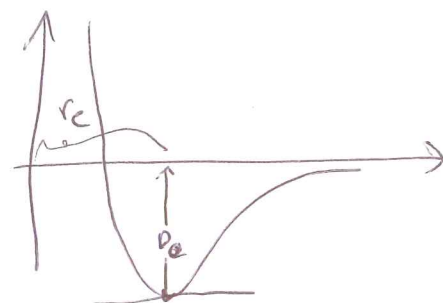


$$K_c(T) = \frac{[q_{\text{Na}_2}(T,V)/V]}{[q_{\text{Na}}(T,V)/V]^2}$$

$$q_{\text{Na}_2}(T,V) = q_{\text{trans}}^{\text{Na}_2} q_{\text{elec}}^{\text{Na}_2} q_{\text{rot}}^{\text{Na}_2} q_{\text{vib}}^{\text{Na}_2} q_{\text{nuc}}^{\text{Na}_2}$$

$$q_{\text{trans}}^{\text{Na}_2} = \frac{\lambda_{\text{trans}}^3}{V} \quad \lambda_{\text{trans}} = \left(\frac{h}{2\pi m_{\text{Na}_2} kT} \right)^{1/2}$$

$$q_{\text{nuc}}^{\text{Na}_2} = \omega_{\text{oe}} e^{+\beta D_e}$$



$$q_{\text{rot}}^{\text{Na}_2} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta \bar{B} J(J+1)}$$

$$\bar{B} = \frac{h^2}{2I}$$

$$I = m_{\text{Na}_2} r_e^2$$

$$= \int_0^{\infty} dx_J e^{-\beta \bar{B} x_J}$$

$$x_J = J(J+1)$$

$$dx_J = (2J+1) dJ \quad (dJ=1)$$

$$= - \frac{e^{-\beta \bar{B} x_J}}{\beta \bar{B}} \Big|_0^{\infty} = \frac{1}{\beta \bar{B}}$$

$$q_{\text{rot}}^{\text{Na}_2} = \frac{kT}{\bar{B}}$$

$$q_{\text{vib}}^{\text{Na}_2} = \sum_{n=0}^{\infty} e^{-\beta h \omega (n + 1/2)} = \frac{e^{-\beta h \omega / 2}}{1 - e^{-\beta h \omega}}$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$q_{\text{nuc}}^{\text{Na}_2} = \omega_{\text{oe}}^{\text{Na}_2}$$

$$q_{\text{Na}_2}(T,V) = \frac{V}{\lambda_{\text{trans}}^3} \omega_{\text{oe}} e^{+\beta D_e} \frac{kT}{\bar{B}} \frac{e^{-\beta h \omega / 2}}{1 - e^{-\beta h \omega}} \omega_{\text{oe}}^{\text{Na}_2}$$

$$= \frac{V}{\lambda_{\text{trans}}^3} \omega_{\text{oe}} \frac{kT}{\bar{B}} \frac{e^{\beta D_0}}{1 - e^{-\beta h \omega}} \omega_{\text{oe}}^{\text{Na}_2}$$

$$D_0 = D_e - \frac{h \omega}{2}$$

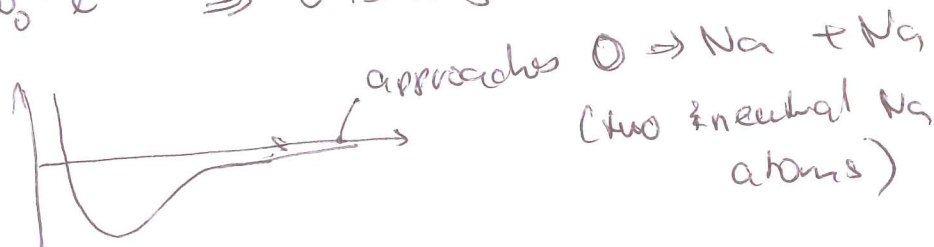
need also

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$$q_{Na}(T, V) = q_{trans}^{Na} q_{elec}^{Na} q_{nuc}^{Na}$$

$$q_{trans}^{Na} = \frac{\lambda_{trans}^3}{V} \frac{V}{\lambda_{trans}^3} \quad \lambda_{trans} = \left(\frac{h}{2\pi m_{Na} kT} \right)^{1/2}$$

$$q_{elec}^{Na} = \omega_0^{Na} e^{-\beta \epsilon_0} \Rightarrow 0 \text{ is the ground state energy}$$



$$\omega_0^{Na} \Rightarrow 2S_{1/2} \text{ is the ground state}$$

$\Rightarrow$ degeneracy of 2

$$q_{elec}^{Na} = 2$$

$$q_{nuc} = \omega_s^{Na} \quad (\omega_s^{Na})^2 = \omega_s^{Na_2}$$

$$K_c(T) = \frac{V^2 \lambda_{trans}^3 \omega_0^{Na_2} \frac{hT}{B} e^{-\beta \epsilon_0} \omega_s^{Na_2} \frac{1}{(1 - e^{-\beta h \omega_s})}}{V^2 \left[\omega_0^{Na} \right]^2 (\omega_s^{Na})^2}$$

$\Rightarrow$ in real life often given in bars of partial pressures

$$\text{calc.: } K_p(T) \approx 0.45 \text{ atm}$$

$$\text{exp.: } K_f(T) \approx 0.50 \text{ atm}$$

Phase transitions

①

- macroscopic matter exists in a number of phases
- phase changes occur abruptly at critical temperatures (but there can ~~sign~~ ^{sign} ~~even~~ ^{even} away from T_c)
- mapping out phase changes

⇒ phase diagram

transition point: where two or more phases coexist

coexist = are in equilibrium with each other

- phases can exchange matter and energy (but not volume)

⇒ condition for coexistence: chemical potentials are equal for a given value of μ and T (or other parameters like pressure...)

- phase transition ⇒ chemical potentials of phases

⇒ Gibbs free energy ⇒ change continuous

- not necessarily true for derivatives of Gibbs free energy

- if first derivative discontinuous

(as a fn. of pressure/temperature/etc.)

⇒ first-order transition

- if discontinuity occurs in higher derivative

⇒ second-order or continuous transition

- critical point ⇒ most phase transitions have one (solid-liquid does not)

as critical point is approached from "above"

fluctuations increase, new order parameter emerges at critical point

- approach of critical point ⇒ characterized by critical exponents

Phase Coexistence: Gibbs Phase Rule

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- most systems can exist in a number of phases
 - $\Rightarrow$ different macroscopic / microscopic behaviour
- phase realized for a particular set of external parameters
 - $\Rightarrow$ lowest free energy
- coexisting phases: thermal & mechanical equilibrium can exchange matter

$\Downarrow$
temperature and chemical potential must be equal between coexisting phases

- example: PVT system pure substance (one component) at a particular pressure / temperature

$$\mu^I(\gamma, T) = \mu^{II}(\gamma, T) \Rightarrow \text{coexistence}$$

$\Downarrow$ $\Downarrow$
it follows that there is a function $\gamma = \gamma(T)$ at which phases can coexist

if there are three phases

$$\mu^I(\gamma, T) = \mu^{II}(\gamma, T) = \mu^{III}(\gamma, T)$$

$\Rightarrow$ coexistence is possible only at one point

four phases cannot coexist

three equations / two unknowns

- example: k different type of particles

$k+2$ phases can coexist

show this by considering that

there are $k+1$ independent variables for each phase

$$\Rightarrow P, T, x_1, \dots, x_{l-1}$$

x_i - concentration of ~~each~~ compound i

(3)

if we have r - phases coexisting

$$\mu_1^I(P, T, x_1^I, \dots, x_{l-1}^I) = \mu_1^{II}(P, T, x_1^{II}, \dots, x_{l-1}^{II}) = \dots = \mu_1^r(P, T, x_1^r, \dots, x_{l-1}^r)$$

$$\vdots$$

$$\mu_l^I(P, T, x_1^I, \dots, x_{l-1}^I) = \mu_l^{II}(P, T, x_1^{II}, \dots, x_{l-1}^{II}) = \dots = \mu_l^r(P, T, x_1^r, \dots, x_{l-1}^r)$$

$\Downarrow$

$\Downarrow$

$\Downarrow$

$l(r-1)$ equations $2 + r(l-1)$ unknowns

$\Downarrow$

$$l(r-1) \leq 2 + r(l-1) \Rightarrow r \leq l+2$$

for an l -component system, ~~at~~ at most $l+2$ phases can coexist

Classification

Gibbs free energies: $G = \sum_j n_j \mu_j$

constant $P, T \Rightarrow dG = \sum_j \mu_j dn_j$

phase transition: $\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{P, T, \{n_i \neq j\}}$ are equal for different j

no restriction on other derivatives

$$V = - \left(\frac{\partial G}{\partial P} \right)_{T, \{n_j\}} \quad S = - \left(\frac{\partial G}{\partial T} \right)_{P, \{n_j\}}$$

if these derivatives are discontinuous

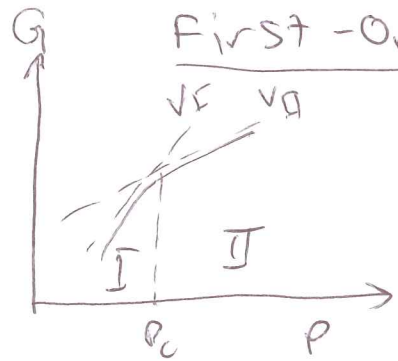
$\Rightarrow$ first-order transition

$\Rightarrow$ finite change in V and S

as ~~T_c or P_c~~ $\rightarrow$ 0
as phase line is crossed
($P(T)$)

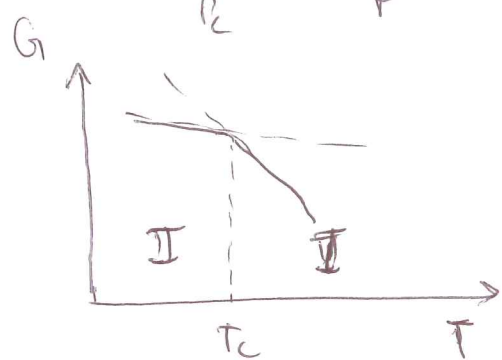
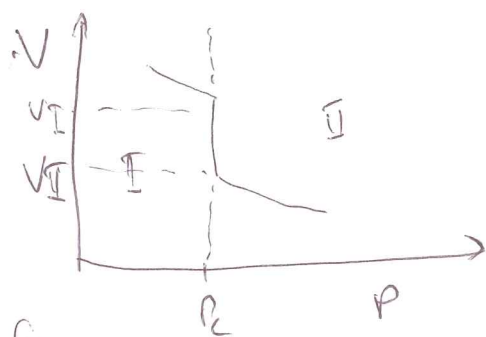
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First-Order phase transition



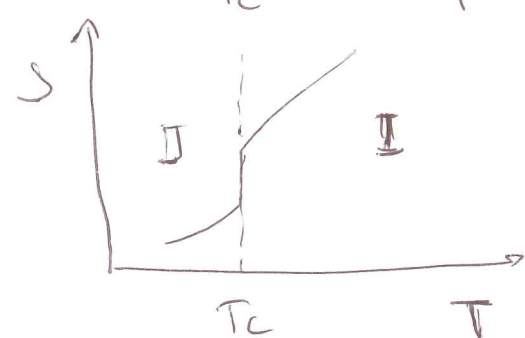
$$V = - \left(\frac{\partial G}{\partial P} \right)_{T, z_{nj}}$$

$$\Delta V = V^I - V^{II} = \left(\frac{\partial G}{\partial P} \right)_{T, z_{nj}}^{II} - \left(\frac{\partial G}{\partial P} \right)_{T, z_{nj}}^I$$



$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, z_{nj}}$$

$$\begin{aligned} \Delta S &= S^I - S^{II} \\ &= \left(\frac{\partial G}{\partial T} \right)_{P, z_{nj}}^{II} - \left(\frac{\partial G}{\partial T} \right)_{P, z_{nj}}^I \end{aligned}$$



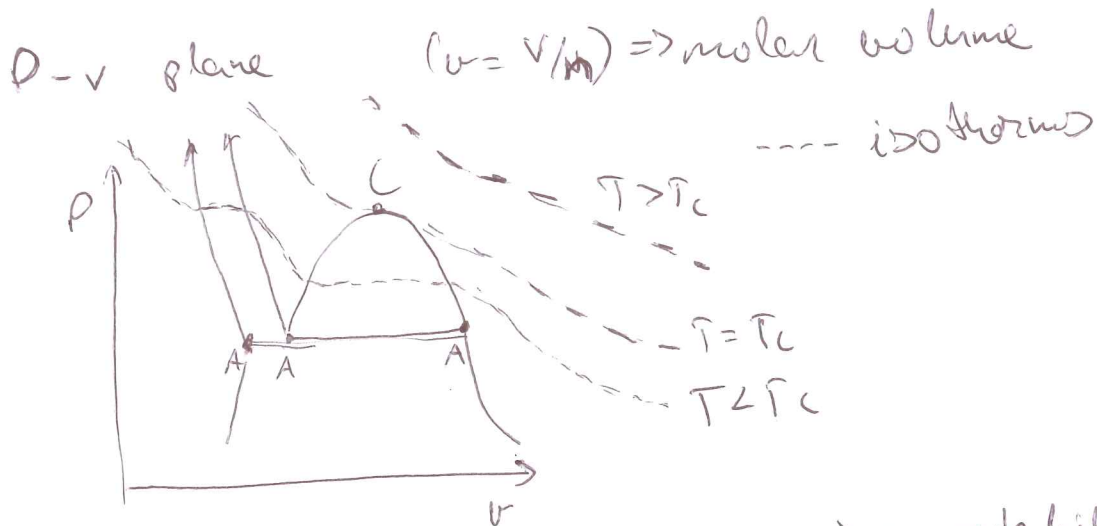
recall! $H = G + TS$

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enthalpy changes during a phase transition

$$\Delta H = T \Delta S$$

enthalpy difference $\rightarrow$ latent heat

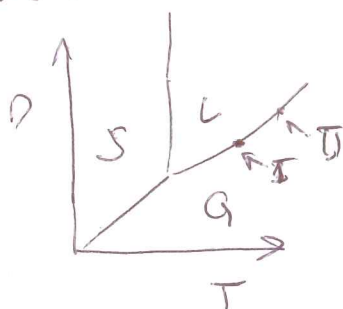


not $(\partial P / \partial v)_T \leq 0 \Rightarrow K_T > 0$ stability condition

flat part of lines $\Rightarrow$ coexistence regions

expansion in volume takes place at constant T, P

- consider moving along a coexistence curve



go from I $\rightarrow$ II

Gibbs free energies must change by equal amounts

$$dg^I = dg^{II} \quad (\Delta G^I = \Delta G^{II})$$

$$v^I dp - s^I dT = v^{II} dp - s^{II} dT$$

(molar quantities used $v = V/n$ $s = S/n$)

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{s^I - s^{II}}{v^I - v^{II}} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T \Delta v}$$

(Clausius-Clapeyron equation)

Vaporization Curve



$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta h_{\text{eg}}}{T \Delta v}$$

assume: Δv due only to changes in volume of gas
gas (vapor) is ideal

$$\Rightarrow \frac{dP}{dT} = \frac{P \Delta h_{\text{eg}}}{T(RT)} \quad PV = nRT \quad \Rightarrow \frac{V}{n} = \frac{RT}{P}$$

$$\frac{dP}{P} = \frac{\Delta h_{\text{eg}}}{R} \frac{dT}{T^2}$$

$$\ln P = -\frac{\Delta h_{\text{eg}}}{R} \frac{1}{T} \Rightarrow \underline{P = P_0 e^{-\frac{\Delta h_{\text{eg}}}{RT}}}$$

as temperature increases $\Rightarrow$ vapor pressure increases

Fusion

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta h_{\text{sl}}}{T \Delta v_{\text{sl}}}$$

$$\text{if } v_{\text{s}} > v_{\text{l}} \Rightarrow \Delta v_{\text{sl}} < 0$$

$$\Rightarrow \frac{dP}{dT} < 0$$

water - negatively sloped fusion curve

$\Rightarrow$ makes ice-skating possible

Sublimation Curve

Solid $\rightleftharpoons$ gas

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{\Delta h_{sg}}{T \Delta v_{sg}}$$

- again assume:

1.) volume change due mainly to change in volume of gas

2.) gas is ideal

$$\Downarrow$$
$$\Delta h_{sg} = -R \frac{d \ln P}{d(1/T)}$$

$$\begin{aligned} dh &= T ds + v dp \\ &= T \left(\frac{\partial s}{\partial T}\right)_p dT + T \left(\frac{\partial s}{\partial p}\right)_T dp + v dp \\ &= c_p dT + \left(v + T \left(\frac{\partial v}{\partial T}\right)_p\right) dp \end{aligned}$$

from Maxwell relation

$$\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$$

$$= c_p dT + v (1 + T \alpha_p) dp$$

α_p - thermal expansivity

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$$

neglect vapor pressure variations

$$\Delta h_{sg} = \Delta h_{sg}^0 + \int_{T_0}^T (c_p^g - c_p^s) dT$$

$$-R \ln P = \Delta h_{sg}^{(0)} d\left(\frac{1}{T}\right) + \int_{T_0}^T (c_p^g - c_p^s) dT' d\left(\frac{1}{T}\right)$$

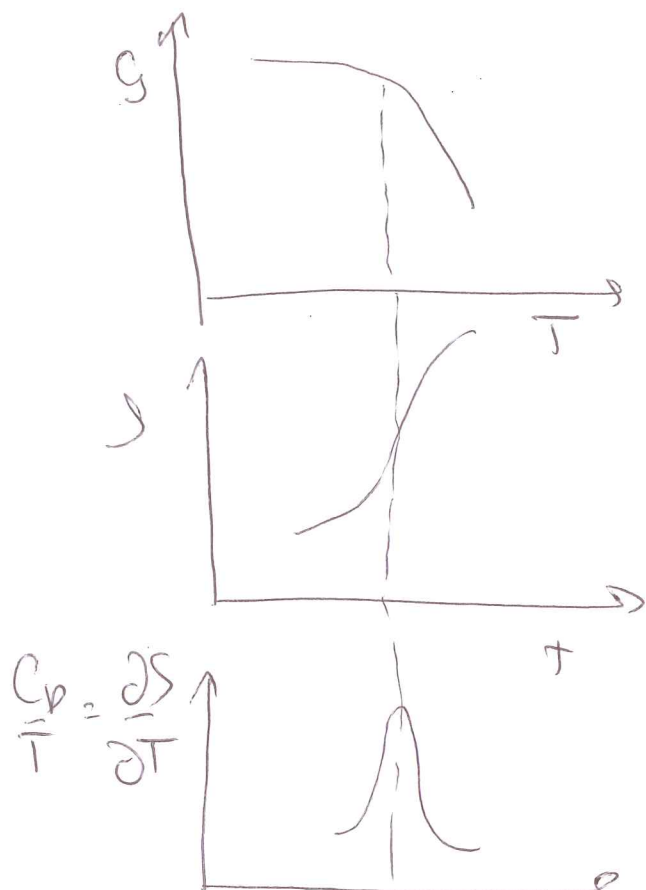
integrate

$$-R \ln \frac{P}{P_0} = \Delta h_{sg}^{(0)} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \int_{T_0}^T \frac{1}{T''} \int_{T_0}^{T'} (c_p^g - c_p^s) dT'' dT'$$

sublimation equation

Continuous phase transition

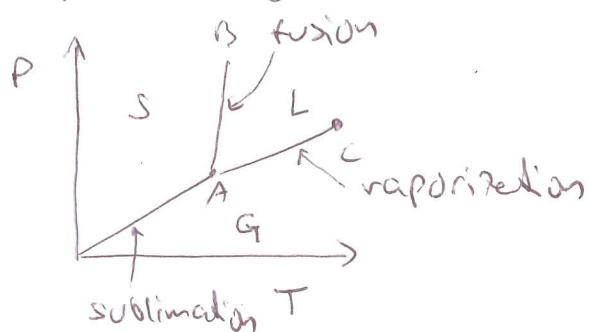
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peak in heat capacity
(or susceptibility in
other cases)

PVT Systems

- one type of molecule
- typical phase diagram:



A - triple point
(all three phases
coexist)
C - critical point

solid - liquid liquid - gas solid - gas

all first order transitions $\Rightarrow$ accompanied by
change in volume, latent heat