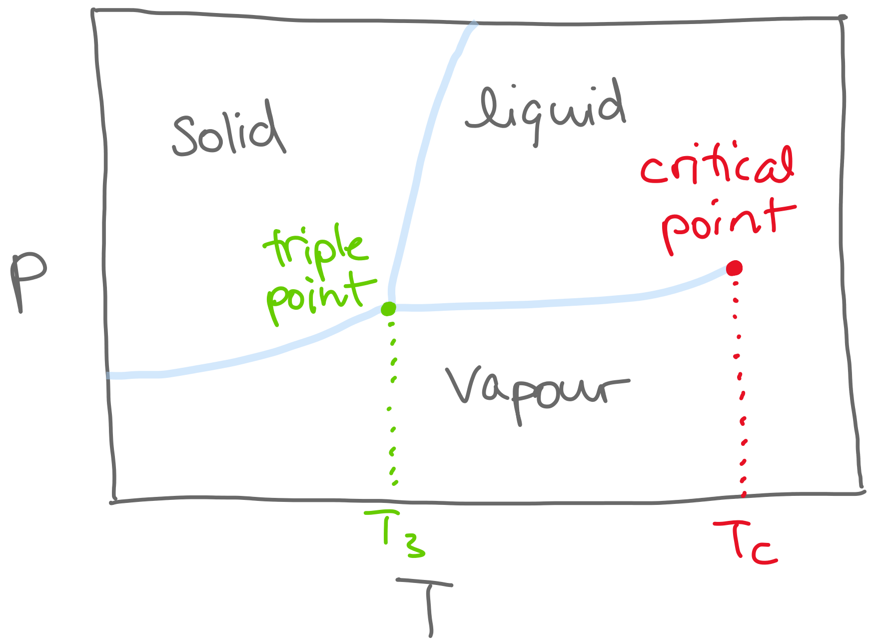
# Lecture 13

Thursday, October 24, 2024 10:00

## Phase Diagrams Continued




## Phase Rule :

$P = 1, \ F = 2$

$P = 2, \ F = 1$

What about three phases in mutual equilibrium?

Phases $\alpha, \beta, \gamma$

$$\mu(\alpha; p, T) = \mu(\beta; p, T)$$

$$\mu(\beta; p, T) = \mu(\gamma; p, T)$$

Two equations with two unknowns; single solution.

$P = 3$, $F = 0$

Four phases cannot be in mutual equilibrium.

$$\mu(\alpha; p, T) = \mu(\beta; p, T)$$
$$\mu(\beta; p, T) = \mu(\gamma; p, T)$$
$$\mu(\gamma; p, T) = \mu(\delta; p, T)$$

Three equations with only two variables. No solution.

When $C = 1$, $F = 3 - P$

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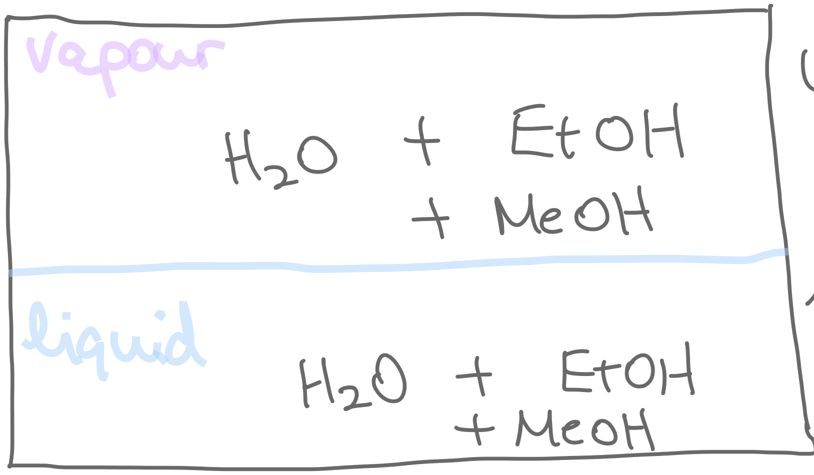
Generalize to any number of components:

components




y : mole fraction in vapour phase

x : mole fraction in liquid phase

How many intensive variables do we have?

$$\boxed{P, T}\,,\ \left.\begin{array}{l} \overbrace{x_{H_2O},\ x_{EtOH},\ x_{MeOH},}^{\text{number of components}} \\ y_{H_2O},\ y_{EtOH},\ y_{MeOH} \end{array}\right\}\ \text{number of phases}$$

$$x_{H_2O} + x_{EtOH} + x_{MeOH} = 1$$

$$y_{H_2O} + y_{EtOH} + y_{MeOH} = 1$$

$$\boxed{P(C-1)+2}$$

At equilibrium, the chemical potential of a component J is the same in every phase.

$$\left.\begin{aligned}
&\mu_{H_2O}(\alpha; p, T) = \mu_{H_2O}(\beta; p, T) \\
&\vdots \\
&\mu_{H_2O}(P-1; p, T) = \mu_{H_2O}(P; p, T)
\end{aligned}\right] \text{P-1 equations}$$

$$\mu_{EtOH}(\alpha; p, T) = \mu_{EtOH}(\beta; p, T)$$

$$\vdots$$

$$\mu_{MeOH}(\alpha; p, T) = \mu_{MeOH}(\beta; p, T)$$

$$\vdots$$

$$P(C-1) + 2 - C(P-1)$$

$$= PC - P + 2 - CP + C$$

$$\boxed{F = C - P + 2}$$ phase rule

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Topic 4B: Thermodynamic Aspects

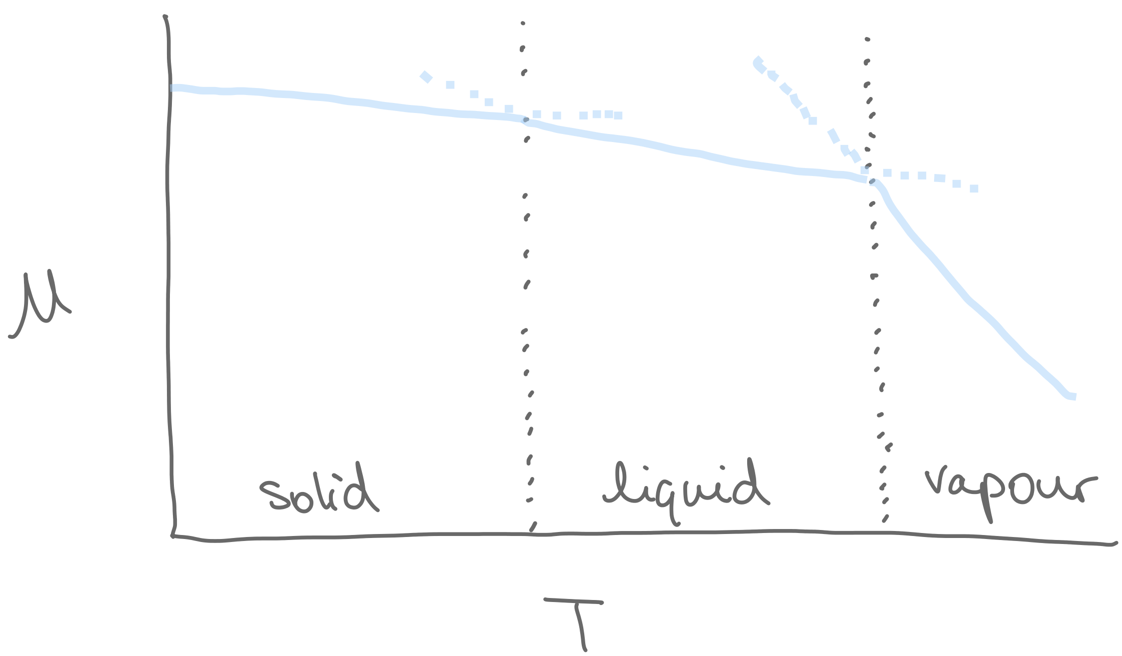
# Topic 1c: Thermodynamic Aspects of Phase Transitions

$$dG = V\,dp - S\,dT$$

$\mu = G_m$ for a one-component system

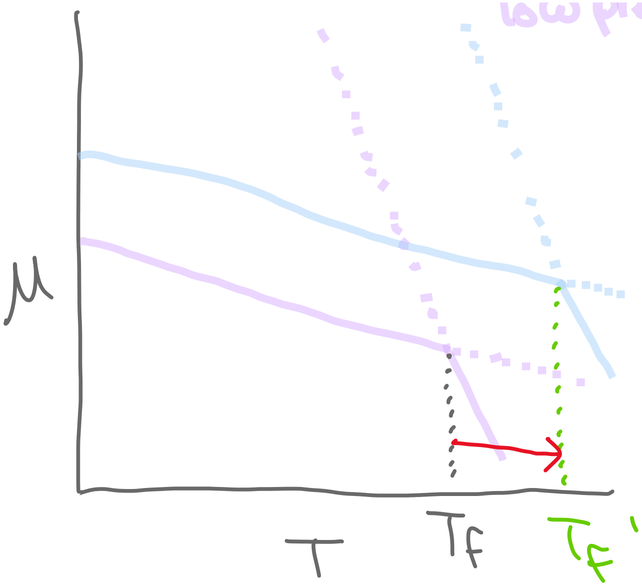
$$d\mu = V_m\,dp - S_m\,dT$$

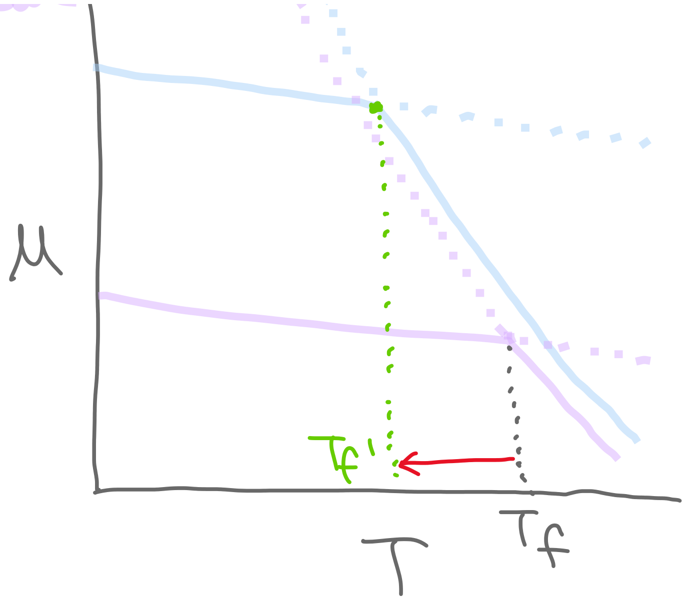
$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m \,, \quad \left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$




The response of melting to applied pressure :

high pressure




$V_m(l) > V_m(s)$

melting point increases as pressure increases

$V_m(l) < V_m(s)$

melting point decreases as pressure increases

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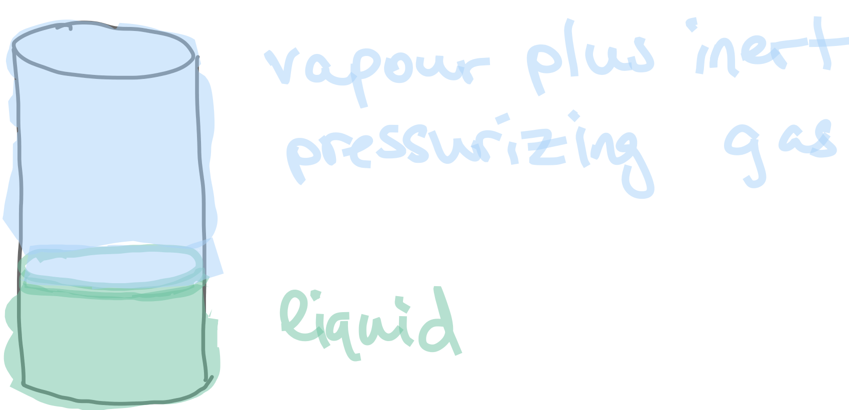
## The Vapour Pressure of a Liquid Subjected to Pressure




$\mu(l) = \mu(g)$

$d\mu(l) = d\mu(g)$

Consider applying additional pressure $dP$.

$d\mu(l) = V_m(l)\,dP$

$d\mu(g) = V_m(g)\,dp$ ← vapour pressure

Assume perfect gas:

$d\mu(g) = \frac{RT}{p}\,dp$

At equilibrium,

$V_m(l)\,dP = \frac{RT}{p}\,dp$

Limits of integration:

if no additional pressure acts on the liquid, $P = p^*$, and $p = p^*$

with additional pressure $\Delta P$,

$P = p^* + \Delta P$

$p^* + \Delta P$ $\qquad$ $p$

$$\int_{p^*} V_m(l)\, dP = RT \int_{p^*} \frac{1}{p'} dp'$$

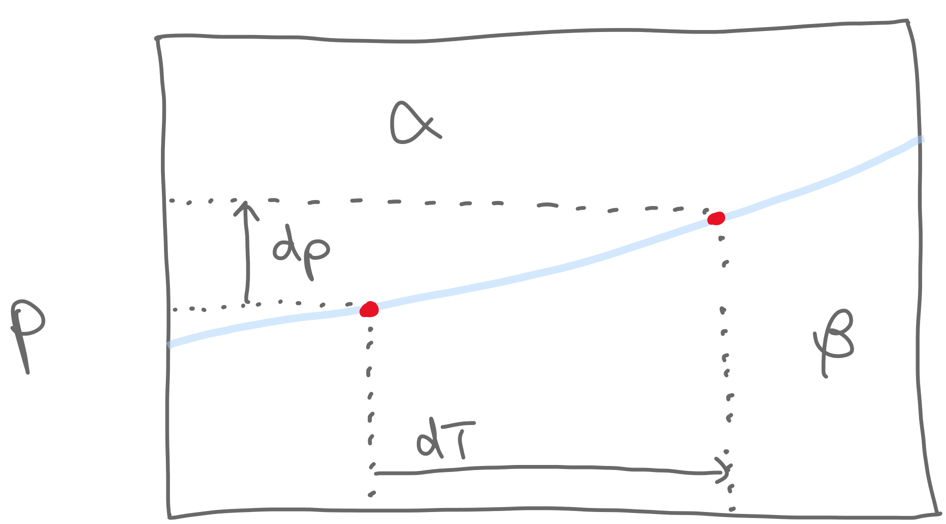
$$V_m(l) \int_{p^*}^{p^*+\Delta P} dP = RT \ln \frac{p}{p^*}$$

$$\frac{V_m(l)}{RT} \Delta P = \ln \frac{p}{p^*}$$

$$\boxed{p = p^* e^{V_m(l)\Delta P / RT}}$$

effect of applied pressure $\Delta P$ on partial vapour pressure $p$

## The Location of Phase Boundaries



T

$$dG = V\,dp - S\,dT$$

$$d\mu = V_m\,dp - S_m\,dT$$

$$d\mu(\alpha) = d\mu(\beta)$$

$$V_m(\alpha)\,dp - S_m(\alpha)\,dT = V_m(\beta)\,dp - S_m(\beta)\,dT$$

$$\underbrace{[S_m(\beta) - S_m(\alpha)]}_{\Delta_{trs} S}\,dT = \underbrace{[V_m(\beta) - V_m(\alpha)]}_{\Delta_{trs} V}\,dp$$

$$\Delta_{trs} S\,dT = \Delta_{trs} V\,dp$$

$$\boxed{\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}}$$

Clapeyron Equation

$$\frac{dT}{dp} = \frac{\Delta_{trs} V}{\Delta_{trs} S}$$