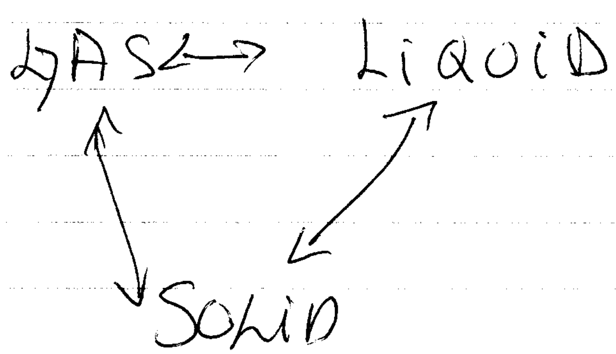
Phase = FORM OF MATTER THAT IS UNIFORM AT THE MICRO AND MACRO SCALES.

GAS
LIQUID
SOLID

TRANSITIONS $\Rightarrow$ PHASE TRANSITIONS




PHASE EQUILIBRIA

GAS $\rightleftharpoons$ LIQUID

GAS $\rightleftharpoons$ SOLID

LIQUID $\rightleftharpoons$ SOLID

In General

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{TP} \quad \text{FOR ONE COMPONENT}$$

$$G = nG_m$$

$$\Rightarrow \quad \mu = G_m$$

$$dG_m = d\mu$$

$$d\mu = -S_m dT + V_m dP$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m > 0$$

$$S_m^{gas} > S_m^{liq} > S_m^{sol.}$$

# P-T DIAGRAMS

AT EQUILIBRIUM $\mu_\alpha(T,P) = \mu_\beta(T,P)$

$$d\mu_\alpha(T,P) = d\mu_\beta(T,P)$$

$$d\mu_\alpha = -S_m^\alpha dT + V_m^\alpha dP = -S_m^\beta dT + V_m^\beta dP$$

$$(S_m^\beta - S_m^\alpha)dT = (V_m^\beta - V_m^\alpha)dP$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}}$$

CLAPEYRON EQUATION

AT THE MELTING TEMP

$$\Delta G_m^{fus} = \Delta H_m^{fus} - T_f \Delta S_m^{fus} = 0$$

$$\Rightarrow \Delta S_m^{fus} = \frac{\Delta H_m^{fus}}{T}$$

FROM TABLES

AN AVERAGE VALUE OF $\Delta S_m$

$$\Delta S_m^{fus} \simeq 22 \frac{J}{mol\,K}$$

$$\Delta V_m^{fus} \simeq 4 \times 10^{-6} \frac{m^3}{mol}$$

$$\left(\frac{dP}{dT}\right)_{fus} \simeq 55 \frac{bar}{K}$$

## VAPORIZATION

Trouton's rule $\Rightarrow \Delta S_m^{vap} \simeq 90 \frac{J}{mol\,K}$

$$\Delta V_m^{vap} > 0$$

$$\Delta V_m^{vap} \simeq 20 \times 10^{-3} \frac{m^3}{mol}$$

$$\left(\frac{dP}{dT}\right)_{vap} \simeq 5 \times 10^3 \frac{Pa}{K} = 5 \times 10^{-2} \frac{bar}{K}$$

$$\left(\frac{dT}{dP}\right)_{vap} \simeq 20 \frac{K}{bar}$$

Sublimation

$$\left(\frac{dP}{dT}\right) = \frac{\Delta S_m^{sub}}{\Delta V_m^{sub}}$$

$$\Delta S_m^{sub} = \Delta S_m^{fus} + \Delta S_m^{vap}$$

$$\Delta V_m^{sub} \simeq \Delta V_m^{vap}$$

$$\left(\frac{dP}{dT}\right)_{sub} \gtrsim \left(\frac{dP}{dT}\right)_{vap}$$

# Vapor pressures $P(T)$

$$\left(\frac{dP}{dT}\right)_{vap} = \frac{\Delta S_m^{vap}}{\Delta V_m^{vap}}$$

$$\Delta S_m^{vap} = \frac{\Delta H^{vap}}{T}$$

$$dP = \Delta H_m^{vap} \frac{dT}{T\Delta V_m^{vap}}$$

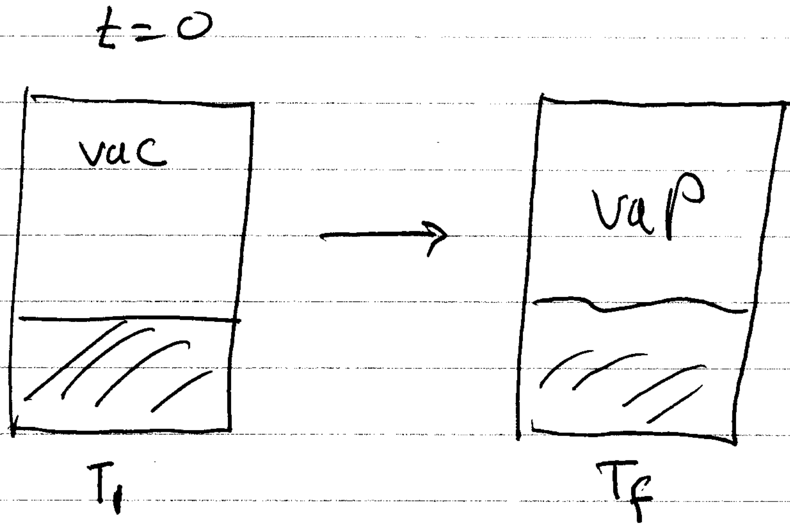
$$\Delta V_m^{vap} \simeq V_m^{gas} \simeq \frac{RT}{P}$$

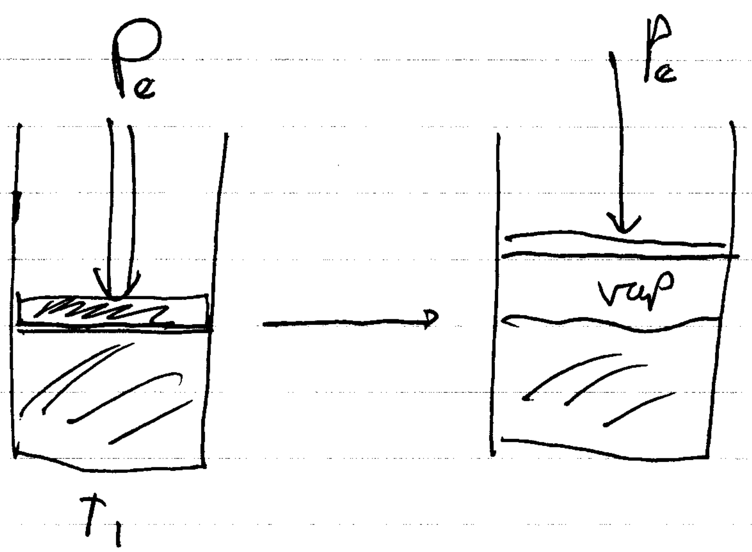
$$dP \simeq \Delta H_m^{vap} P \frac{dT}{RT^2}$$

$$\frac{dP}{P} \simeq \frac{\Delta H_m^{vap}}{R} \frac{dT}{T^2}$$

$$\boxed{\ln\left(\frac{P_f}{P_i}\right) = -\frac{\Delta H_m^{vap}}{R}\left[\frac{1}{T_f} - \frac{1}{T_i}\right]}$$

# PURE SUBSTANCE




$$\mu_{liq}(T, P_e) = \mu_{gas}(T, P)$$

$$\left(\frac{\partial \mu_{liq}}{\partial P_e}\right)_T = \left(\frac{\partial \mu_{gas}}{\partial P}\right)_T \left(\frac{\partial P}{\partial P_e}\right)_T$$

$$d\mu = -S_m dT + V_m dP$$

$$\Rightarrow \quad \left(\frac{\partial \mu}{\partial P}\right)_T = V_m$$

$$V_m^{liq} = V_m^{gas} \left(\frac{\partial P}{\partial P_e}\right)_T$$

$$\left(\frac{\partial P}{\partial P_e}\right)_T = \frac{V_m^{liq}}{V_m^{gas}} = \frac{V_m^{liq} P}{RT}$$

$$RT \frac{dP}{P} = V_m^{liq} dP_e$$

$$\boxed{RT \ln\left(\frac{P}{P^0}\right) = V_m^{liq} (P_e - P^0)}$$

$P^0$ Vapor pressure with $P_e = 0$ (VACUMM)

$P_e = 1 \text{bar}$

$P_o = 0.0316 \text{ bar}$

$V_m^{liq} = 1.8 \times 10^{-5} m^3$

$P = 1.0007 P_o \doteq 0.0316$

At $P_e = 100 \text{ bar}$

$P = 0.0339 \text{ bar}$