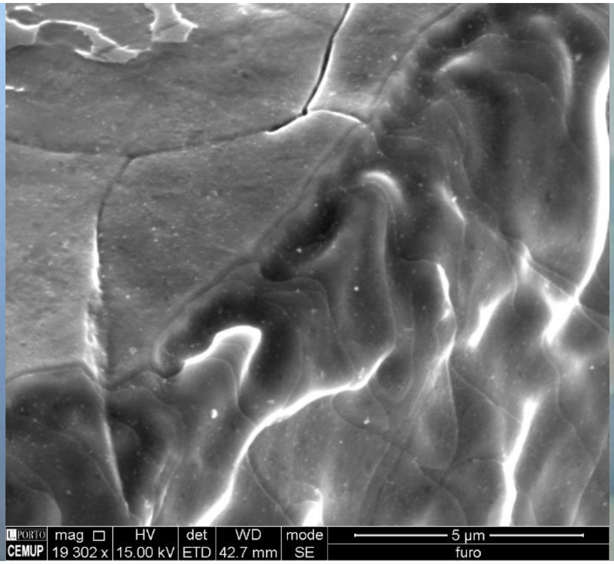
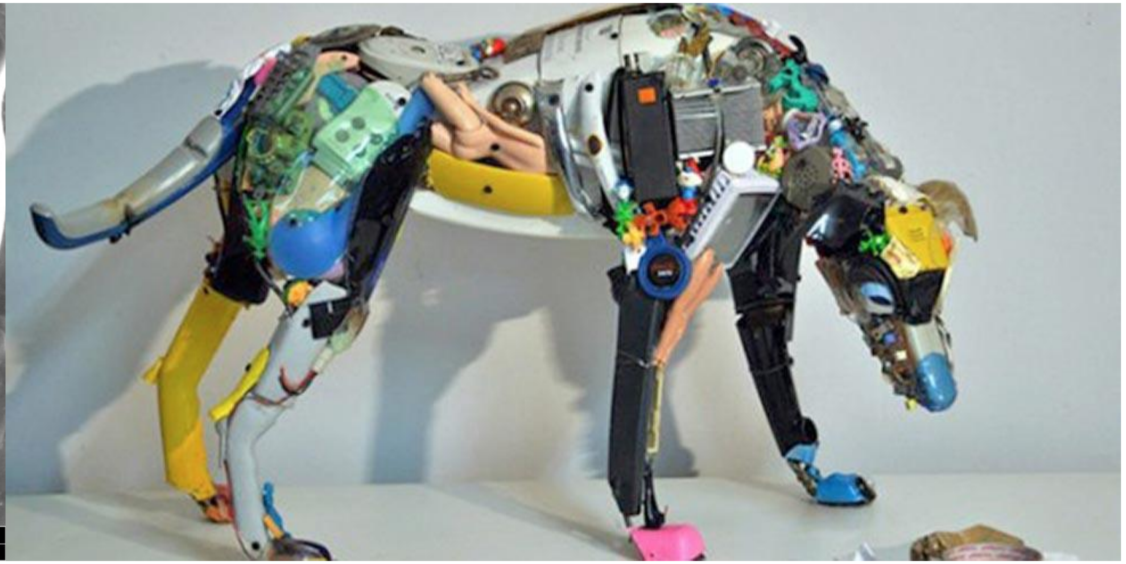
Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.

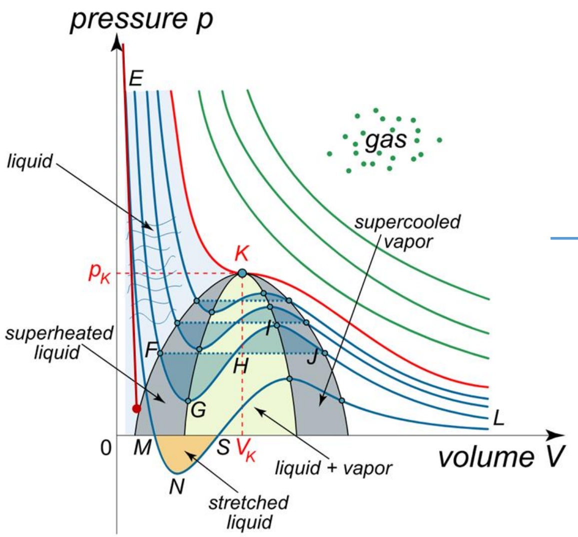


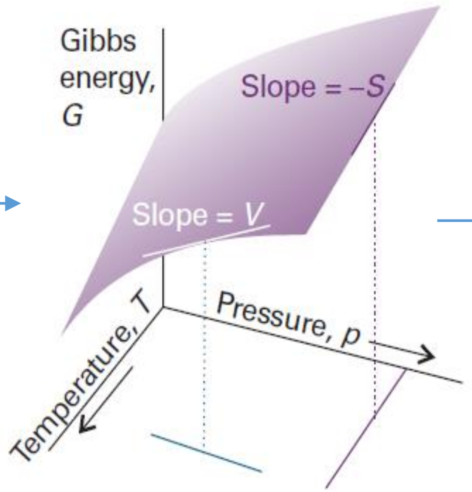


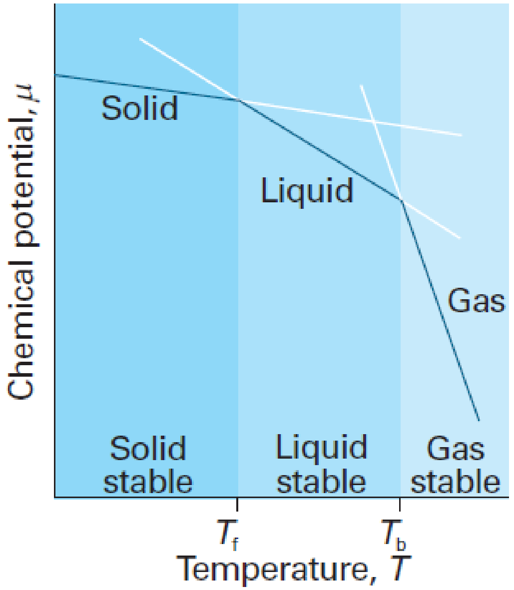
Physical transformations of pure substances

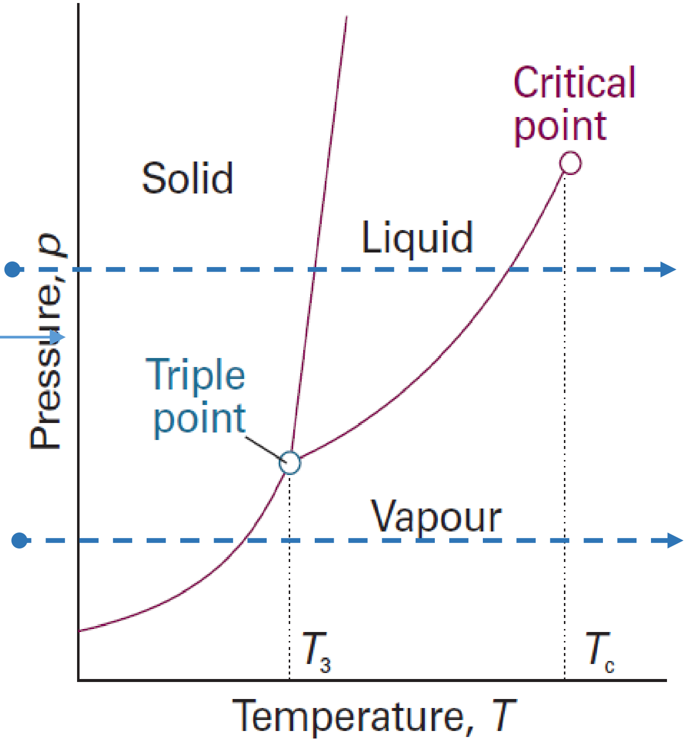
EoS

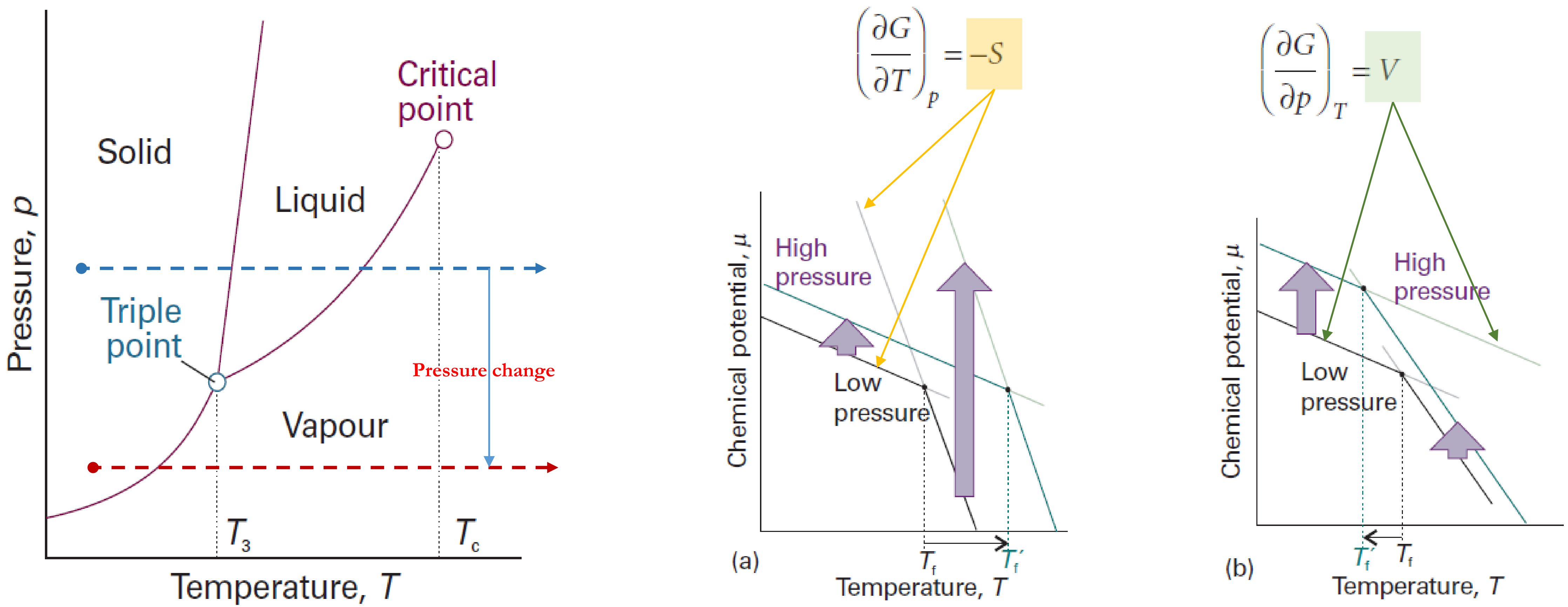
$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$










Critical point
Solid
Liquid
Pressure, p
Triple point
Pressure change
Vapour
T_3
T_c
Temperature, T
$\left(\frac{\partial G}{\partial T}\right)_p = -S$
High pressure
Low pressure
Chemical potential, μ
(a)
T_f
T_f'
Temperature, T
$\left(\frac{\partial G}{\partial p}\right)_T = V$
High pressure
Low pressure
Chemical potential, μ
(b)
T_f'
T_f
Temperature, T

Physical transformations of pure substances

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

Clapeyron equation

Shape of the curve!

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

Phase equilibrium !

$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

Phase_α ⇄ Phase_β

V_m (α)	V_m(β)
S_m (α)	S_m(β)

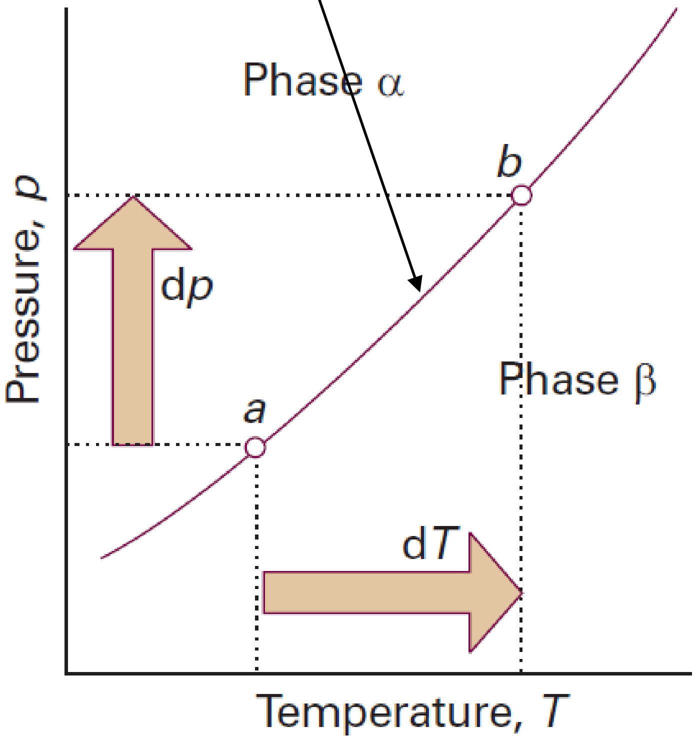
$$dG = Vdp - SdT$$

$$G_\alpha(p,T) = G_\beta(p,T)$$

$$dG_\alpha(p,T) = dG_\beta(p,T)$$

$$-S_{\alpha,m}dT + V_{\alpha,m}dp = -S_{\beta,m}dT + V_{\beta,m}dp$$

$$(V_{\beta,m} - V_{\alpha,m})dp = (S_{\beta,m} - S_{\alpha,m})dT$$



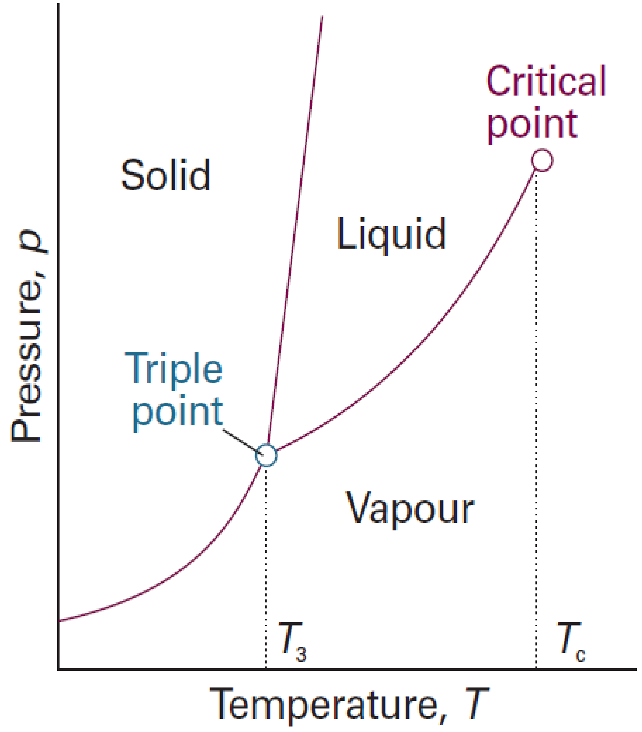
Physical transformations of pure substances

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

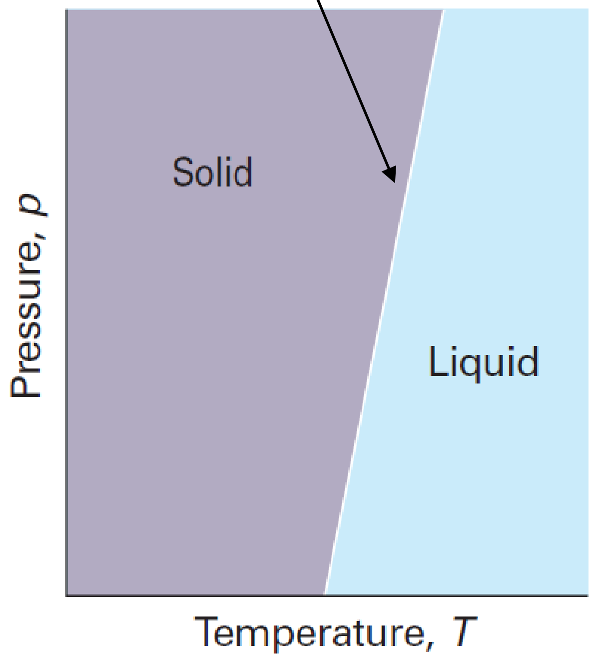
Clapeyron equation

Solid -Liquid ..condensed phases

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$



Slope could be **positive** or **negative**!!



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

$\Delta_{fus} S = S_m(l) - S_m(s)$

$\Delta_{fus} V = V_m(l) - V_m(s)$

$\Delta_{fus} S = \Delta_{fus} H / T_{fus}$

$$\frac{dp}{dT} = \frac{\Delta_{fus} H}{T\Delta_{fus} V}$$

$\Delta_{fus} V$ Could be **positive** or **negative**!!

Physical transformations of pure substances

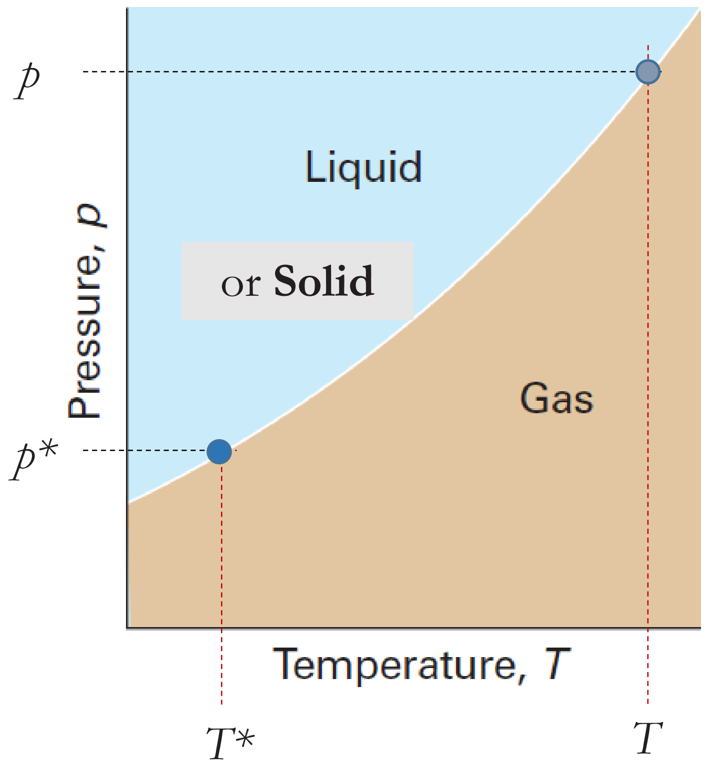
CHAP . #4

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

The liquid–vapour boundary

Clapeyron equation

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



$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

$$\Delta_{vap}V \approx V_m(g)$$

$$V_m(g) = RT/p$$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)}$$

Liquid–Vapour and **Solid–Vapour** phase boundaries

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

Clausius–Clapeyron equation
(liquid (or solid) /gas)

$$\int_{\ln p^*}^{\ln p} d\ln p = \frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{dT}{T^2} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$p = p^* e^{-\chi} \qquad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

Gibbs–Helmholtz equation

$$G = H - TS$$

$$\frac{G}{T} = \frac{H}{T} - S$$

$$\left(\frac{\partial}{T}\frac{G}{T}\right)_p = \frac{H}{T} - dS \rightarrow \left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = -\frac{H}{T^2}$$

$$\left(\frac{\partial}{\partial T}\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2}$$

The Gibbs–Helmholtz equation

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G/T = \Delta H/T - \Delta S$$

$$\left(\frac{\partial}{\partial T}\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2}$$

$$G_m(p) = G_m^{\ominus} + RT\ln\frac{p}{p^{\ominus}}$$

$$\Delta G = -RTln(p)$$

$$\Delta G/T = -Rln(p)$$

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

Physical transformations of pure substances

The liquid–vapour boundary

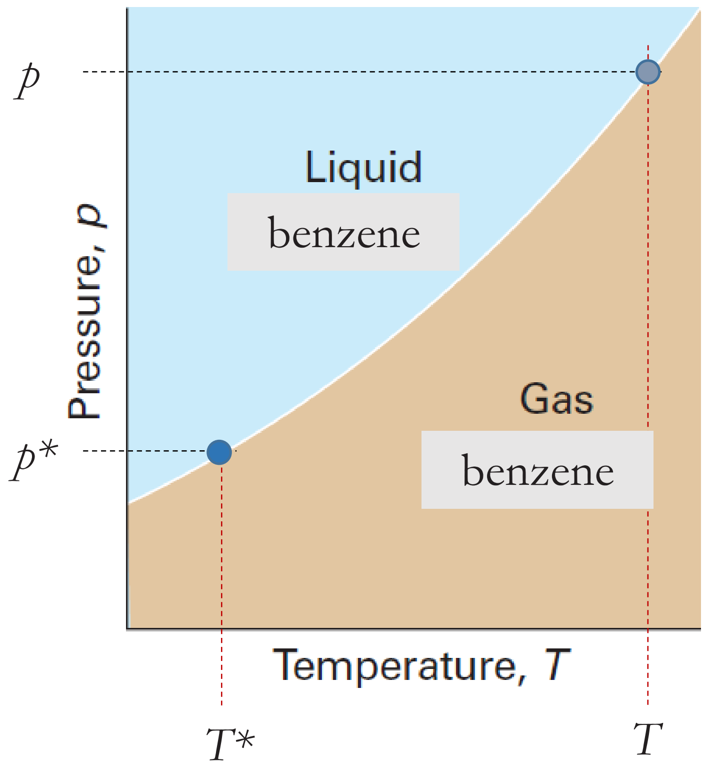


Illustration 4.2 *The effect of temperature on the vapour pressure of a liquid*

Equation 4.12 can be used to estimate the vapour pressure of a liquid at any temperature from its normal boiling point, the temperature at which the vapour pressure is 1.00 atm (101 kPa). Thus, because the normal boiling point of benzene is 80°C (353 K) and (from Table 2.3), $\Delta_{vap}H^{\ominus} = 30.8\ \text{kJ mol}^{-1}$, to calculate the vapour pressure at 20°C (293 K), we write

$$\chi = \frac{3.08\times10^4\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{293\ \text{K}} - \frac{1}{353\ \text{K}}\right) = \frac{3.08\times10^4}{8.3145}\left(\frac{1}{293} - \frac{1}{353}\right)$$

with $p^* = 101$ kPa. (1 atm)

The result is 12 kPa. The experimental value is 10 kPa. (0.1 atm)

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

Clausius–Clapeyron equation
(liquid (or solid) /gas)

$$\int_{\ln p^*}^{\ln p} d\ln p = \frac{\Delta_{vap}H}{R}\int_{T^*}^{T}\frac{dT}{T^2} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$p = p^* e^{-\chi}$$

$$\chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

First & Second ORDER Phase transitions

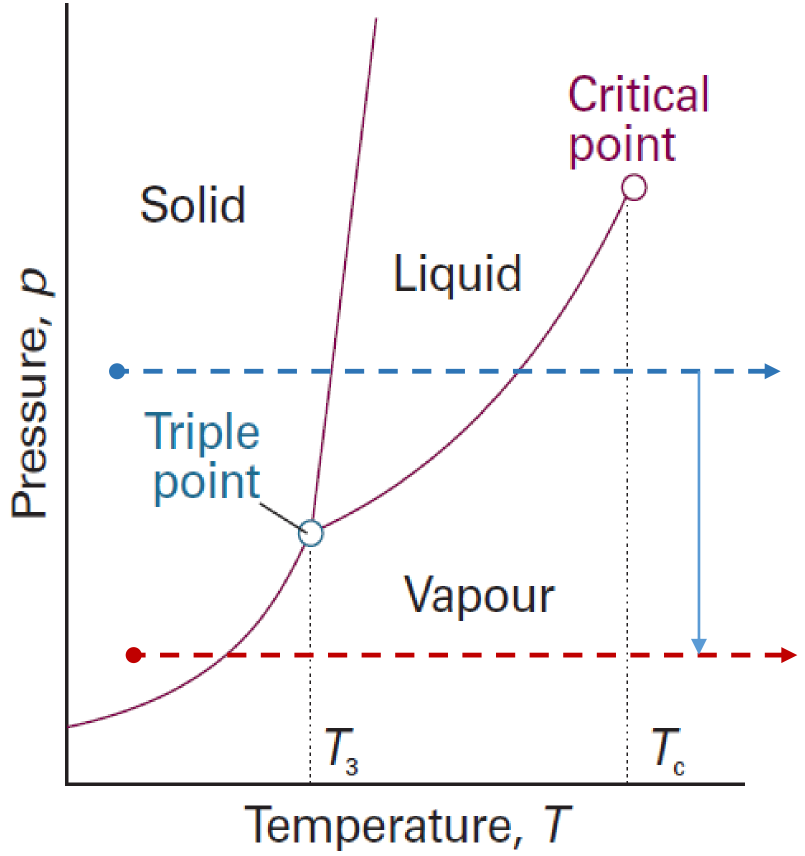
First-order phase transition

A transition for which the first derivative of the μ, with respect to ***temperature is discontinuous***

e.g… fusion, vaporization ..etc

Second-order phase transition the first derivative of μ, with respect to temperature is continuous but its second derivative is discontinuous.

e.g… some ….. solid- solid ..etc



First & Second ORDER Phase transitions

First-order phase

e.g… fusion, vaporization ..etc

Second-order

e.g… some ….. solid- solid ..etc

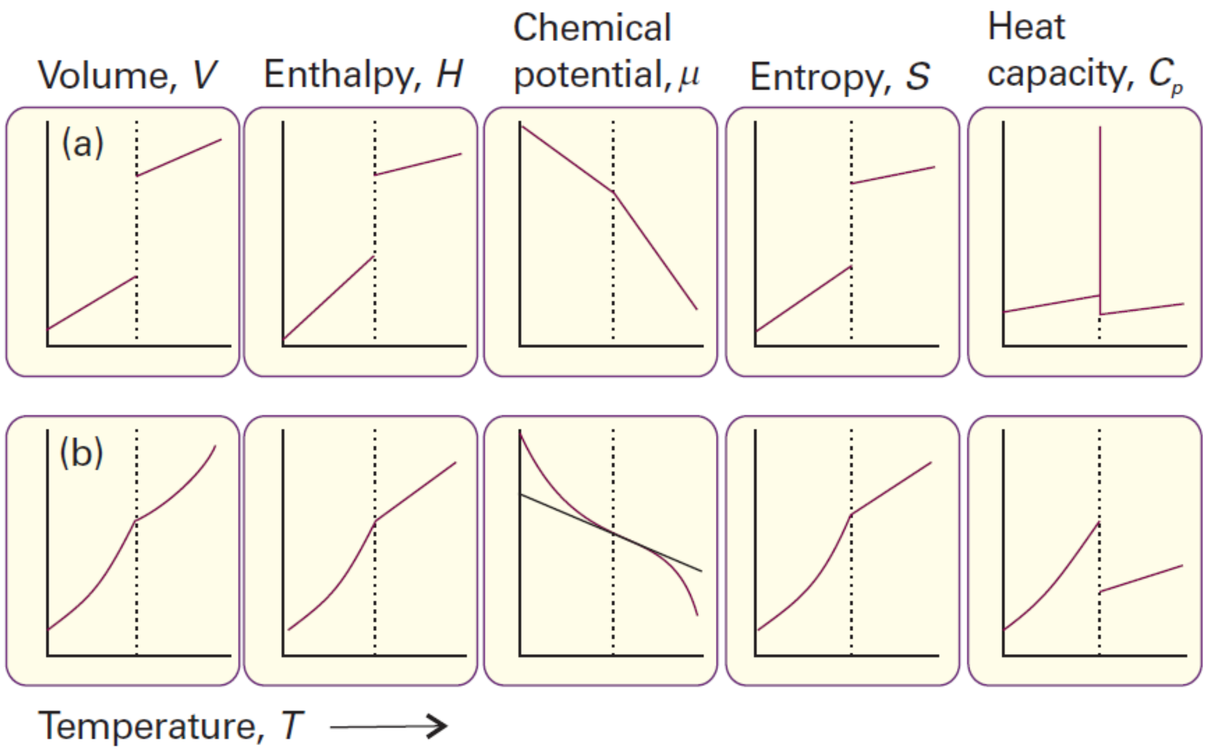


Fig. 4.16 The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

First & Second ORDER Phase transitions

IL, $[Cnmim[PF_6]$