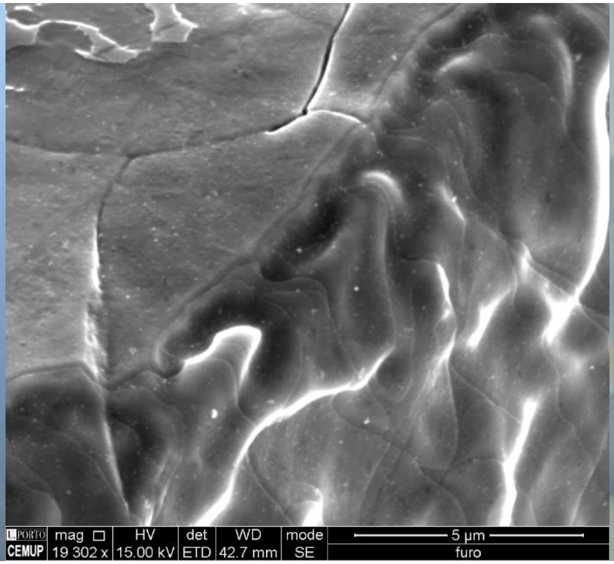
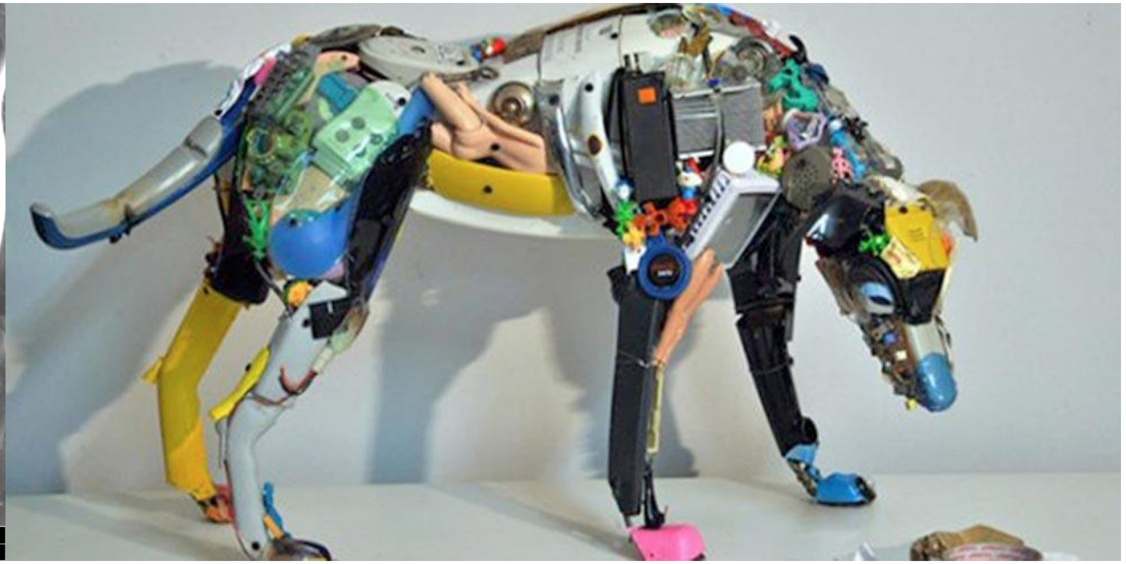
Physical Chemistry

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

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



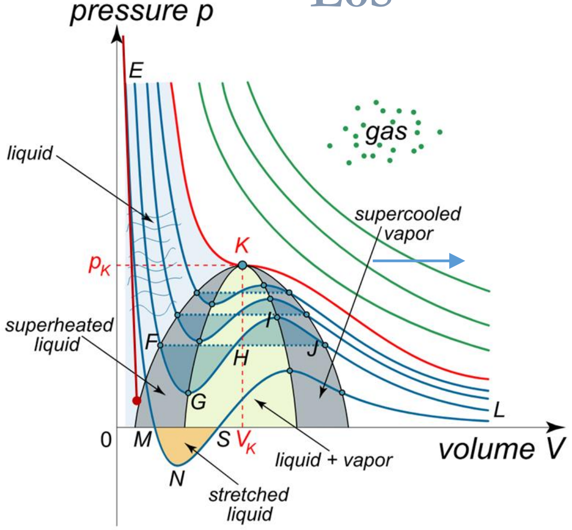


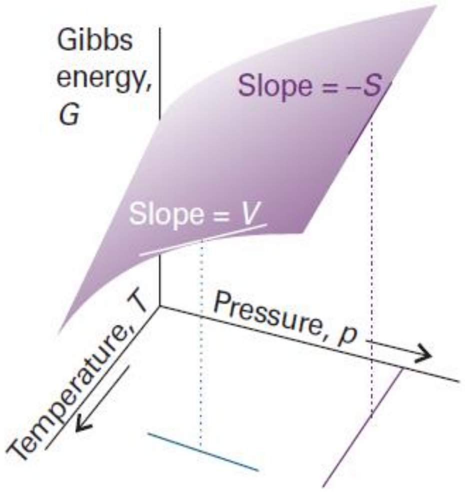
Physical transformations of pure substances

Gibbs energy

$$G = H - TS \rightarrow dG = Vdp - SdT \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

EoS





The **Gibbs–Helmholtz** equation

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

Clapeyron Equation

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

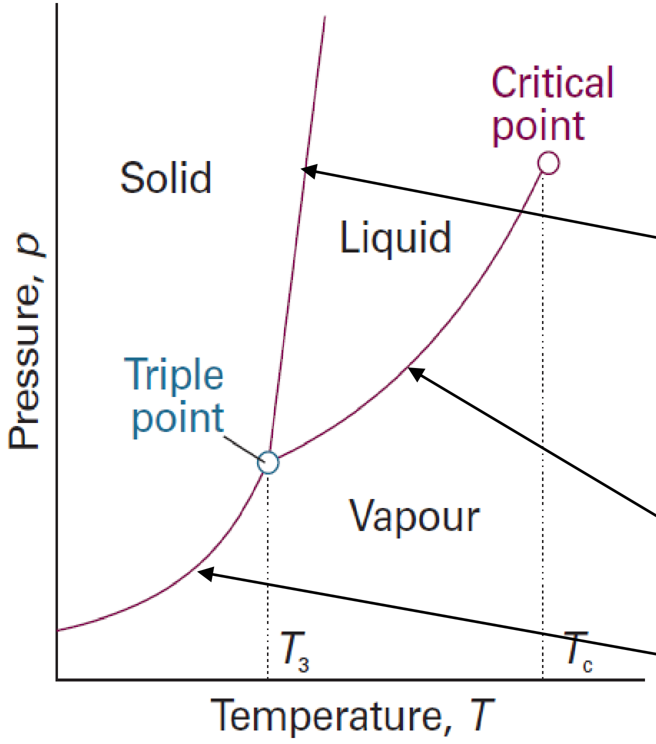
Physical transformations of pure substances

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

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

Clapeyron equation

Shape of the curve!



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

Clausius–Clapeyron

Solid -Liquid ..condensed phases

High slope !! **Vertical line**

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

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

Clausius–Clapeyron equation

(liquid (or solid) /gas)

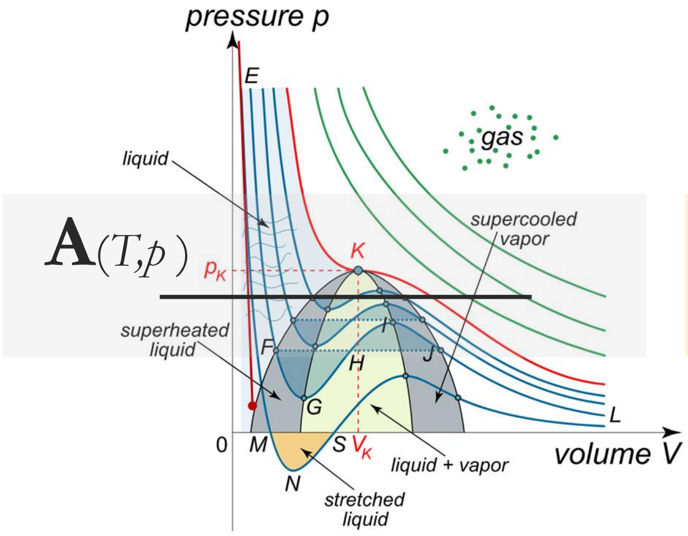
Exponential dependence

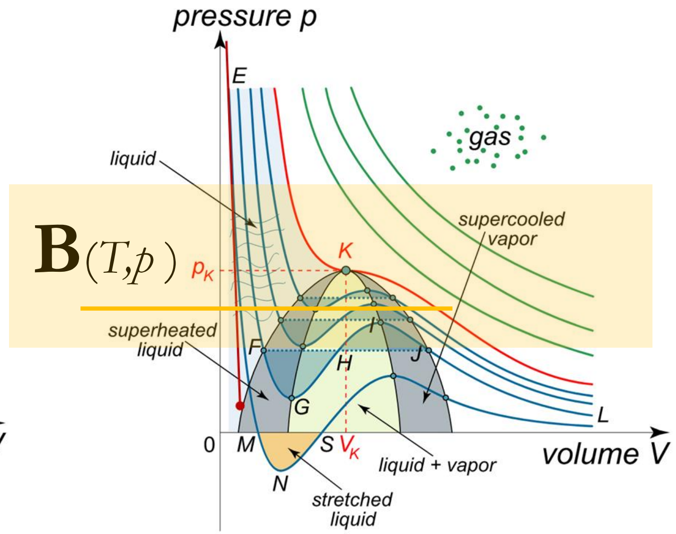
The thermodynamic description of mixtures

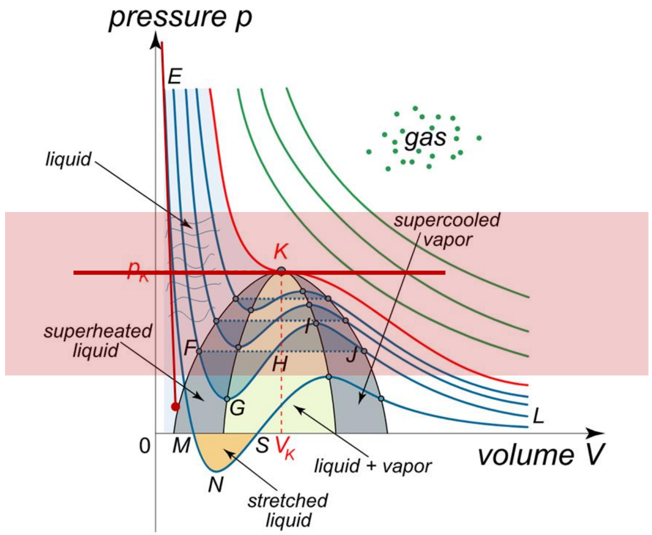
EoS .. **A**

EoS .. **B**

EoS .. **A+B** $(T,p,\ n_A + n_B)$





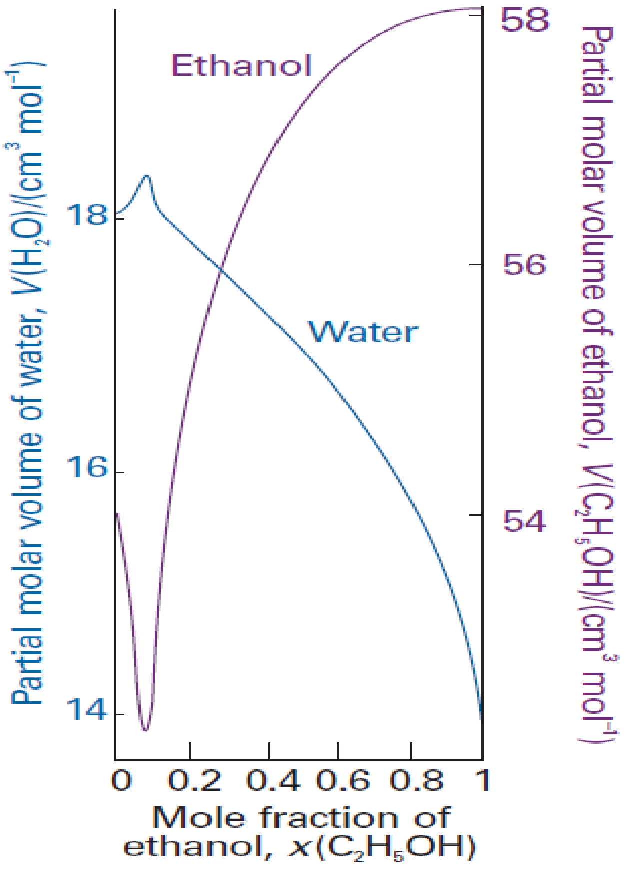


Water, n_A

Ethanol, n

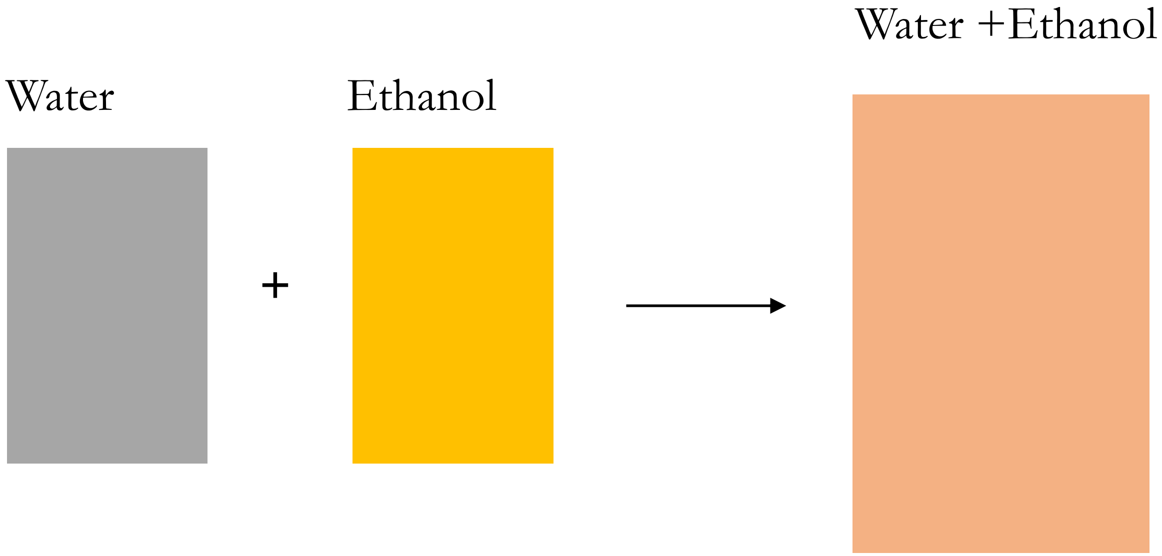
(T,p) **A** + **B** → **A + B** Water +Ethanol

Partial molar quantities

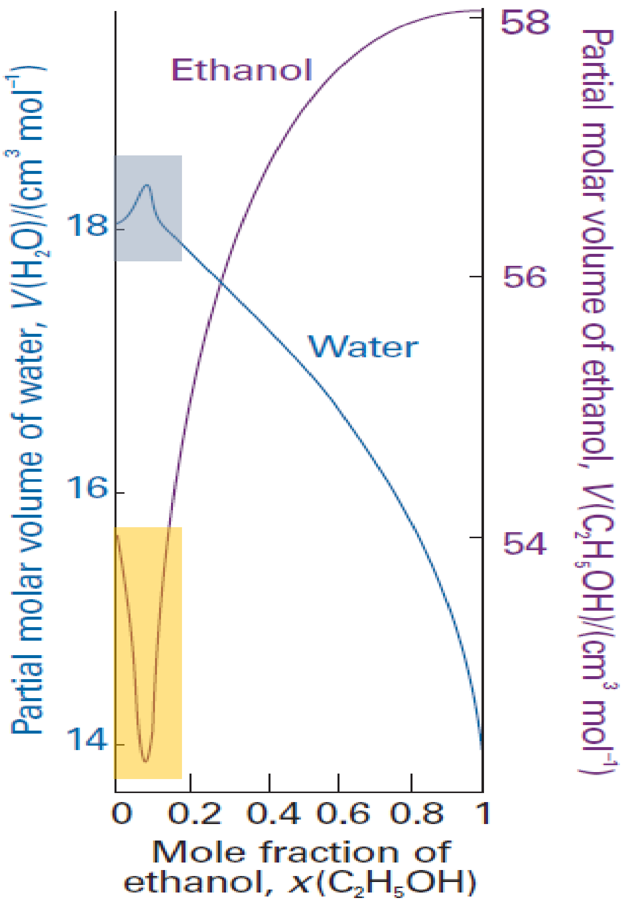


Partial molar volume of a substance A in a mixture
volume per mole of A added to a large volume of the mixture.

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$$



Partial molar quantities



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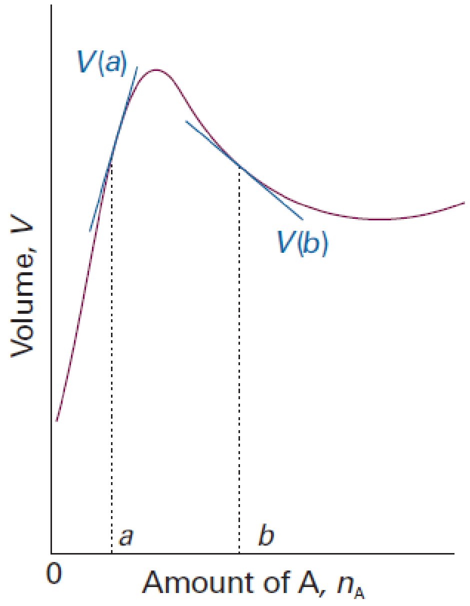


$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B$$

$$V_A dn_A + V_B dn_B$$

A B

Partial molar quantities

Partial molar volume of a substance A in a mixture
volume per mole of A added to a large volume of the mixture.

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$$

Change of de **volume**

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B$$

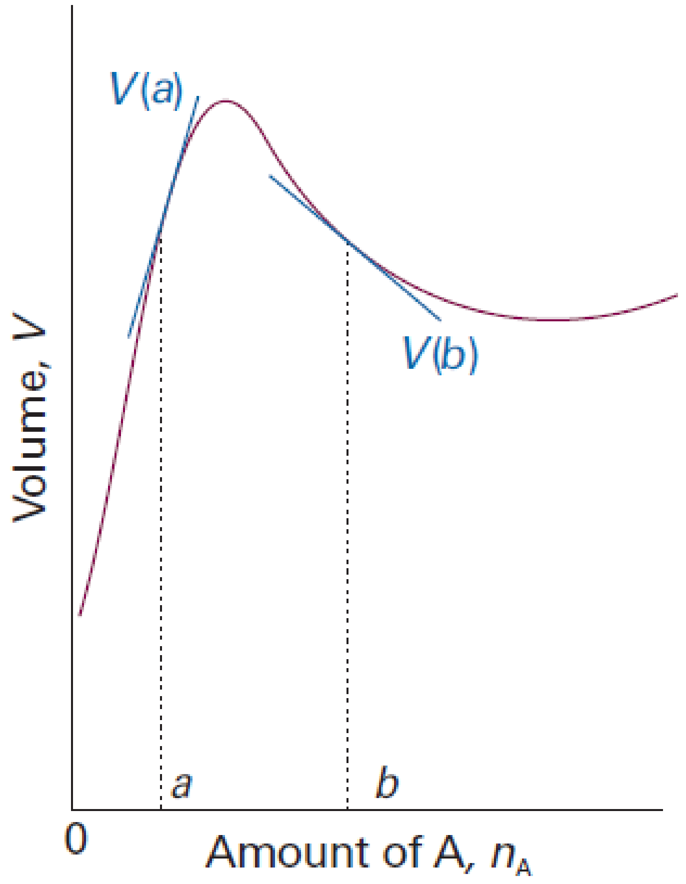
Total **Volume** of mixture

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B$$

$$= V_A n_A + V_B n_B$$

A B

hypothetical
Volume of A and B



Partial molar quantities

Partial molar volume of a substance A in a mixture
volume per mole of A added to a large volume of the mixture.

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$$

Minimum @ ~ 20% mass

A polynomial fit to measurements of the total volume of a water/ethanol mixture at 25°C that contains 1.000 kg of water is

$$v = 1002.93 + 54.6664x - 0.363\,94x^2 + 0.028\,256x^3$$

where $v = V/\text{cm}^3$, $x = n_E/\text{mol}$, and n_E is the amount of CH_3CH_2OH present. The partial molar volume of ethanol, V_E, is therefore

$$V_E = \left(\frac{\partial V}{\partial n_E}\right)_{p,T,n_W} = \left(\frac{\partial(V/\text{cm}^3)}{\partial(n_E/\text{mol})}\right)_{p,T,n_W} \text{cm}^3\,\text{mol}^{-1} = \left(\frac{\partial v}{\partial x}\right)_{p,T,n_W} \text{cm}^3\,\text{mol}^{-1}$$

Then, because

$$\frac{dv}{dx} = 54.6664 - 2(0.36394)x + 3(0.028256)x^2$$

we can conclude that

$$V_E/(\text{cm}^3\,\text{mol}^{-1}) = 54.6664 - 0.72788x + 0.084768x^2$$

Figure 5.3 is a graph of this function.

Parabolic Funtion!!

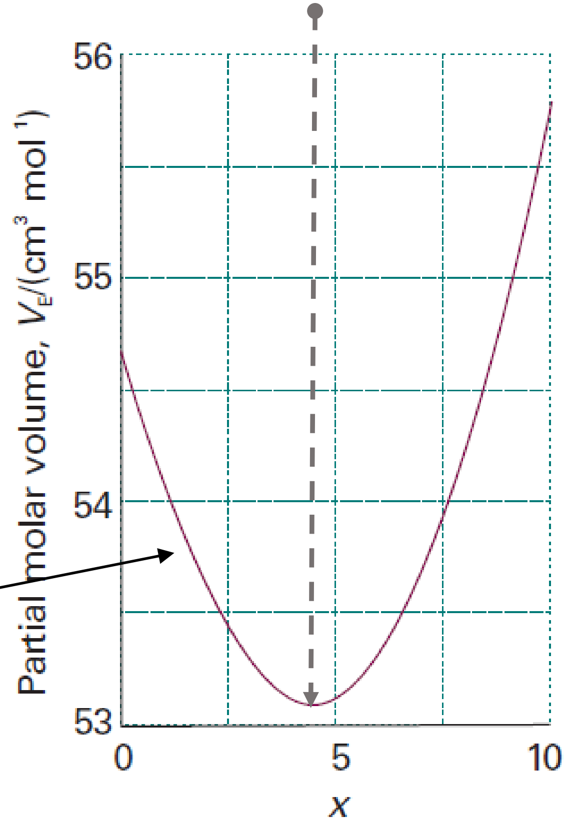


Fig. 5.3 The partial molar volume of ethanol as expressed by the polynomial in

Partial molar quantities

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$$

State 1

$\boldsymbol{V}(T, p, n_i, n_j)$

volume

→

State 2

$\boldsymbol{V}(T, p, n_i, n_j) + \mathbf{dV}$

volume

By changing
T, p, n

Change of
de **volume**

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,T,n_i,n_j} . dT + \left(\frac{\partial V}{\partial p}\right)_{p,T,n_i,n_j} . dp + \left(\frac{\partial V}{\partial ni}\right)_{p,T,n_i} . dn_i$$

Temperature
effect
(Thermal Expansion)

Pressure
effect
(Isothermal compressibility)

Composition
effect

Partial molar **Gibbs** energies

Partial molar quantity can be extended to any extensive state function

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

$$G = n_A\mu_A + n_B\mu_B$$

Total **Volume** of mixture

$$V_A n_A + V_B n_B$$

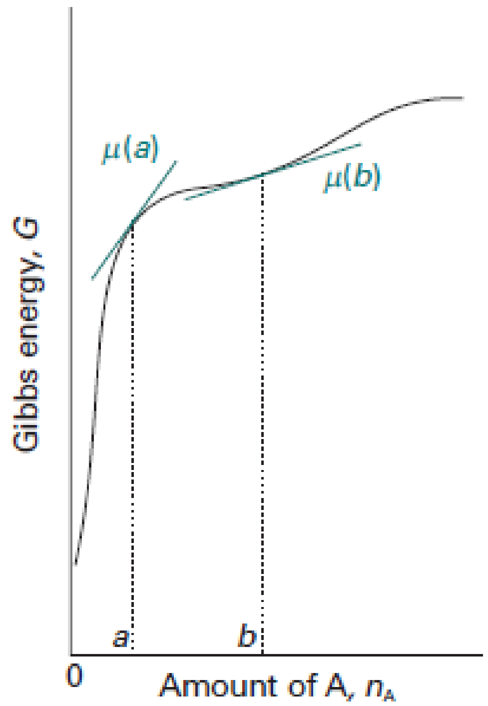


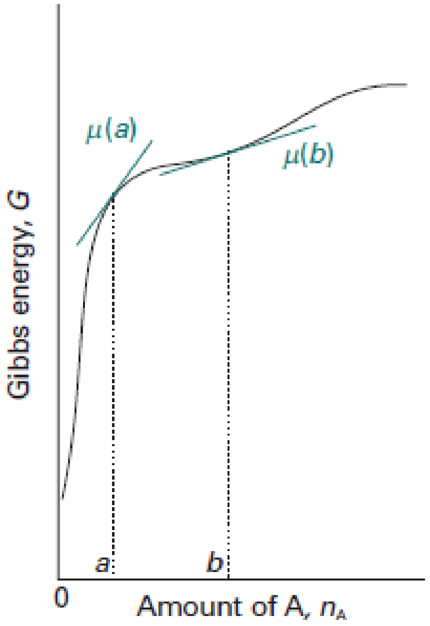
Fig. 5.4 The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition, as shown for the two values at *a* and *b*. In this case, both chemical potentials are positive.

Partial molar **Gibbs** energies

$$G = U + pV - TS$$

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

$$G = n_A\mu_A + n_B\mu_B$$



Change of **Gibbs** energies

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$$

Pressure effect

Temperature effect

Composition effect

Partial molar quantities

$$G = U + pV - TS$$

Gibbs–Duhem equation

$$G = n_A\mu_A + n_B\mu_B$$

chemical potential is the contribution of that substance to the **total Gibbs energy** of the mixture

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

→ Because ***G*** **is a state function**

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots$$

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$\sum_J n_J d\mu_J = 0$$

→

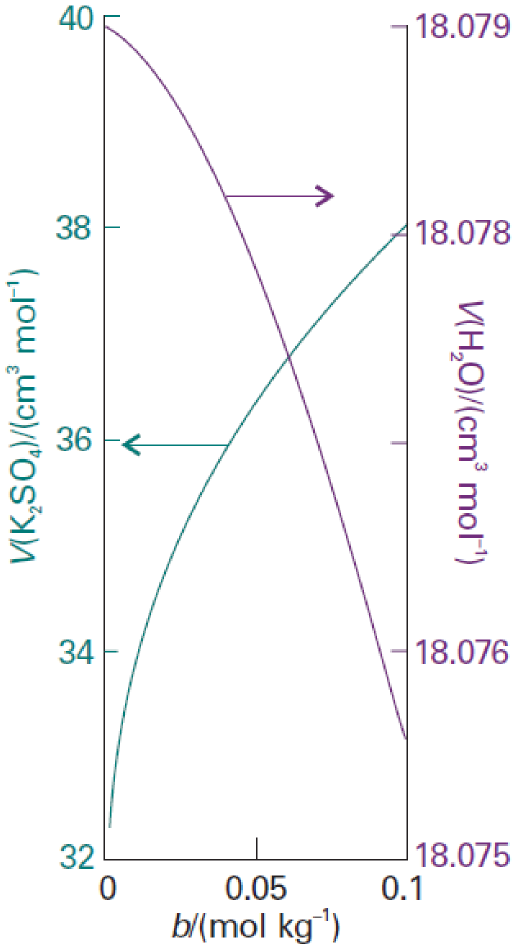
$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Gibbs–Duhem equation |
the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

Gibbs–Duhem equation

$$G = n_A\mu_A + n_B\mu_B$$

$$\sum_J n_J \mathrm{d}\mu_J = 0 \quad \rightarrow \quad \mathrm{d}\mu_B = -\frac{n_A}{n_B}\mathrm{d}\mu_A$$



Gibbs–Duhem equation |
the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

Applies to all partial molar quantities !!!

Gibbs–Duhem equation

$$\sum_J n_J d\mu_J = 0$$

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Applies to all partial molar quantities !!!

For the partial **molar volume:**

$$n_A dV_A + n_B dV_B = 0.$$

$$dv_A = -(n_B/n_A)dv_B$$