Chemical potential and internal energy

$$G = U + pV - TS$$

$$U = -pV + TS + G$$

$$dU = -pdV - Vdp + SdT + TdS + dG$$

$$= -pdV - Vdp + SdT + TdS$$
$$+ (Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots)$$

$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \cdots$$

at constant volume and entropy,

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

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

$$\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'}$$

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

Gibbs-Duhem equation

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

μ_A and μ_B are the chemical potentials of components A and B, representing the change in Gibbs free energy per mole of each component.

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- The Gibbs free energy is an extensive property, meaning it depends on the amount of substance present.
- The total Gibbs free energy of the system is the sum of the contributions from each component.

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

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

At constant pressure and temperature:

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At constant pressure and temperature

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

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

In a binary mixture, the chemical potentials of the components are not independent: a change in μ_A directly influences μ_B. (at constant T and P)

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

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

$$\sum_{i=1}^{N} n_i d\mu_i = 0$$

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amount of substance of component i

For a multi-component system

$$\sum_{i=1}^{N} n_i d\mu_i = 0$$

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chemical potential of component i
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number of components in the system

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Changes in chemical potentials of the components are related to each other.

$$\sum_{i=1}^{N} n_i d\mu_i = 0$$

Gibbs–Duhem equation

chemical potential of component i
(partial molar Gibbs energy)

Gibbs-Duhem equation

$$\sum_{J} n_J \mathrm{d}V_J = 0$$

Gibbs-Duhem equation

partial molar volume

↑

$$\sum_J n_J \mathrm{d}V_J = 0$$

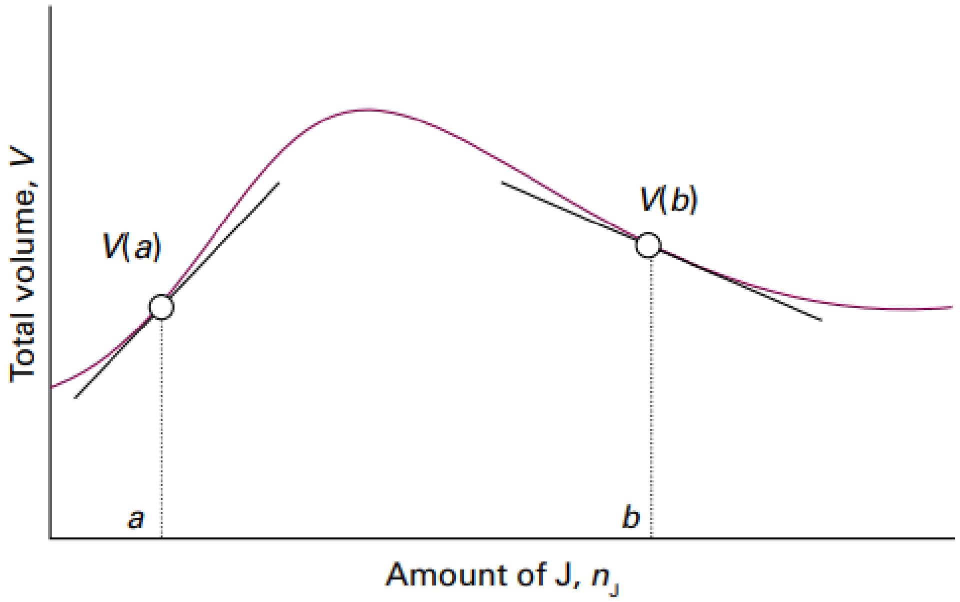
Gibbs-Duhem equation

partial molar volume

$$\sum_J n_J \mathrm{d}V_J = 0$$

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

change in volume per mole of J added to a large volume of the mixture



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For a binary mixture,

$$\mathrm{d}V_B = -\frac{n_A}{n_B}\mathrm{d}V_A$$

The larger the molar fraction of A,
the system is highly sensitive to its changes

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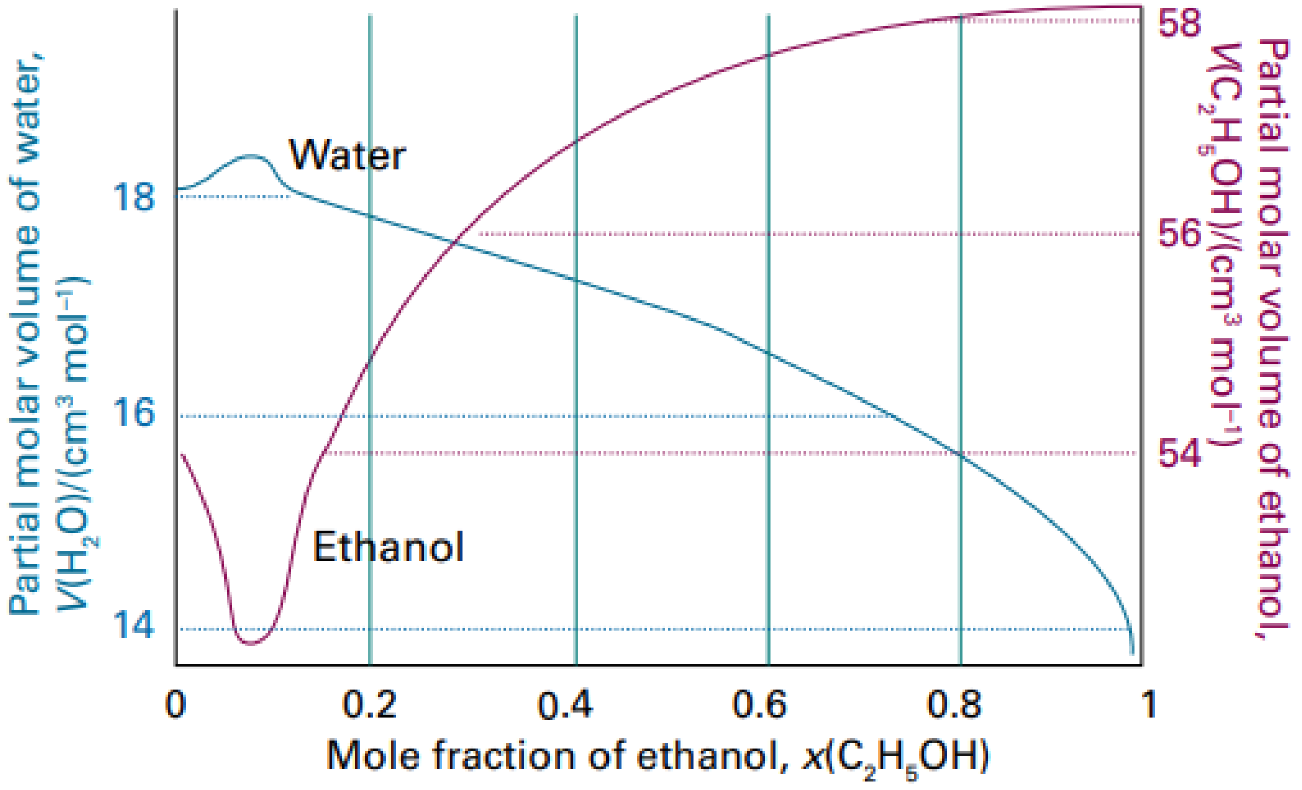
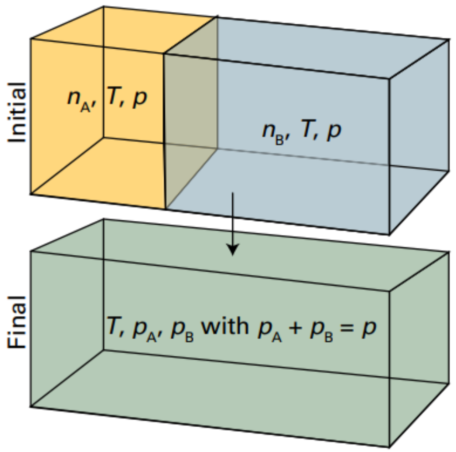


Thermodynamics of mixing perfect gases



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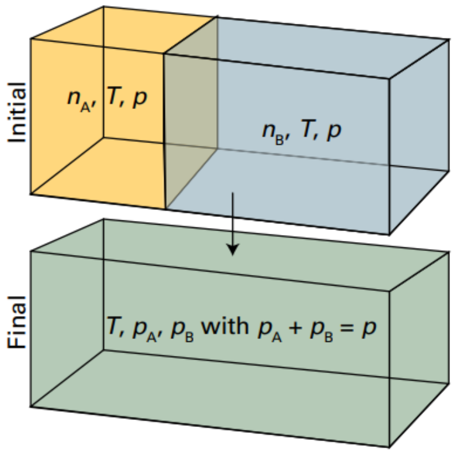

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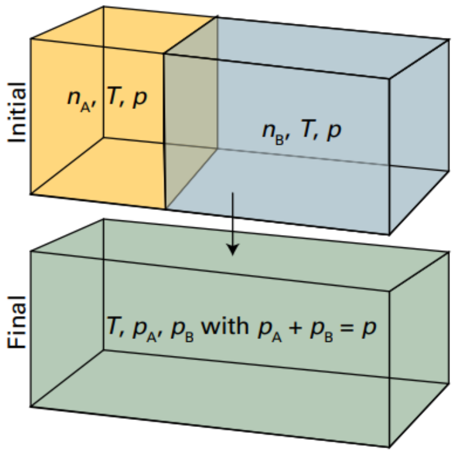

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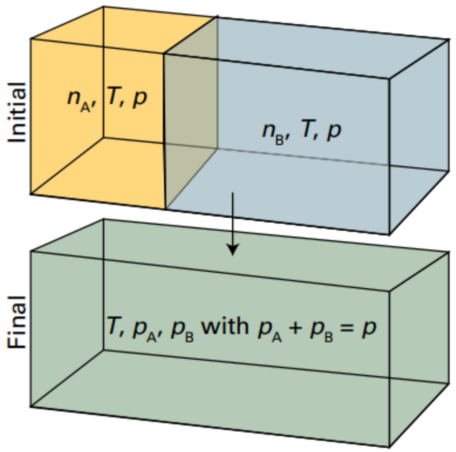

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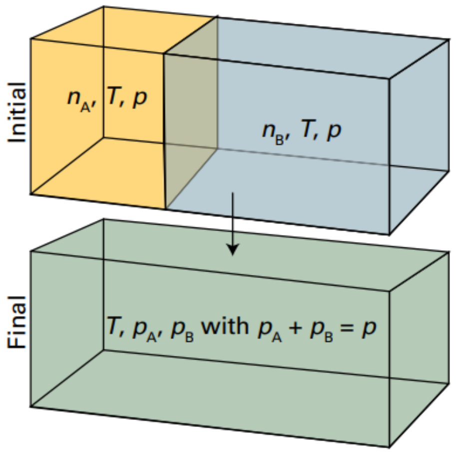

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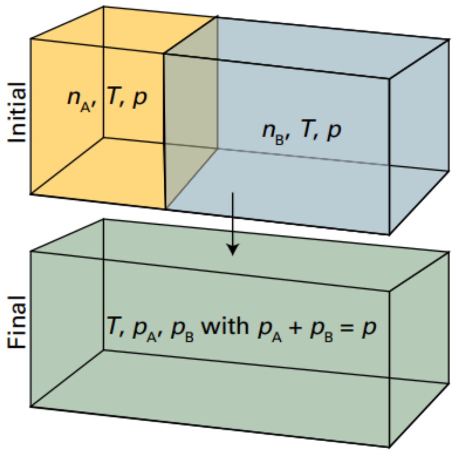

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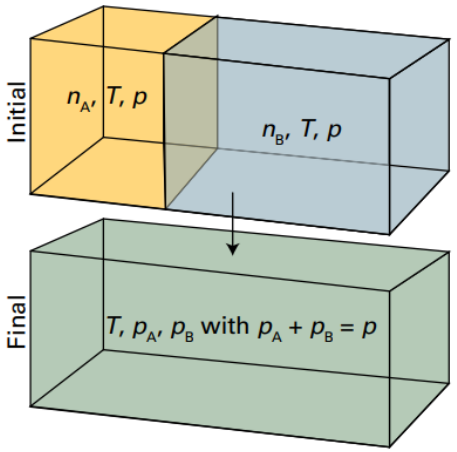

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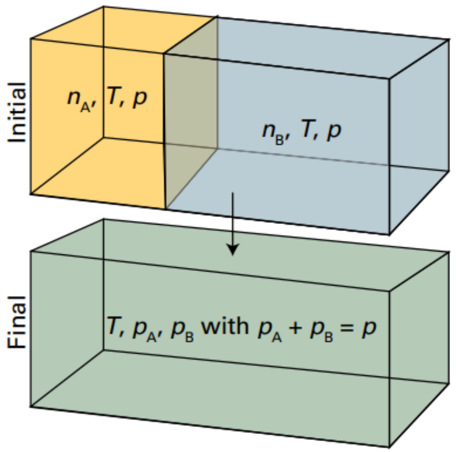

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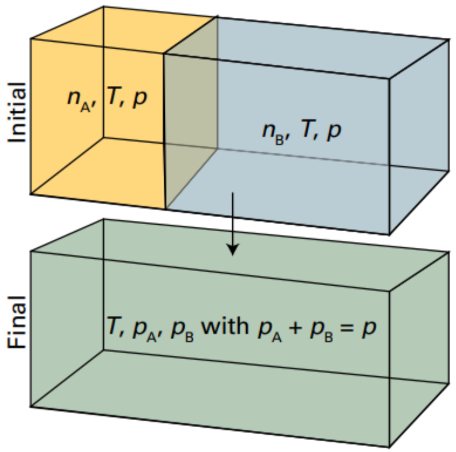
Partial pressure: the pressure exerted by a single component of a mixture if it alone occupied the entire volume of the mixture (at the same temperature)

Thermodynamics of mixing perfect gases



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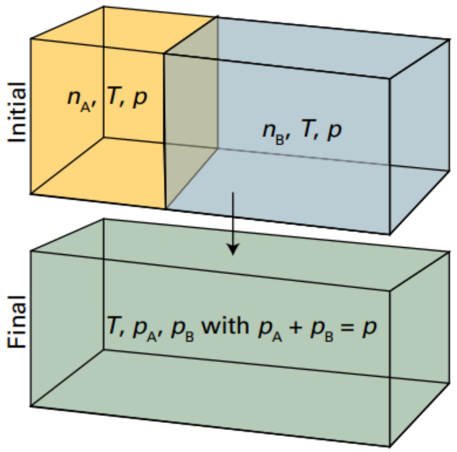

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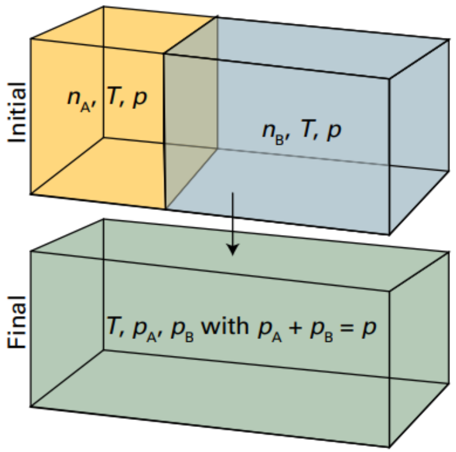

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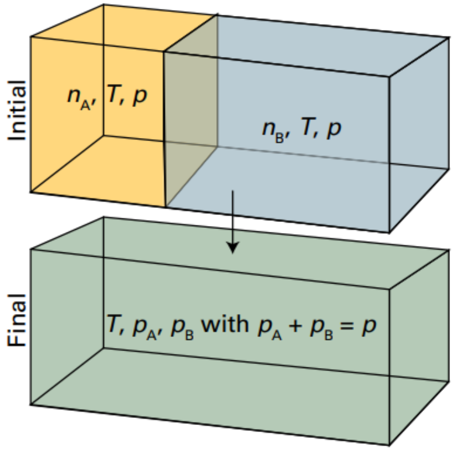
Gibbs energy of mixing [perfect gas]

Thermodynamics of mixing perfect gases



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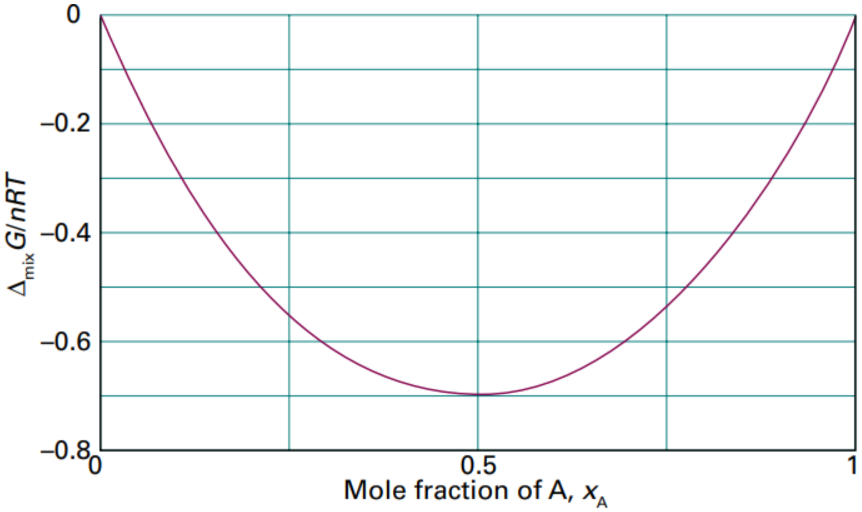

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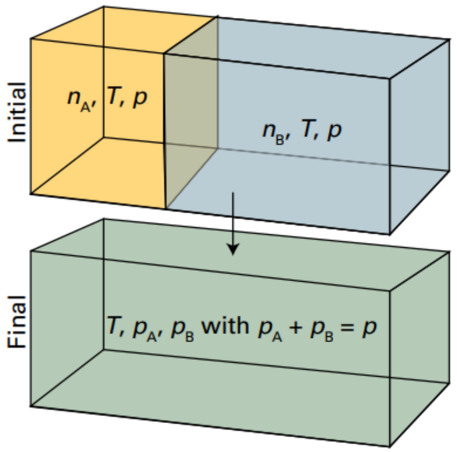

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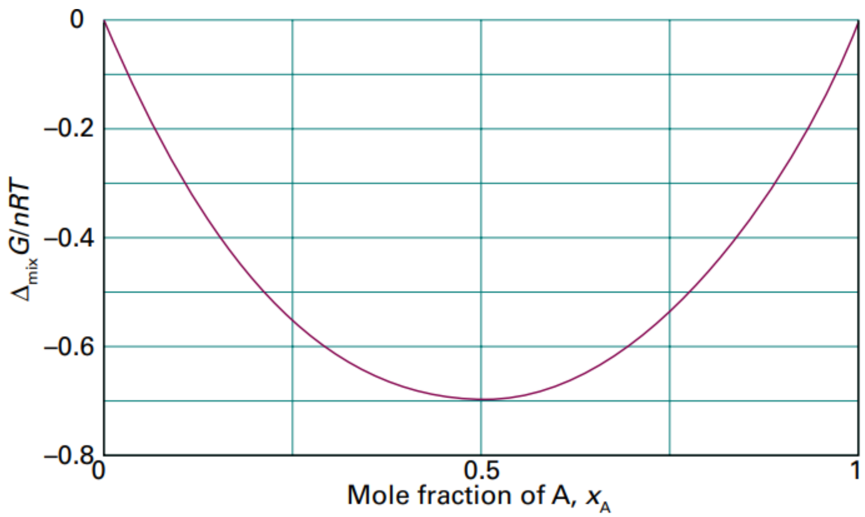

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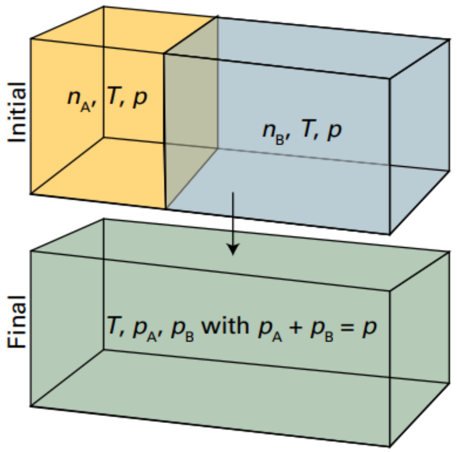

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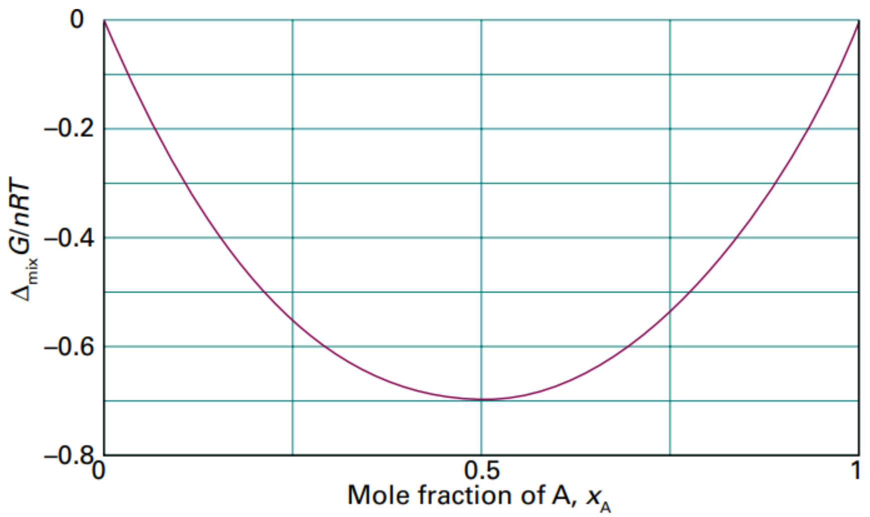

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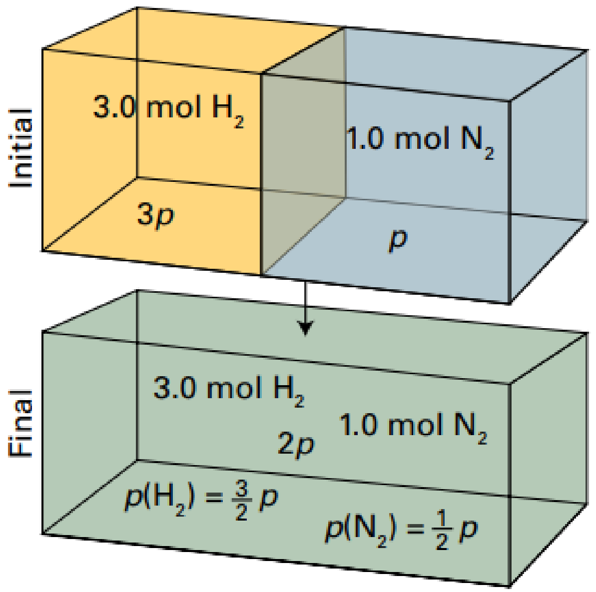
Gibbs energy of mixing [perfect gas]

Perfect gases mix spontaneously in all proportions!

Example

A container is divided into two equal compartments One contains 3.0 mol $H_2(g)$ at 25 °C; the other contains 1.0 mol $N_2(g)$ at 25 °C. Calculate the Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.



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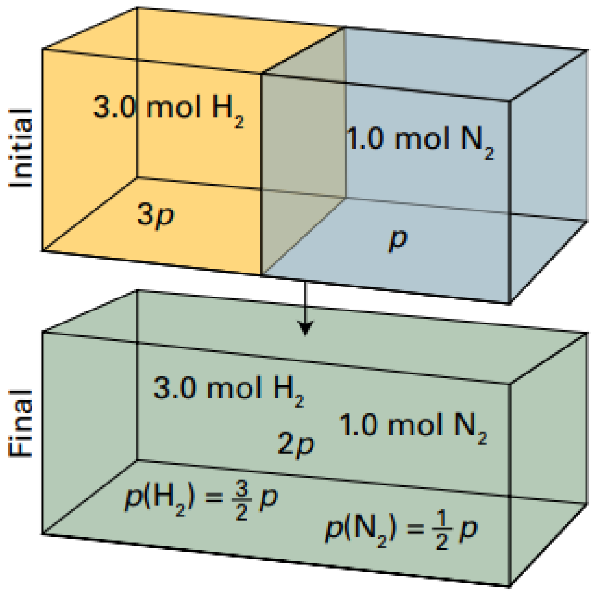

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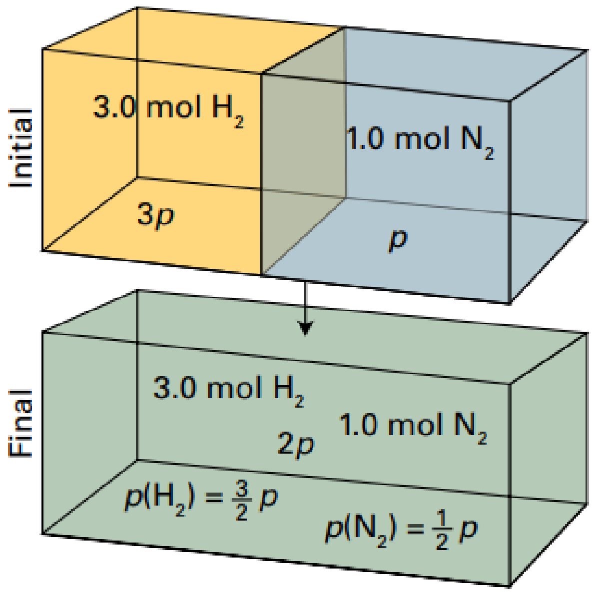

$$G_i = (3.0\,\mathrm{mol})\{\mu^{\ominus}(H_2) + RT\ln 3p\}$$
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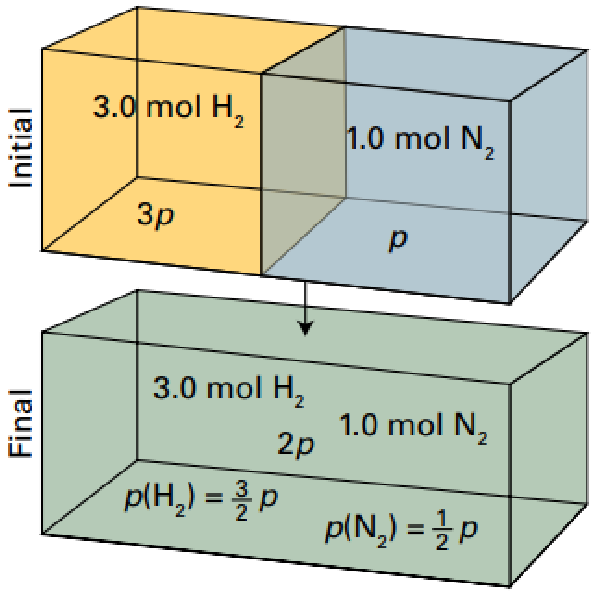

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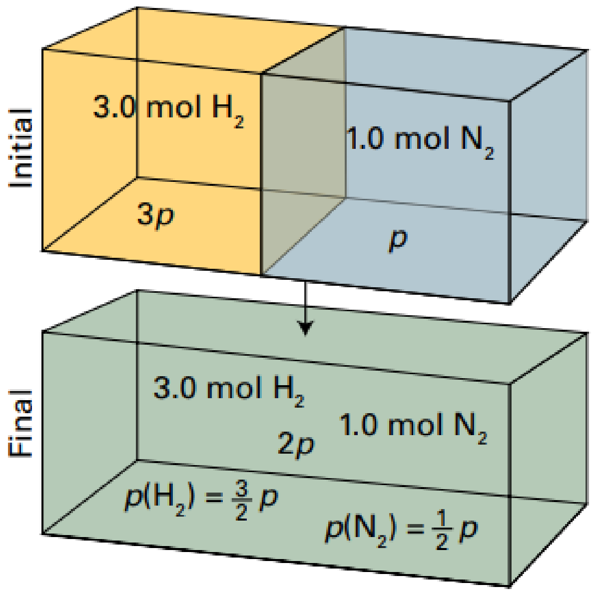

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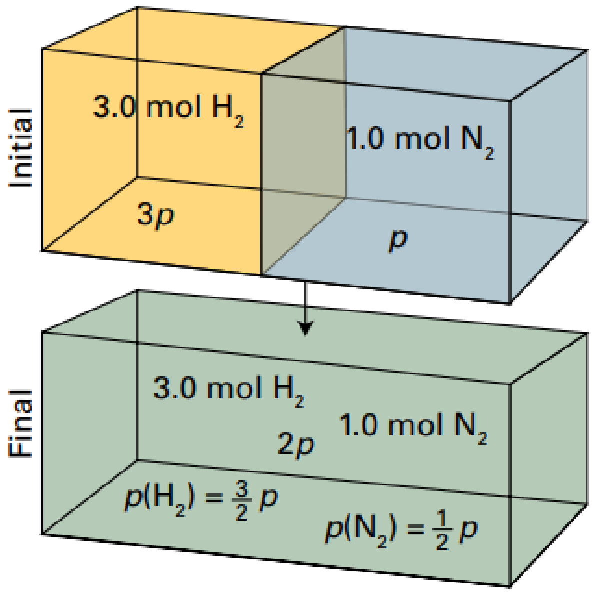

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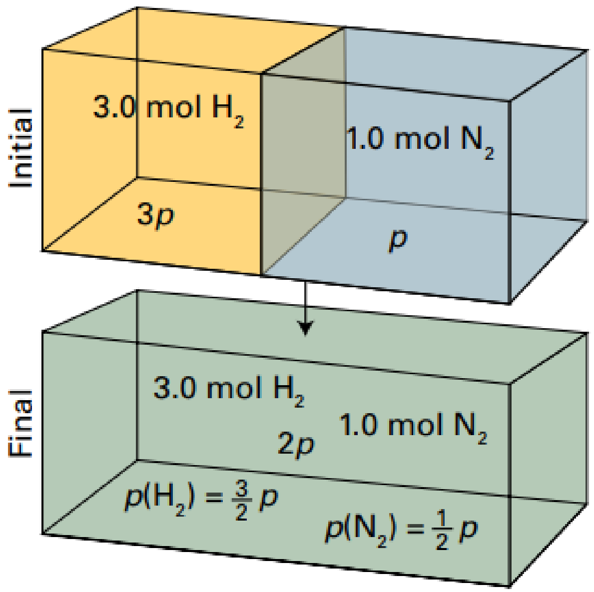

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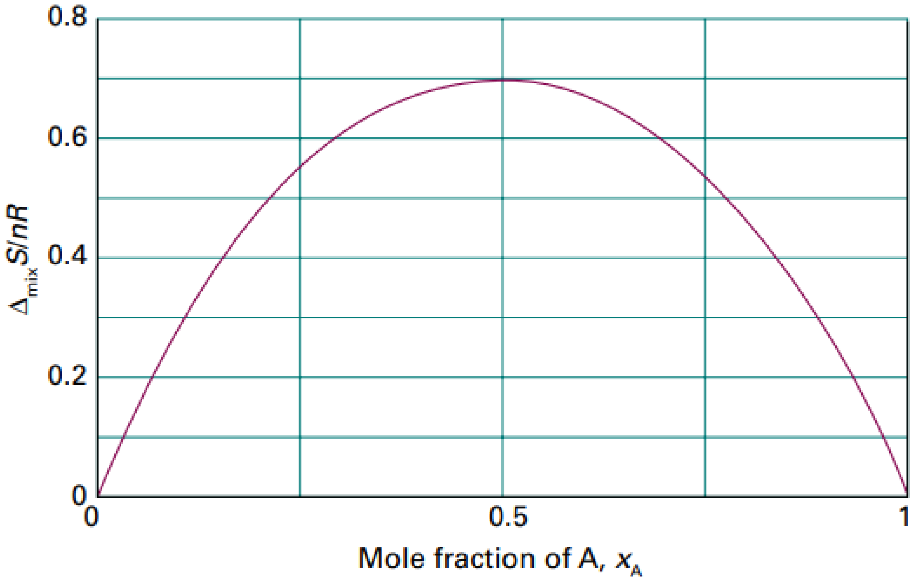

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