CHEM3520 - Spring 2023

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 16: Molecules in motion

Focus 17: Chemical kinetics

Focus 18: Reaction dynamics

Focus 5: Simple mixtures

- TD description of mixtures
- Properties of solutions
- Phase diagrams of binary systems
- Phase diagrams of ternary systems
- Thermodynamic activity

Partial molar quantities

Partial molar quantities are fundamental in understanding the thermodynamic behavior of mixtures

Contribution that a component of a mixture makes to the total property of a sample.

Partial molar quantities

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

Mathematical Representation

conditions could be different

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Mathematical Representation

conditions could be different

The partial molar quantity of a component in a mixture is the change in the total extensive property of the mixture when an infinitesimal amount of that component is added to the mixture, with all other components held constant

Partial molar volume

The partial molar volume of substance j in a mixture is the change in volume per mole of j added to the mixture.

Provide insight into how the addition of a particular component affects the overall volume of the mixture

Partial molar volume

The partial molar volume of substance J in a mixture is the change in volume per mole of J added to a large volume of the mixture.

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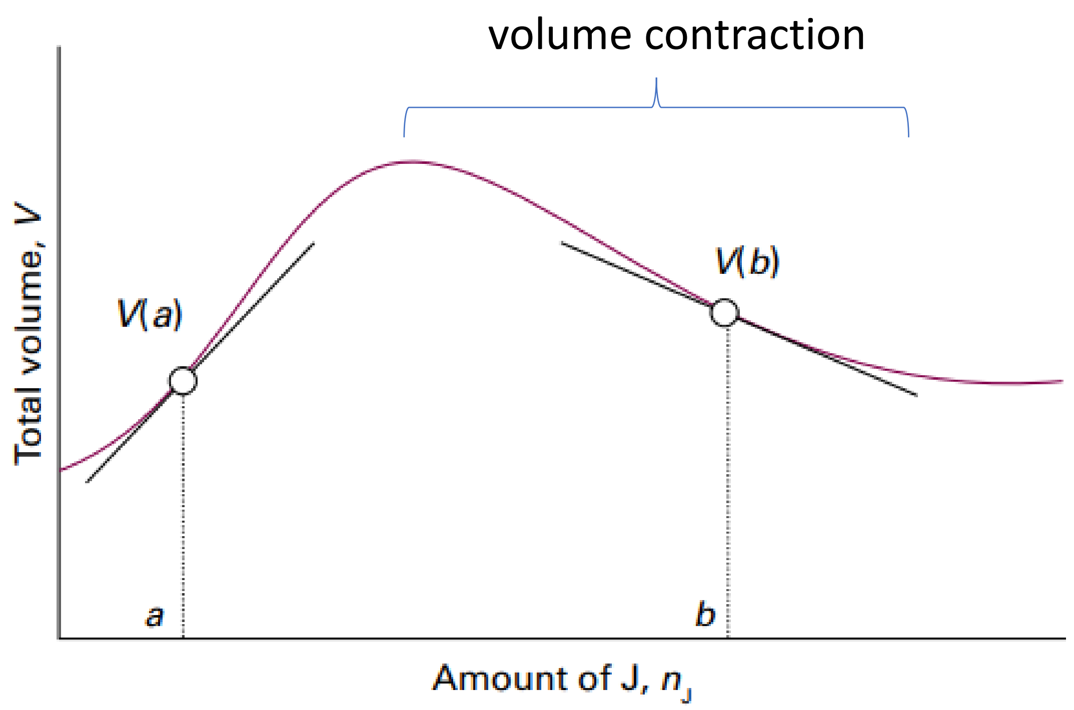

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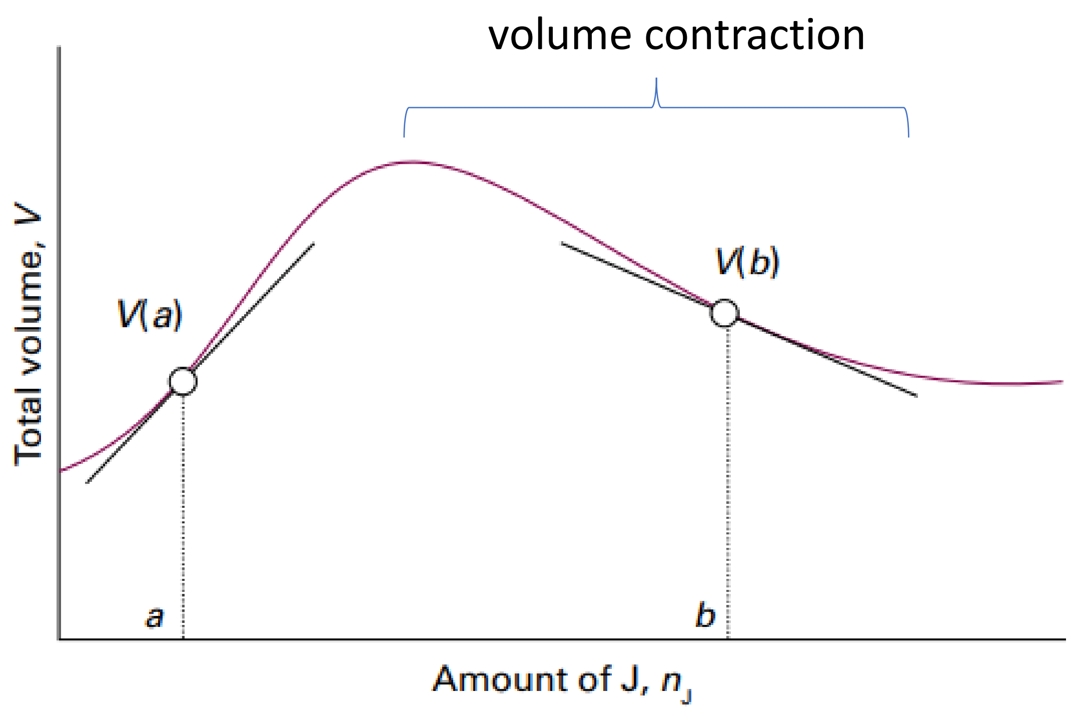

- V_J depends on the relative composition
- Could be negative.

Partial molar volume

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

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Partial molar volume

$$\mathrm{d}V = \left(\frac{\partial V}{\partial n_\mathrm{A}}\right)_{p,T,n_\mathrm{B}} \mathrm{d}n_\mathrm{A} + \left(\frac{\partial V}{\partial n_\mathrm{B}}\right)_{p,T,n_\mathrm{A}} \mathrm{d}n_\mathrm{B}$$

$$= V_\mathrm{A}\mathrm{d}n_\mathrm{A} + V_\mathrm{B}\mathrm{d}n_\mathrm{B}$$

$$V = \int_0^{n_\mathrm{A}} V_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \int_0^{n_\mathrm{B}} V_\mathrm{B}\,\mathrm{d}n_\mathrm{B}$$

Partial molar volume

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If A:B ratio constant

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

If a mixture preserves constant relative composition, the partial molar volumes V_A and V_B are constant.

Partial molar volume

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Chemical potential of a mixture

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- Then, chemical potential μ_j of a component is defined as:

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Partial molar Gibbs energies

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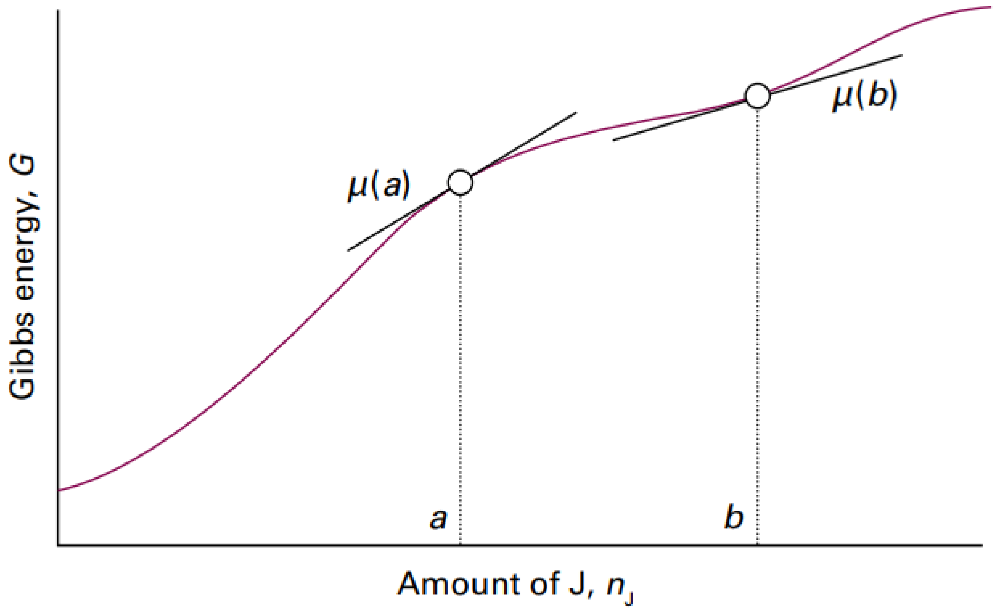

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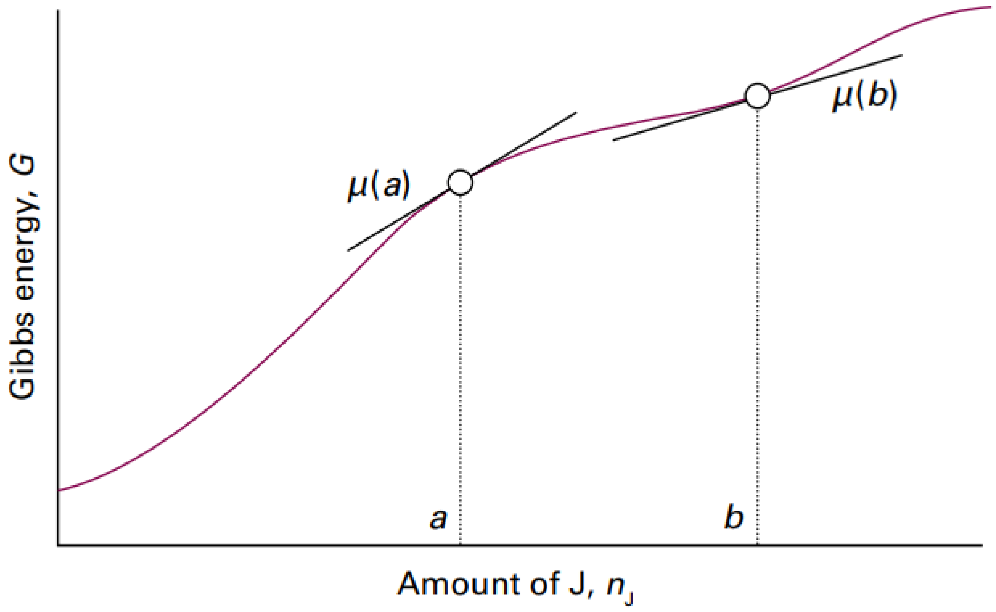

$$G = n_A\mu_A + n_B\mu_B$$

change in composition contributes to the total Gibbs energy

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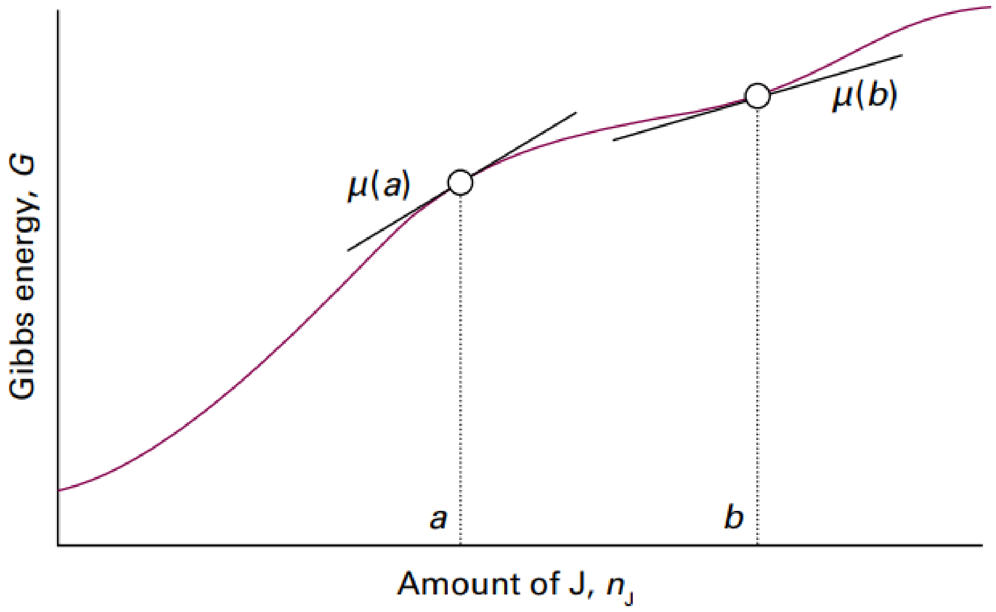

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$$dG = Vdp - SdT$$

In a constant composition system

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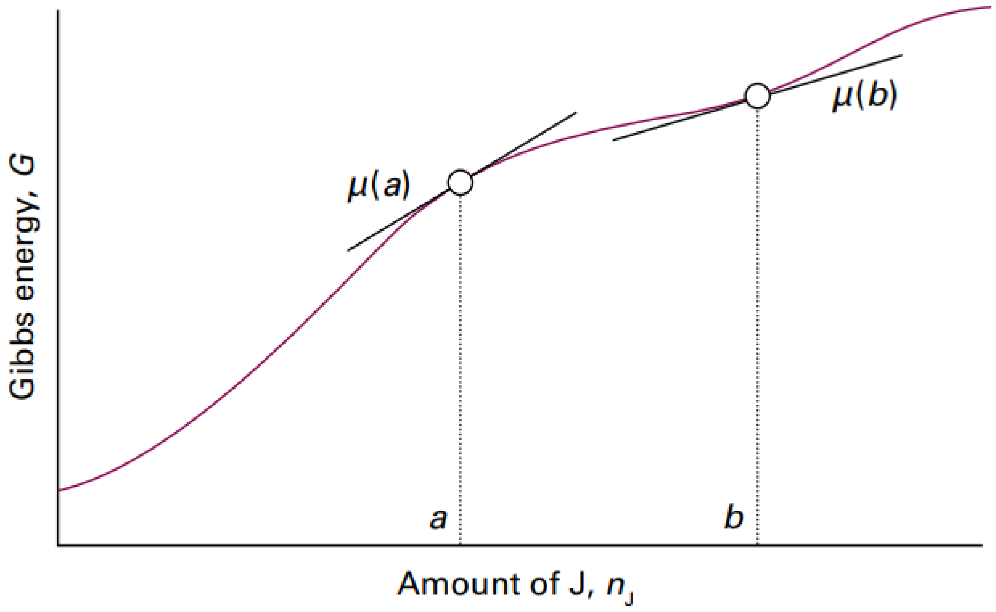

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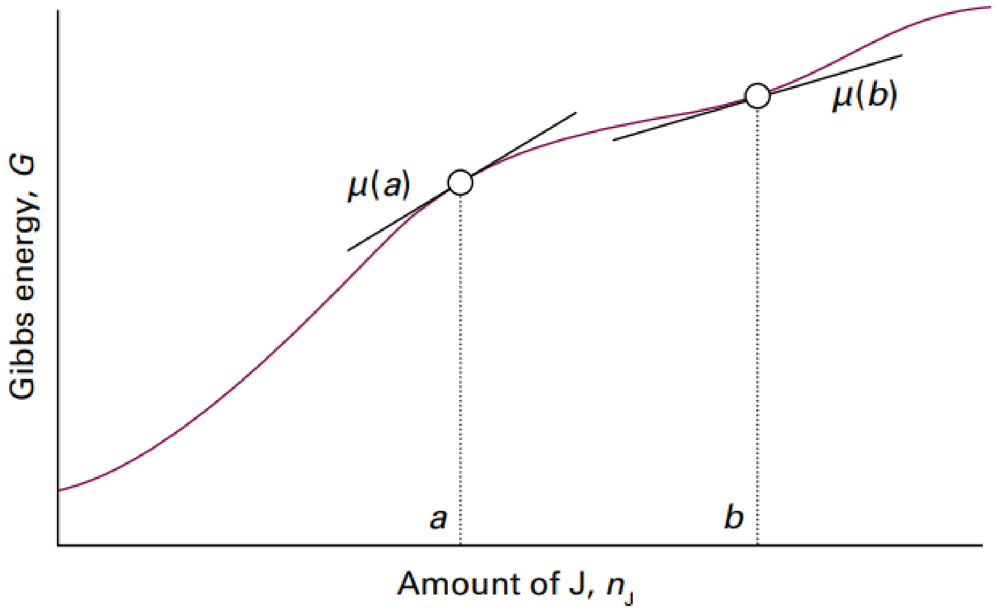

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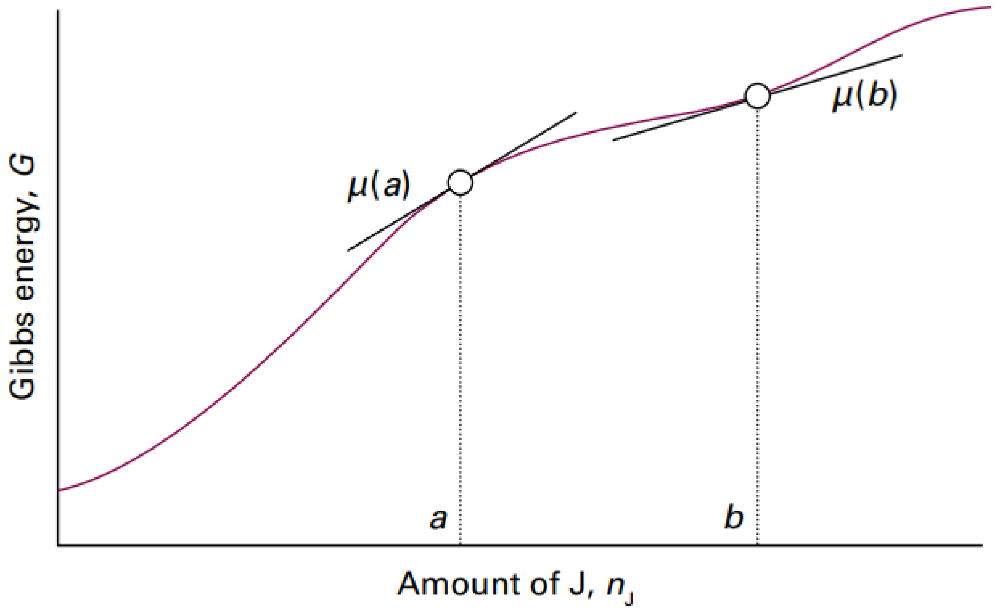

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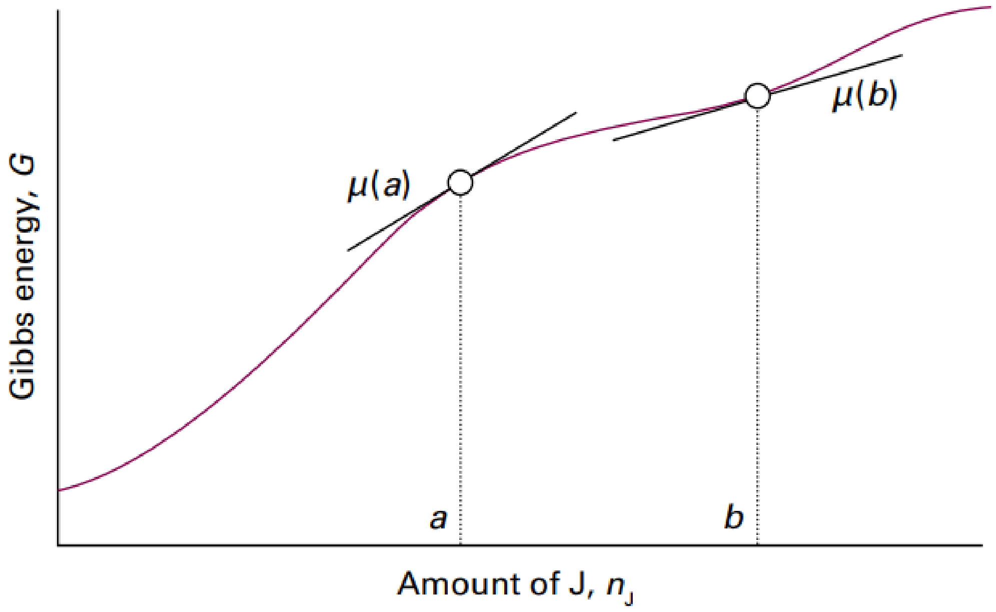

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↑

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$$+ (V\mathrm{d}p - S\mathrm{d}T + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + \cdots)$$

$$= -p\mathrm{d}V + T\mathrm{d}S + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + \cdots$$

A more generalized form of the equation:
dU = T dS- P dV

Chemical potential and internal energy

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

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

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at constant volume and entropy,

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