Focus 3: The Second and Third Laws

Entropy

Entropy changes in processes

Entropy measurement

Free energy

Combining 1st and 2nd laws

The fundamental equation

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$$dU = dq + dW$$

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a reversible change in a closed system

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The fundamental equation

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a reversible change in a closed system

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This equation applies to any change in U—reversible or irreversible—of a closed system that does no additional (non-expansion) work!

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$$U(S,V)$$

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$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

The fundamental equation

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$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Maxwell relations

Maxwell relations

An infinitesimal change in a function $f(x,y)$

$$df = g dx + h dy$$

where:

- g is the partial derivative of f with respect to x, i.e., $g = \frac{\partial f}{\partial x}$.
- h is the partial derivative of f with respect to y, i.e., $h = \frac{\partial f}{\partial y}$.

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$$\mathrm{d}f = g\mathrm{d}x + h\mathrm{d}y$$

mathematical criterion for $\mathrm{d}f$ being an exact differential

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

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For df to be an **exact differential**, meaning it represents the total derivative of some function $f(x, y)$, the mixed second partial derivatives must be equal:

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

- This is a necessary and sufficient condition for the differential *df* to be exact, which is fundamental in vector calculus, thermodynamics, and differential equations.

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Use the Maxwell relations to show that the entropy of a perfect gas is linearly dependent on ln V, that is, $S = a + b \ln V$.

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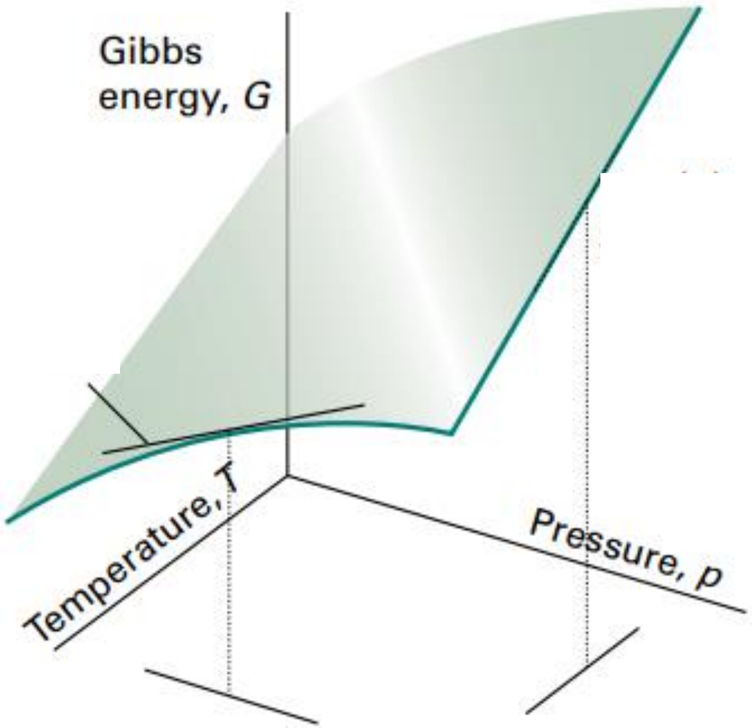

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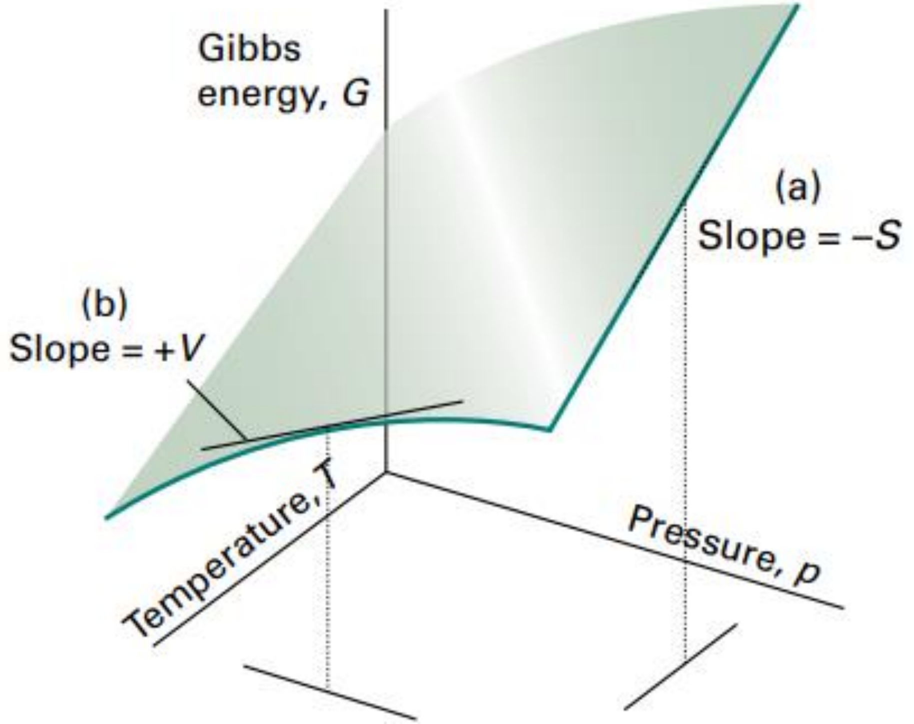

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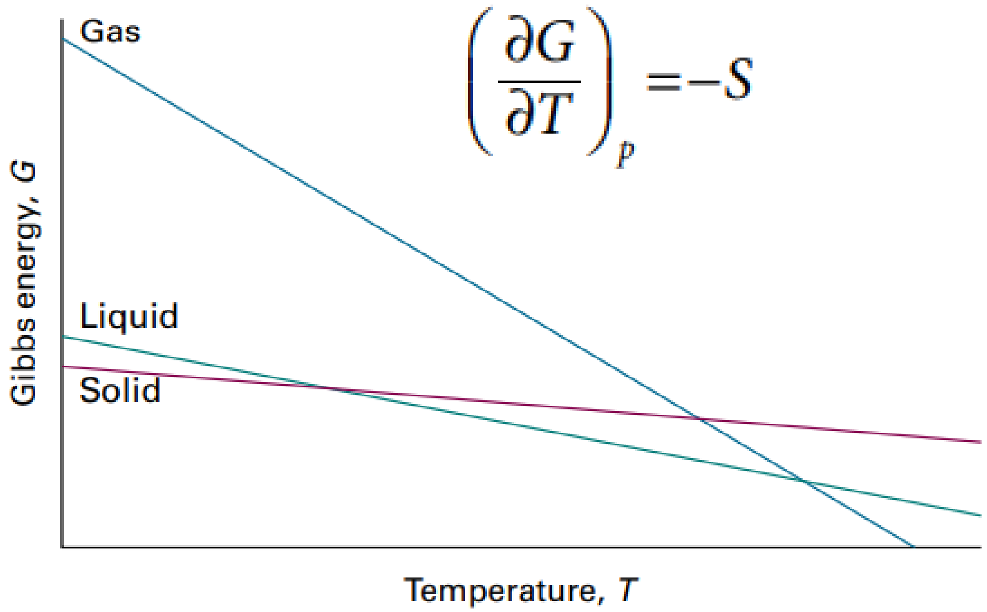

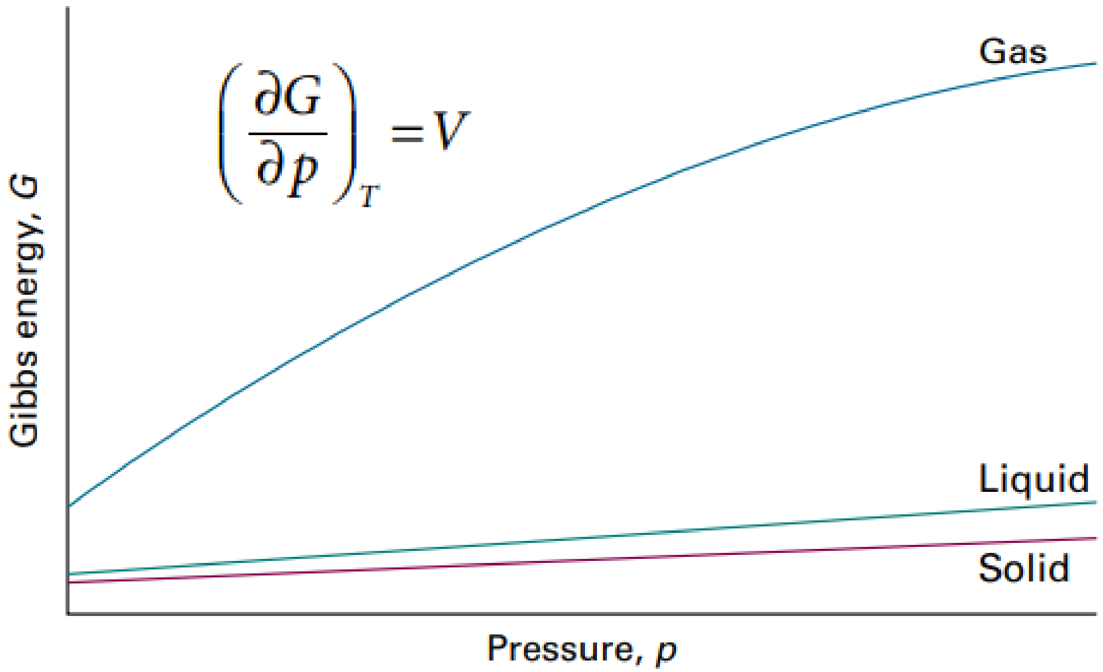

Variations of Gibbs energy with temperature

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

Gibbs–Helmholtz equation

- The equation relates Gibbs free energy to enthalpy (H) and temperature.
- It shows how G/T varies with temperature, which is important in determining equilibrium constants and spontaneity of reactions.

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Gibbs–Helmholtz equation

when it is applied to changes,

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If the change in enthalpy is known,
then how the change in Gibbs energy varies
with temperature is also known.

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$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$$

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Gibbs energy change at constant T: $\mathrm{d}T = 0$

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$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\,dp$$

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Molar Gibbs energy [incompressible substance]

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$$= G_m(p_i) + RT \ln \frac{p_f}{p_i}$$

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if $p_i = p^{\ominus}$ (the standard pressure of 1 bar)

set $p_f = p$

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

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[perfect gas, constant T]