CHM 421/621 Statistical Mechanics

Lecture 9 Deriving fundamental relations

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

Legendre Transformed Representations

Stability of Thermodynamic Systems

Equilibrium Relations

The Gibbs-Duhem Relations: An example

Find the relation among *T, P* and μ for the system with the fundamental equation

$$U = C\frac{S^4}{NV^2}$$

C is a positive constant.

Hint: Find equations of state and use the Gibbs-Duhem equation.

Answer:

$$\ln\left(\frac{\mu}{\mu_0}\right) = 4\,\ln\left(\frac{T}{T_0}\right) - 2\,\ln\left(\frac{P}{P_0}\right)$$

Equilibrium Relations

Deriving the fundamental relation from equations of state

The equations of state can be used to derive the fundamental relation for a system.
Example: Ideal gas

$$PV = NRT$$

$$U = cNRT$$

Answer:

$$s = s_0 + c\,R\,\ln\left(\frac{u}{u_0}\right) + R\,\ln\left(\frac{v}{v_0}\right)$$

Equilibrium Relations

Deriving the fundamental relation from equations of state

The equations of state can be used to derive the fundamental relation for a system.
Example: Ideal gas

$$U = \frac{1}{2}PV$$

$$T^2 = \frac{AU^{\frac{3}{2}}}{VN^{\frac{1}{2}}}$$

Answer:

$$S = 4A^{-\frac{1}{2}}U^{\frac{1}{4}}V^{\frac{1}{2}}N^{\frac{1}{4}} + Ns_0$$

Equilibrium Relations

Conjugate variables

Energetic variables

$$T \longleftrightarrow S$$

$$-P \longleftrightarrow V$$

$$\mu \longleftrightarrow N$$

$$B \longleftrightarrow I$$

Related through derivatives of the *U*.

Magnetic system

$$U = T\ S - p\ V + B\ I + \mu\ N$$

Task: Write for entropic variables

Equilibrium Relations

Second derivatives of U and S

Molar heat capacity, coefficient of thermal expansion, adiabatic/isothermal compressibility, susceptibility

Molar heat capacity @ constant pressure

$$c_P \equiv T\left(\frac{\partial s}{\partial T}\right)_P$$

Isotermal compressibility

$$\kappa_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

Coefficient of thermal expansion

$$\alpha \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

In general, the derivatives are connected to each other.

Why are these 2nd derivatives?

Equilibrium Relations

Second derivatives of U and S

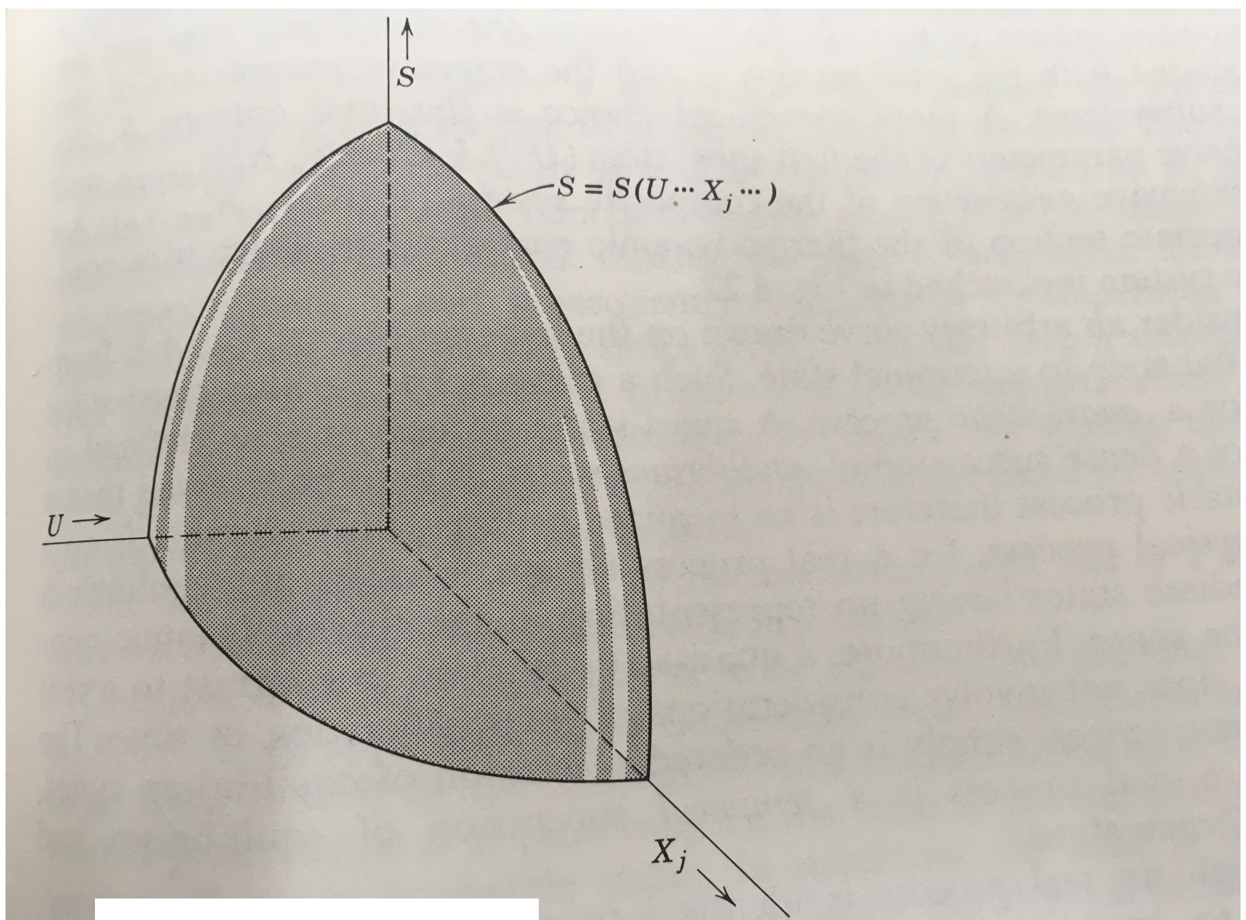
Show that

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

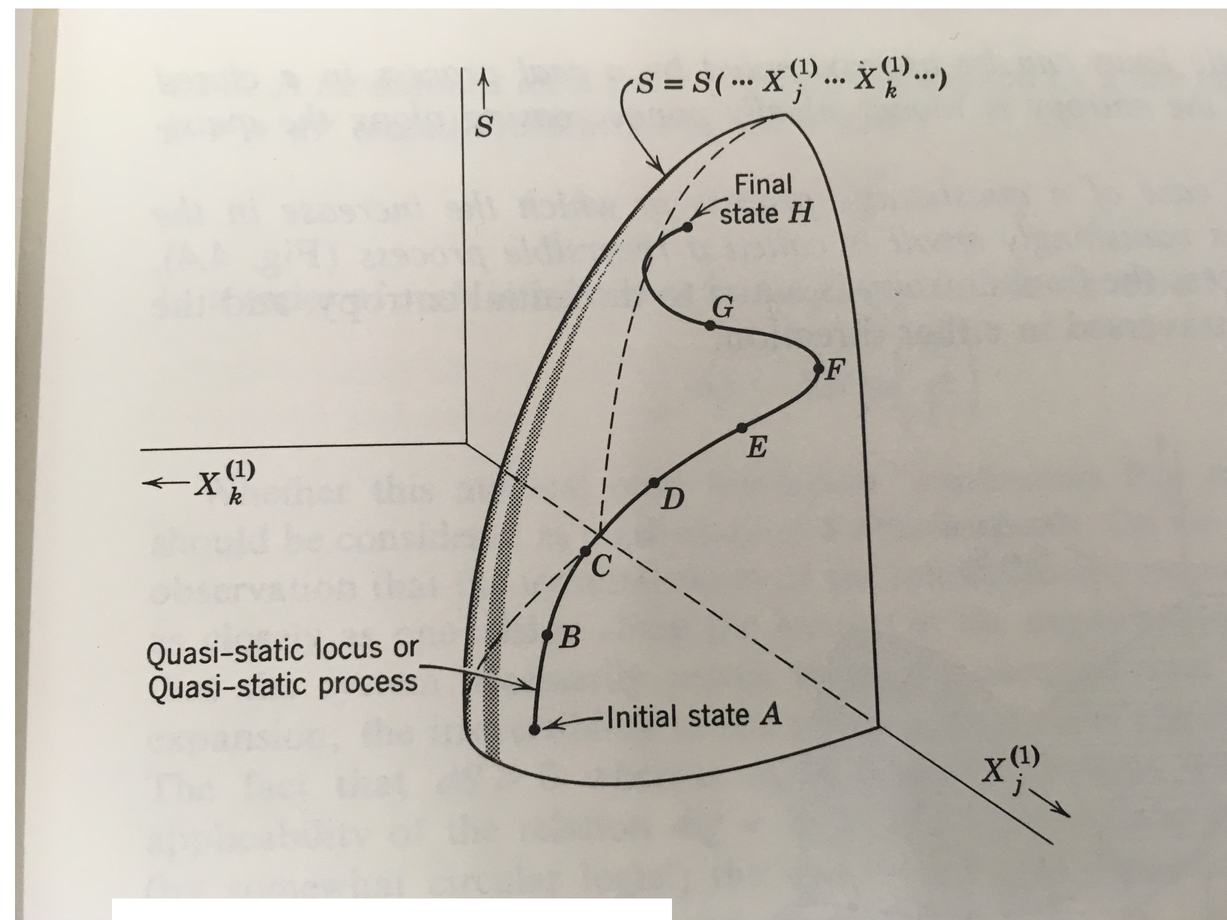
Equilibrium Relations

Quasi-static and reversible processes

Thermodynamic configuration space



Simple system



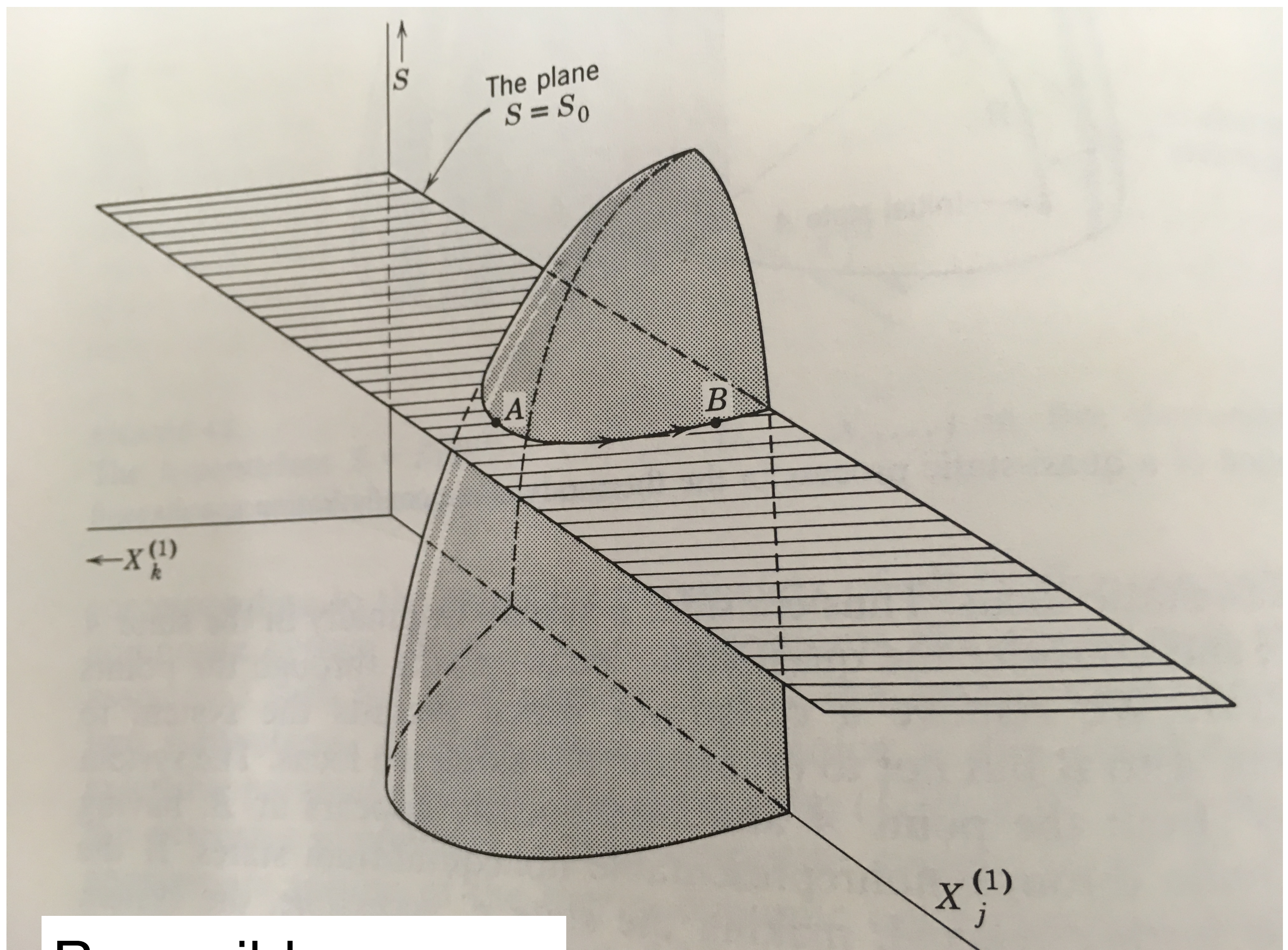
Composite system

Taken from Callen, Sec. 4-2.

Equilibrium Relations

Quasi-static and reversible processes

Thermodynamic configuration space



Reversible process

Taken from Callen, Sec. 4-2.