CHM 421/621
Statistical Mechanics

Lecture 8 Conditions for Equilibrium

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

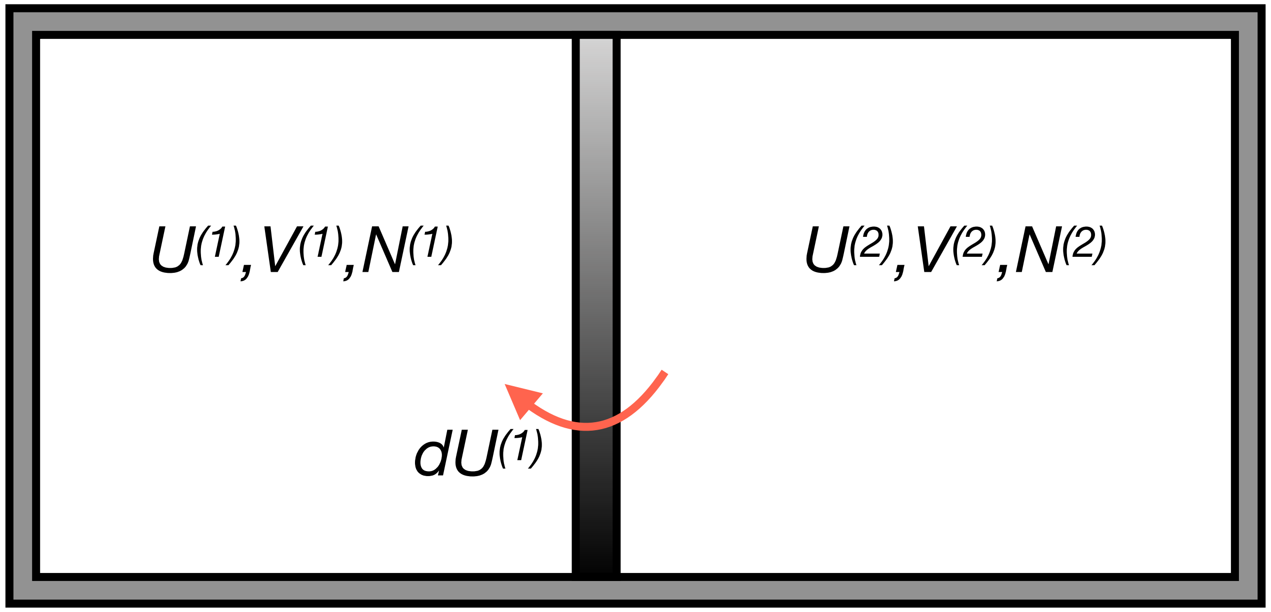
Legendre Transformed Representations

Stability of Thermodynamic Systems

Conditions of Equilibrium

Thermal

Consider a closed system with a rigid, adiabatic and impermeable partition separating two subsystems 1 and 2.



Partition is made diathermal. Under what conditions would no heat flow occur?

$$U = U^{(1)} + U^{(2)} = \text{Constant}$$

$N, V, N^{(i)}, V^{(i)}$ are Constant

$$S = S^{(1)} + S^{(2)}$$

At equilibrium, an infinitesimal transfer of internal energy *dU* from system 2 to 1 will not change the entropy of the system

$$dS = dS^{(1)} + dS^{(2)} = 0$$

Conditions of Equilibrium

Thermal

$$dS = dS^{(1)} + dS^{(2)} = 0$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU^{(1)} = 0$$

Since *dN* and *dV* are 0 for both subsystems

$$\implies \boxed{T_1 = T_2}$$

Thus, the heat flow would stop when the two temperatures are equal.

<u>Direction of flow</u>

If T_1 and T_2 are initial temperatures (differing only slightly) before the wall is made diathermal then

$$\Delta S \approx \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta U > 0$$

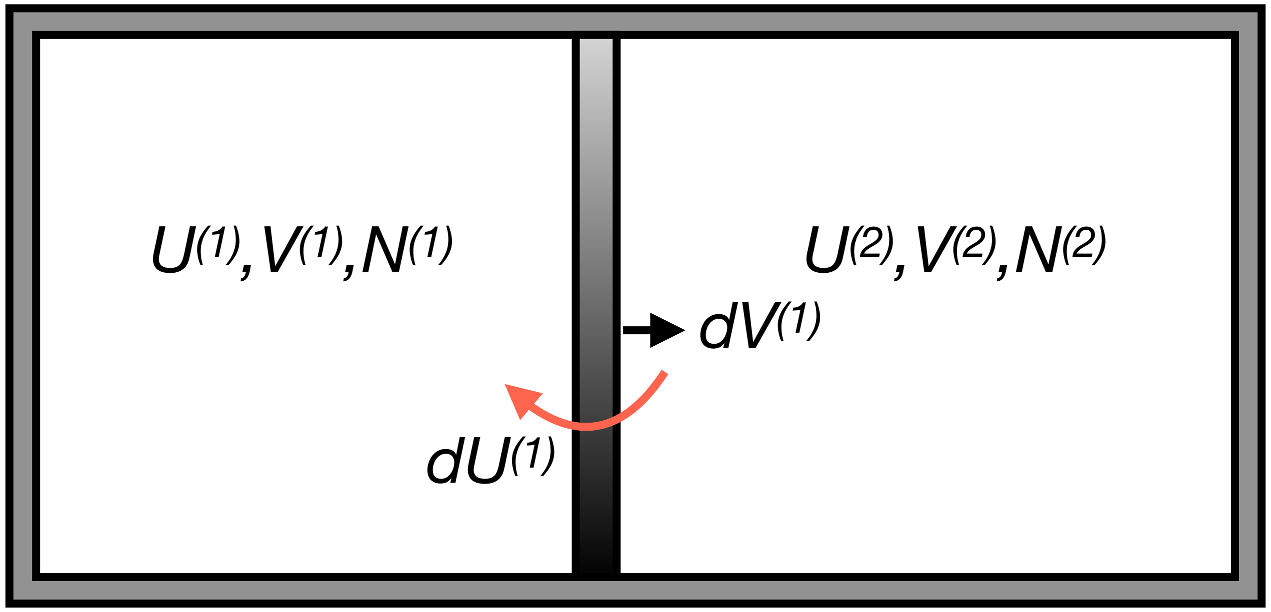
Thus, the direction of transfer is from high to low temperature.

$$T_1 > T_2 \implies \Delta U < 0$$

Conditions of Equilibrium

Mechanical

Consider a closed system with a movable, diathermal and impermeable partition separating two subsystems 1 and 2.



Under what conditions would no heat flow and no volume change occur?

$$U = U^{(1)} + U^{(2)} = \text{Constant}$$
$$V = V^{(1)} + V^{(2)} = \text{Constant}$$

N, $N^{(i)}$ are Constant

$$S = S^{(1)} + S^{(2)}$$

At equilibrium, an infinitesimal transfer of internal energy *dU* from system 2 to 1 will not change the entropy of the system

$$dS = dS^{(1)} + dS^{(2)} = 0$$

Conditions of Equilibrium

Mechanical

$$dS = dS^{(1)} + dS^{(2)} = 0$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU^{(1)} + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV^{(1)} = 0$$

Since *dN* is 0
for both subsystems

$$\implies \boxed{T_1 = T_2 \qquad \text{And} \qquad p_1 = p_2}$$

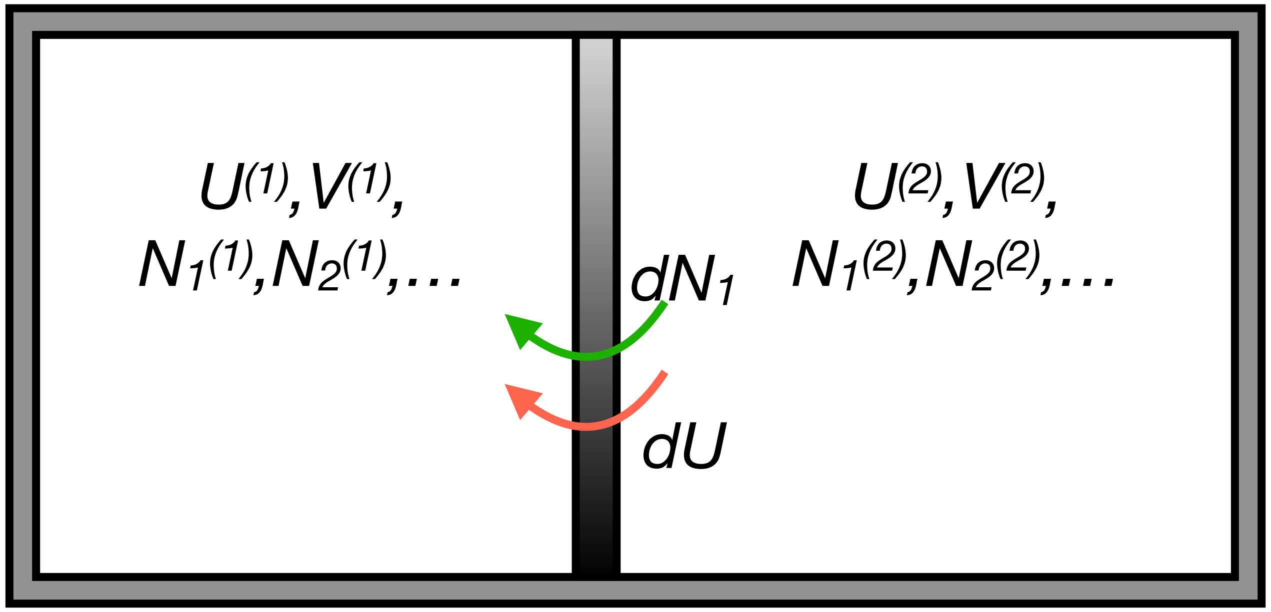
Thus, the heat flow and volume change would stop when the two temperatures as well as pressures are equal.

Direction of movement of partition is from high pressure side to low pressure side.

Conditions of Equilibrium

Matter Flow

Consider a closed system with a rigid and diathermal partition separating two subsystems 1 and 2, permeable only to molecules of species 1.



Under what conditions would no heat flow and no transfer of species 1 occur?

$$U = U^{(1)} + U^{(2)} = \text{Constant}$$
$$N_1 = N_1^{(1)} + N_1^{(2)} = \text{Constant}$$

$V, V^{(i)}, N_2^{(i)}, N_3^{(i)}, \ldots$ are Constant

$$S = S^{(1)} + S^{(2)}$$

At equilibrium, an inifinitesimal transfer of internal energy *dU* from system 2 to 1 Will not change the entropy of the system

$$dS = dS^{(1)} + dS^{(2)} = 0$$

Conditions of Equilibrium

Matter Flow

$$dS = dS^{(1)} + dS^{(2)} = 0$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU^{(1)} - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1^{(1)} = 0$$

Since *dN* is 0
for both subsystems

$$\Longrightarrow \boxed{T_1 = T_2 \qquad \text{And} \qquad \mu_1 = \mu_2}$$

Thus, the heat flow and *N₁* change would stop when the two temperatures as well as corresponding electrochemical potentials are equal.

Direction of transfer of species 1 is from chemical potential to low chemical potential.

Conditions of Equilibrium

Matter Flow: An application to Chemical Equilibrium

Consider a chemical reaction at equilibrium

$$0 \rightleftharpoons \sum_j \nu_j A_j$$

where the ν_j are stoichiometric coefficients bearing negative signs for reactants and positive for products

For a virtual chemical process involving transfer of infinitesimal amount of reactants to products

$$\begin{aligned} dS &= -\sum_j \frac{\mu_j}{T} dN_j \\ &= -\frac{d\tilde{N}}{T} \sum_j \mu_j \nu_j \ (dN_j = \nu_j d\tilde{N}) \\ &= 0 \end{aligned}$$

At equilibrium

$$\Longrightarrow \boxed{\sum_j \mu_j \nu_j = 0}$$

This equation along with the equation of state of the mixture and overall mole constraints of constituents can yield the equilibrium distribution of moles of various species in the mixtures

Equilibrium Relations

The Euler Equation

Given the homogenous first-order property of the fundamental relation, we can represent that equation in the Euler form.

Consider the energetic fundamental relation

$$U_\lambda \equiv U(\lambda S, \lambda X_1, \lambda X_2, ..., \lambda X_t) = \lambda U(S, X_1, X_2, ..., X_t)$$

Differentiating with respect to λ

$$\frac{\partial U_\lambda}{\partial \lambda} = \frac{\partial U_\lambda}{\partial(\lambda S)}\frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U_\lambda}{\partial(\lambda X_1)}\frac{\partial(\lambda X_1)}{\partial \lambda} + \cdots \quad = U(S, X_1, X_2, ..., X_t)$$

Or

$$\frac{\partial U_\lambda}{\partial(\lambda S)}S + \sum_{j=1}^{t}\frac{\partial U_\lambda}{\partial(\lambda X_j)}X_j = U(S, X_1, \cdots, X_t)$$

Setting $\lambda = 1$ we get

$$\boxed{U = TS + \sum_{j=1}^{t} P_j X_j}$$

Equilibrium Relations

The Euler Equation

In the simple case this amounts to

$$U = TS - PV + \mu_1 N_1 + \mu_2 N_2 + \cdots + \mu_r N_r$$

Similarly, from the entropic fundamental relation one can show that

$$S = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \sum_{k=1}^{r} \left(\frac{\mu_k}{T}\right) N_k$$

Equilibrium Relations

The Gibbs-Duhem Relations

Relations among intensive parameters can be derived in a differential form from the Euler relation

$$U = TS + \sum_{j=1}^{t} P_j X_j$$

$$dU = TdS + SdT + \sum_{j=1}^{t} (P_j dX_j + X_j dP_j) \qquad \mathbf{1}$$

But, from the fundamental relation we also know that

$$dU = TdS + \sum_{j=1}^{t} P_j dX_j \qquad \mathbf{2}$$

Therefore, **1-2** implies that

$$\boxed{SdT + \sum_{j=1}^{t} X_j dP_j = 0}$$

Equilibrium Relations

The Gibbs-Duhem Relations

For a single component system we get

$$SdT - VdP + Nd\mu = 0$$

Or $$\boxed{d\mu = -sdT + vdP}$$

where *s* and *v* are molar entropy and volume, respectively.

This relation shows that $$\boxed{\mu \equiv \mu(T, P)}$$

=> only 2 intensive parameters are independent.

Number of intensive parameters capable of independent variation is called the number of *thermodynamic degrees of freedom* of a given system.

“A simple system of *r* components has *r+1* thermodynamic degrees of freedom.”

In order to obtain the integrated form above one must know the equations of state.