

Recitation: 4

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Third Law

For elements in equilibrium state at 0 K , $S \equiv 0$

For compounds: Apply the third law: At $T = 0$, the magnitude of entropy change in any reversible reaction will be zero.

- Heat capacity is 0, at $T \rightarrow 0$
- Absolute zero is unattainable: There is only one adiabat that crosses the $T = 0$ temperature. Starting from a finite temperature, it is impossible to find an adiabatic process that will take the system at a final temperature equal to zero.

See Callen, first part.

Internal Energy: Intensive, Extensive Parameters

$$U = U(S, V, N)$$

and we know (from first law) that

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V,N} dS + \left(\frac{\partial U}{\partial V} \right)_{S,N} dV + \left(\frac{\partial U}{\partial N} \right)_{S,V} dN$$

where

$$\begin{aligned} \left(\frac{\partial U}{\partial S} \right)_{V,N} &\equiv T \\ \left(\frac{\partial U}{\partial V} \right)_{S,N} &\equiv -P \\ \left(\frac{\partial U}{\partial N} \right)_{S,V} &\equiv \mu \end{aligned}$$

Therefore,

$$dU = TdS - PdV + \mu dN$$

Equations of State

$$\begin{aligned} T &= T(S, V, N) \\ P &= P(S, V, N) \\ \mu &= \mu(S, V, N) \end{aligned}$$

- Intensive parameters as a function of extensive parameters.
- Homogeneous zero order:

$$T(\lambda S, \lambda V, \lambda N) = T(S, V, N)$$

To completely determine the thermodynamic behavior of the system we need a number of equations of state equal to the number of conjugate pairs that exist in the energy equation.

Euler Relation

Energy is an extensive variable:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

Differentiating with respect to λ

$$\frac{\partial U}{\partial \lambda} = \frac{\partial U}{\partial \lambda S} \cdot \frac{\partial \lambda S}{\partial \lambda} + \frac{\partial U}{\partial \lambda V} \cdot \frac{\partial \lambda V}{\partial \lambda} + \frac{\partial U}{\partial \lambda N} \cdot \frac{\partial \lambda N}{\partial \lambda}$$

If $\lambda = 1$:

$$U = TS - PV + \mu N$$

Thermodynamic Equilibrium

- Entropy Maximum Principle: The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total energy.
- Energy Minimum Principle: The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy.

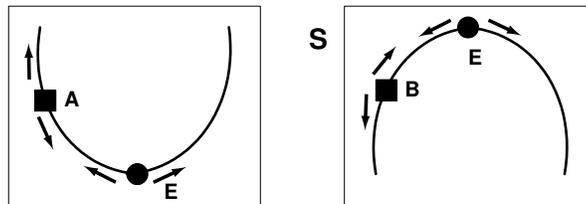


Figure 1: Equilibrium Conditions

Fig. ?? indicates the conditions for equilibrium for both the entropy and the energy.

By looking at the diagram on the left it is evident that, at point E , any possible change in the internal parameters of the system increases its internal energy, $\delta U > 0$, and therefore U is a minimum and the system is at equilibrium. At point A , there are two possibilities: either the internal energy of the system is decreased $\delta U < 0$, or is increased $\delta U > 0$. The criterion for equilibrium establishes that the system has to minimize its energy to achieve equilibrium. Provided there are no constraints that prevent the system from doing so, it will change its internal energy until it reaches point E .

A similar analysis can be done for the diagram on the right: At point E , any possible change in the internal parameters of the system decrease its entropy, $\delta S < 0$. At point B there are two possibilities: either the system increases its entropy, $\delta S > 0$ or it decreases it, $\delta S < 0$. Provided there are no constraints that prevent the system from evolving to the equilibrium condition, the

system will increase its entropy until it reaches a maximum.

The first law and the second law can be combined so we can have a generalized criterion to determine whether any thermodynamic system is at equilibrium:

$$\delta z \equiv dU - TdS - \sum_i Y_i dX_i \geq 0$$

To determine **the allowed** changes in the system, the criterion is inverted:

$$\delta z \equiv dU - TdS - \sum_i Y_i dX_i \leq 0$$

The removal of any internal constraint creates an internal variable. Remove adiabatic wall (leave it diathermal), heat can be exchanged and the internal variable of the system is its temperature.

Using Evolution Equation for Simple System:

For a simple system

$$dU - TdS + PdV \leq 0$$

Isolated System:

$$\begin{aligned} dU &= 0 & dV &= 0 \\ -TdS &\leq 0 \\ dS &\geq 0 \end{aligned}$$

Mechanical System

$$\begin{aligned} dS &= 0 & dV &= 0 \\ dU &\leq 0 \end{aligned}$$

The system is time reversible. There are no dissipative losses.

Isentropic, Isobaric

$$\begin{aligned} dS &= 0 & dP &= 0 \\ d(U + PV) &\leq 0 \\ dH &\leq 0 \end{aligned}$$

Enthalpy is the potential to minimize under constant entropy and pressure conditions.

Isothermal, Isochoric

$$dT = 0 \quad dV = 0$$

$$d(U - TS) \leq 0$$
$$dF \leq 0$$

Helmholtz Free Energy is the potential to minimize under constant temperature and volume conditions.

Isothermal, Isobaric

$$dT = 0 \quad dP = 0$$
$$d(U - TS + PV) \leq 0$$
$$dG \leq 0$$

The Gibbs Free Energy is the potential to minimize under constant pressure and temperature conditions.

This criterion for equilibrium is the most useful for material scientists. It will be shown later on that the Gibbs free energy minimization is related to changes in compositions in inhomogeneous systems, and chemical reactions.

Problem 1

I will try to answer questions regarding P.S. 1...