

Lecture 7

- Calculus of Thermodynamics
- Manipulating derivatives (4 simple rules)
- First derivatives – equations of state
- Second derivatives – use U and G as examples
 - pure second derivatives
 - mixed second derivatives: Maxwell relation
- Calculate ΔU and ΔH in terms of T , V or T , p
- Examples:
 - J-T coefficient
 - pressure dependence of C_p
 - rubber elasticity

Read Ch. 6 Callen Ch. 7.1-7.3 Sandler

Objectives

- Be able to manipulate derivatives using the 4 simple rules for derivatives
- Be able to derive and use Maxwell relations
- Understand meaning of derivatives
- Calculate changes in U and H in terms of T, V or T, P

Four Simple Rules for Derivatives

Reciprocity $\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z}$

Triple product $\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = -1$

Chain/insertion $\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial y}{\partial \phi}\right)_z \left(\frac{\partial \phi}{\partial x}\right)_z$

Maxwell

$$\left(\frac{\partial^2 F}{\partial y \partial x}\right) = \left(\frac{\partial^2 F}{\partial x \partial y}\right)$$

general, F doesn't have to be
a thermodynamic potential

Derivatives

First derivatives

- Conjugate variables to the characteristic variables
- Define generalized equation of state (EOS)

First Derivatives

From fundamental equation $dU = TdS - PdV + \sum_i \mu_i dn_i$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, \{n_i\}}, -P = \left(\frac{\partial U}{\partial V} \right)_{S, \{n_i\}}, \mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{i \neq j}}$$

Each of these first derivatives is an equation of state

$$T = T(S, V, \{n_i\}), P = P(S, V, \{n_i\}), \mu_i = \mu_i(S, V, \{n_i\})$$

The usual P-V-T EOS can be obtained by eliminating (solving for) S in terms of T, P, V, n_i

$$\implies P = P(T, V, \{n_i\})$$

First Derivatives

From fundamental equation $dF = -SdT - PdV + \sum_i \mu_i dn_i$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V, \{n_i\}}, -P = \left(\frac{\partial F}{\partial V}\right)_{T, \{n_i\}}, \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_{i \neq j}}$$

EOSs already in terms of familiar variables

$$S = S(T, V, \{n_i\}), P = P(T, V, \{n_i\}), \mu_i = \mu_i(T, V, \{n_i\})$$

Each of these EOS contains only partial information, since they are only partial derivatives. But if we have all the EOS, that's complete information

Derivatives

Second derivatives

- Pure derivatives all involve conjugate pairs; have definitive sign
- Mixed derivatives give Maxwell relations; no sign requirement

Second Derivatives

Examples using U and G for closed systems

$$dU = TdS - PdV \quad T = \left(\frac{\partial U}{\partial S}\right)_V, -P = \left(\frac{\partial U}{\partial V}\right)_S$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \quad \left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{V\kappa_S} > 0$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \quad \begin{array}{l} \text{adiabatic} \\ \text{compressibility} \end{array}$$

$$\left(\frac{\partial^2 U}{\partial V \partial S}\right) = \left(\frac{\partial^2 U}{\partial S \partial V}\right)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{1}{V\alpha_S} = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S \quad \begin{array}{l} \text{adiabatic thermal} \\ \text{expansivity} \end{array}$$

$$dG = -SdT + VdP \quad S = -\left(\frac{\partial G}{\partial T}\right)_P, V = \left(\frac{\partial G}{\partial P}\right)_T$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_P}{T} < 0 \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T = -V\kappa_T < 0$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{isothermal compressibility}$$

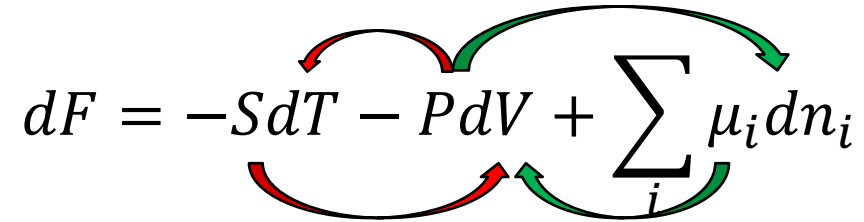
$$\left(\frac{\partial^2 G}{\partial P \partial T}\right) = \left(\frac{\partial^2 G}{\partial T \partial P}\right)$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = V\alpha_P$$

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{isobaric thermal expansivity}$$

Maxwell Relations

Mixed 2nd derivatives from any of the fundamental equations

$$dF = -SdT - PdV + \sum_i \mu_i dn_i$$


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

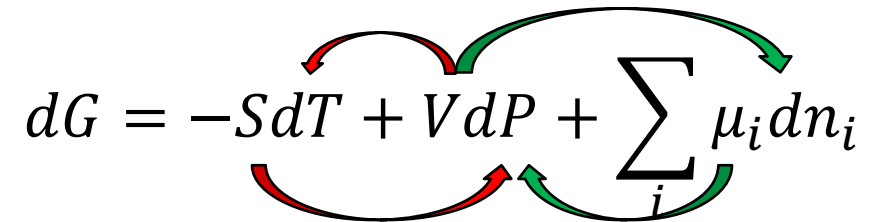
$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j \neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{T,\{n_i\}}$$

$$\left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,V,n_{j \neq i}} = \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,V,n_{i \neq j}}$$

Maxwell relation allows us to express nonobvious derivatives in terms of more familiar derivatives (using just PVT EOS)

Maxwell Relations

Mixed 2nd derivatives from any of the fundamental equations

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$


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

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j \neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\{n_i\}}$$

$$\left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,P,n_{j \neq i}} = \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,P,n_{i \neq j}}$$

Mnemonic for Maxwell Relations

- Looking at bottom variables that are not conjugate to each other
- If bottom variables are conjugates, flip the derivative
- Use the fundamental equation for those characteristic variables

Example: $\left(\frac{\partial S}{\partial V}\right)_P$ **flip** $\left(\frac{\partial V}{\partial S}\right)_P$

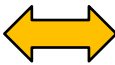
What thermodynamic potential takes P and S as characteristic variables?

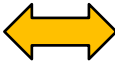
$$dH = TdS + VdP$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad \longrightarrow \quad \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_S$$

Understanding Thermodynamic Derivatives

- Understanding the physical meaning of a derivative
- Turn physical statement into an appropriate derivative

Example: $\left(\frac{\partial P}{\partial T}\right)_S$  how pressure changes with temperature in an isentropic process

or $\left(\frac{\partial T}{\partial P}\right)_S$  how temperature with pressure in an isentropic process
adiabatic, reversible expansion

$$dH = TdS + VdP \quad \Rightarrow \quad dH = VdP$$

For ideal gas $dH = C_P dT \quad \Rightarrow \quad \left(\frac{\partial T}{\partial P}\right)_S = \frac{V}{C_P}$

From Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V}$ entropy increase with volume in an isobaric pressure (has to involve heating)

Changes in U and H in Terms of T, V or T, P

Start from fundamental equation

$$dU = TdS - PdV$$

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

similarly

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

Ideal Gas: $\left(\frac{\partial P}{\partial T} \right)_V = \frac{P}{T}$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{V}{T}$$



$$dU = C_V dT$$

$$dH = C_P dT$$

Joules Thompson Coefficient

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P} \left[V - T \left(\frac{\partial V}{\partial T}\right)_P \right]$$

Pressure Dependence of Cp

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left\{ \frac{\partial}{\partial P} \left[T \left(\frac{\partial S}{\partial T}\right)_P \right] \right\}_T = T \left\{ \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_T \right\}_P = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Entropic Origin of Rubber Elasticity

$$dU = TdS - PdV + fdL$$

$$dG = -SdT + VdP + fdL$$

$$f = \left(\frac{\partial G}{\partial L}\right)_{T,P} = \left(\frac{\partial H}{\partial L}\right)_{T,P} - T \left(\frac{\partial S}{\partial L}\right)_{T,P} = f_H + f_S$$

Maxwell

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

$$f = f_H + T \left(\frac{\partial f}{\partial T}\right)_{L,P}$$

Slope: entropic
Intercept: enthalpic

Experimentally

$$f = A(L)T$$

 Rubber elasticity is entropic in origin!

Questions to Think about

- For a single component system, how many Maxwell relations are there from all possible thermodynamic potentials?
- Show that the total Legendre transform does not yield new Maxwell relations.

Lecture 8

- Equilibrium condition in terms of maximum entropy
- Equilibrium condition in terms of thermodynamic potentials
- Condition for phase equilibrium
- Condition for chemical equilibrium
- Direction of change

Read Ch. 7 Sandler, Chs. 7 and 8 Callen

Objectives

- Master equilibrium condition in terms of entropy and thermodynamic potentials
- Appreciate variational nature of thermodynamics
- Understanding of roles of environment/reservoir
- Understanding roles of constraints
- Know common equilibrium conditions

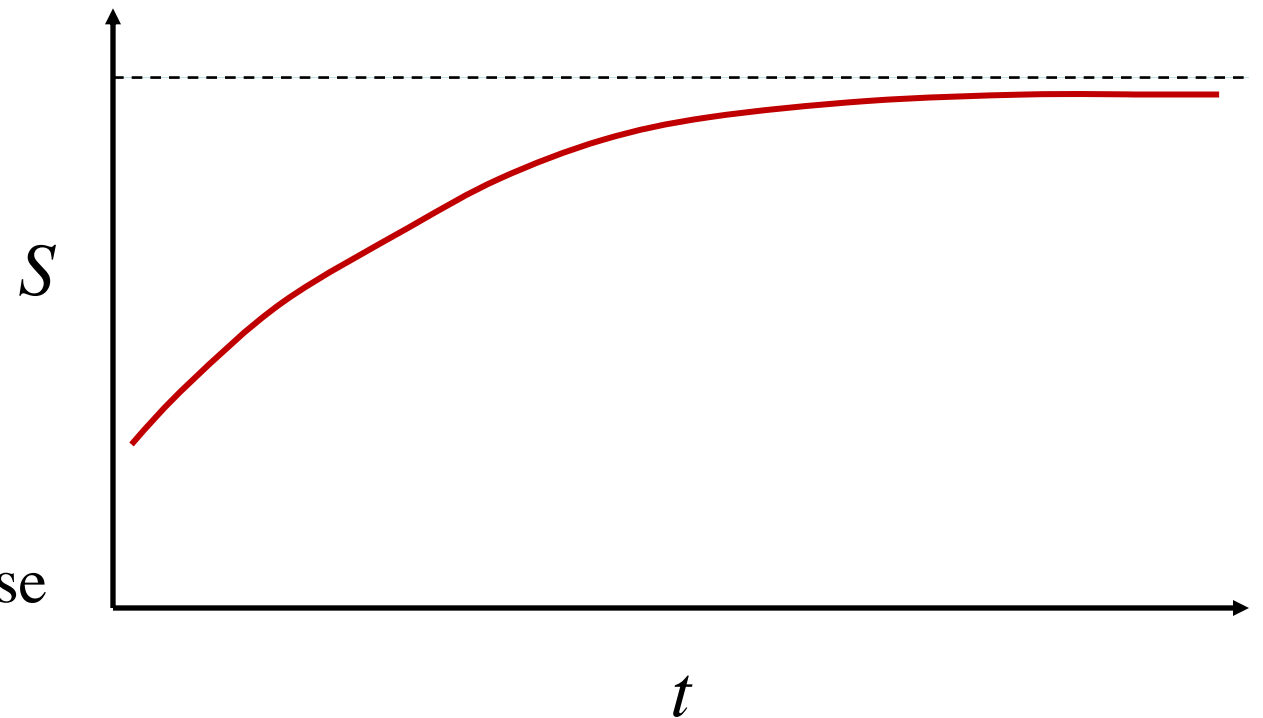
Equilibrium Condition and 2nd Law

- Equilibrium conditions and stability criteria are rooted in 2nd law

For an isolated system

$$dS \geq 0$$

Entropy will keep increasing until system reaches equilibrium, at which point the entropy can increase no more



Entropy is maximum at equilibrium

Entropy Maximization Principle

The equilibrium value of any unconstrained, internal parameter in a closed system with fixed volume and energy is such as to maximize the entropy of the system

Symbolically

$$\left(\frac{\delta S}{\delta X}\right)_{V,U} = 0 \qquad \left(\frac{\delta^2 S}{\delta X^2}\right)_{V,U} < 0$$

Any real or virtual change (hence the notation δ) will lead to *no change at first order* and *decrease at second order*

Equilibrium Condition

| | |
|----------|-------------------------|
| N_{A1} | $N_{A2} = N_A - N_{A1}$ |
| N_{B1} | $N_{B2} = N_B - N_{B1}$ |
| U_1 | $U_2 = U - U_1$ |
| V_1 | $V_2 = V - V_1$ |

Insulated system in rigid container

$$\delta S = \delta S_1 + \delta S_2 = 0$$

Fundamental equation:

$$dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{\mu_A}{T} dn_A - \frac{\mu_B}{T} dn_B$$

$$\delta U_2 = -\delta U_1 \quad \delta V_2 = -\delta V_1 \quad \delta N_{A2} = -\delta N_{A1} \quad \delta N_{B2} = -\delta N_{B1}$$

$$\delta S = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta U_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \delta V_1 - \left(\frac{\mu_{A1}}{T_1} - \frac{\mu_{A2}}{T_2} \right) \delta n_A - \left(\frac{\mu_{B1}}{T_1} - \frac{\mu_{B2}}{T_2} \right) \delta n_B = 0$$

Since δU etc. are completely arbitrary, terms in each pair of parentheses must vanish separately

Equilibrium Condition

$$T_1 = T_2 \quad P_1 = P_2 \quad \mu_{A1} = \mu_{A2} \quad \mu_{B1} = \mu_{B2}$$

- Depending on nature of wall, one or more of these conditions may not be met
- Wall may be virtual, then condition applies to different parts of system. Temperature, pressure, chemical potential, must be equal for all parts of the system

Energy Minimization Principle

The equilibrium value of any unconstrained, internal parameter in a closed system with fixed volume and entropy is such as to minimize the energy of the system

Symbolically

$$\left(\frac{\delta U}{\delta X}\right)_{V,S} = 0 \qquad \left(\frac{\delta^2 U}{\delta X^2}\right)_{V,S} > 0$$

Proof:

If energy weren't a minimum for given entropy. Then we withdraw energy from system adiabatically and reversibly (in the form of work), so entropy remains constant. We then return this energy in the form of heat.

Energy is back to its original value, but entropy has increased due to heat. This means the entropy is not a maximum.

Violates the maximum entropy principle

Enthalpy Minimization Principle

The equilibrium value of any unconstrained, internal parameter in a closed system at fixed entropy in contact with a pressure reservoir is such as to minimize the enthalpy of the system

Symbolically

$$\left(\frac{\delta H}{\delta X}\right)_{P,S} = 0 \qquad \left(\frac{\delta^2 H}{\delta X^2}\right)_{P,S} > 0$$

Helmholtz Free Energy Minimization Principle

The equilibrium value of any unconstrained, internal parameter in a closed system at fixed volume in contact with a thermal reservoir is such as to minimize the Helmholtz free energy of the system

Symbolically

$$\left(\frac{\delta F}{\delta X}\right)_{T,V} = 0 \qquad \left(\frac{\delta^2 F}{\delta X^2}\right)_{T,V} > 0$$

Helmholtz Free Energy

Apply maximum entropy to supersystem

$$S_t(X) = S(X) + S_b[U_t - U(X)]$$

Taylor expand bath entropy

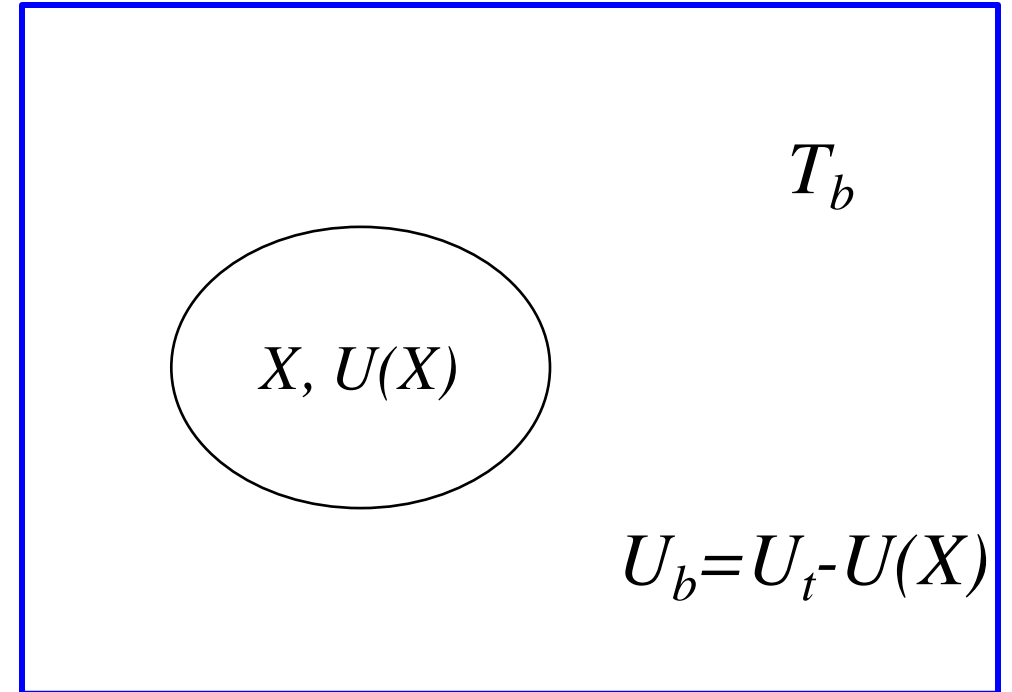
$$\begin{aligned} S_b[U_t - U(X)] &= S_b(U_t) - \left(\frac{\partial S_b}{\partial U_b} \right) U(X) \\ &= S_b(U_t) - \frac{U(X)}{T_b} \end{aligned}$$

$$S_t = S(X) + S_b(U_t) - \frac{U(X)}{T_b} = S_b - \frac{U(X) - T_b S(X)}{T_b} = S_b - \frac{F(X)}{T_b}$$



Maximizing S_t is equivalent to minimizing F

Again shows that F includes effects of surroundings/environment



Gibbs Free Energy Minimization Principle

The equilibrium value of any unconstrained, internal parameter in a closed system in contact with a pressure and thermal reservoir is such as to minimize the Gibbs free energy of the system

Symbolically

$$\left(\frac{\delta G}{\delta X}\right)_{T,P} = 0 \qquad \left(\frac{\delta^2 G}{\delta X^2}\right)_{T,P} > 0$$

Comments on Equilibrium Conditions

- Equilibrium conditions derived from different thermodynamic potentials are the same in form and in principle, but different in practicality and interpretation. Example: thermal equilibrium

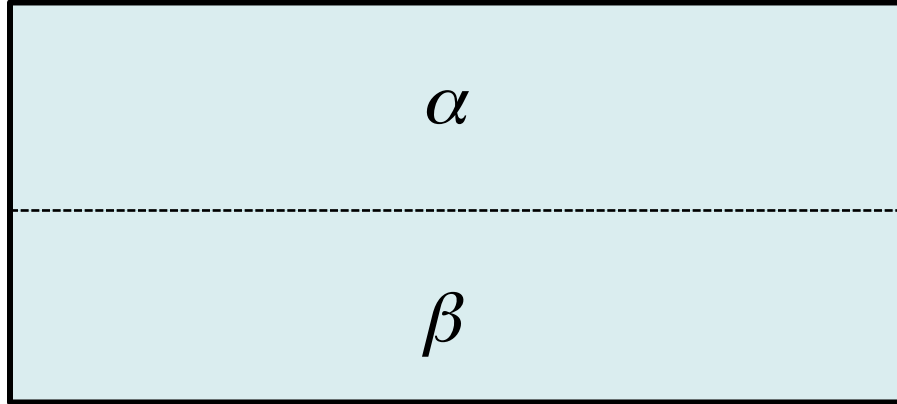
$$T_1 = T_2$$

In entropy formulation, this means $T_1(U_1) = T_2(U - U_1)$ Need for solve for U_1

In Helmholtz free energy formulation, this means $T = T_b$
temperature of system is same as that of the thermal bath

- Using different thermodynamic potentials to derive the equilibrium conditions provides additional insight to the nature of these thermodynamic potentials and Legendre transforms

Phase Equilibrium



- Interface: serves as natural internal boundary for exchanging energy, matter and volume
- Energy, matter and volume are all unconstrained internal variables

$$\delta S = \delta S^{\alpha} + \delta S^{\beta} = 0$$

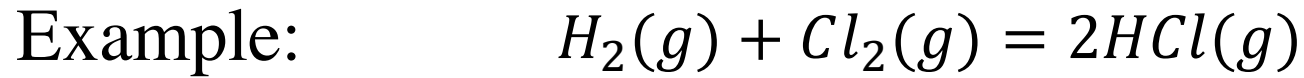
$$T^{\alpha} = T^{\beta} \quad P^{\alpha} = P^{\beta} \quad \mu^{\alpha} = \mu^{\beta}$$

Multiphase:

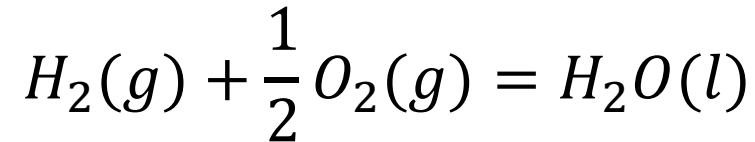
$$T^{\alpha} = T^{\beta} = T^{\gamma} = \dots \quad P^{\alpha} = P^{\beta} = P^{\gamma} = \dots \quad \mu^{\alpha} = \mu^{\beta} = \mu^{\gamma} = \dots$$

Chemical Reactions

Reaction
$$\sum_i \nu_i C_i = 0$$



$$\nu_{H_2} = -1 \quad \nu_{Cl_2} = -1 \quad \nu_{HCl} = 2$$



$$\nu_{H_2} = -1 \quad \nu_{O_2} = -\frac{1}{2} \quad \nu_{H_2O} = 1$$

Stoichiometric coefficients depend on how reaction is written

Extent of reaction
$$\frac{\delta n_1}{\nu_1} = \frac{\delta n_2}{\nu_2} = \dots = \frac{\delta n_r}{\nu_r} \equiv \delta \xi$$

Chemical Equilibrium

Reaction

$$\sum_i \nu_i C_i = 0$$

Equilibrium

$$(\delta S)_{U,V} = - \sum_i \frac{\mu_i}{T} \delta n_i = 0$$

Using entropy formulation
in an insulated rigid box

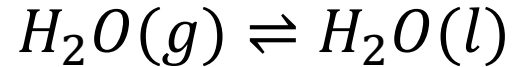
Using extent of reaction

$$\frac{\delta n_1}{\nu_1} = \frac{\delta n_2}{\nu_2} = \dots = \frac{\delta n_r}{\nu_r} \equiv \delta \xi$$

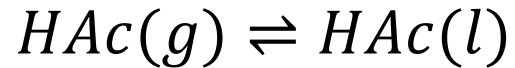
$$- \sum_i \frac{\mu_i \nu_i}{T} \delta \xi = 0$$

$$\sum_i \nu_i \mu_i = 0$$

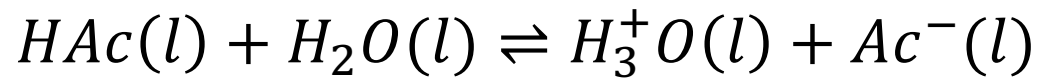
Multiple/Simultaneous Equilibrium



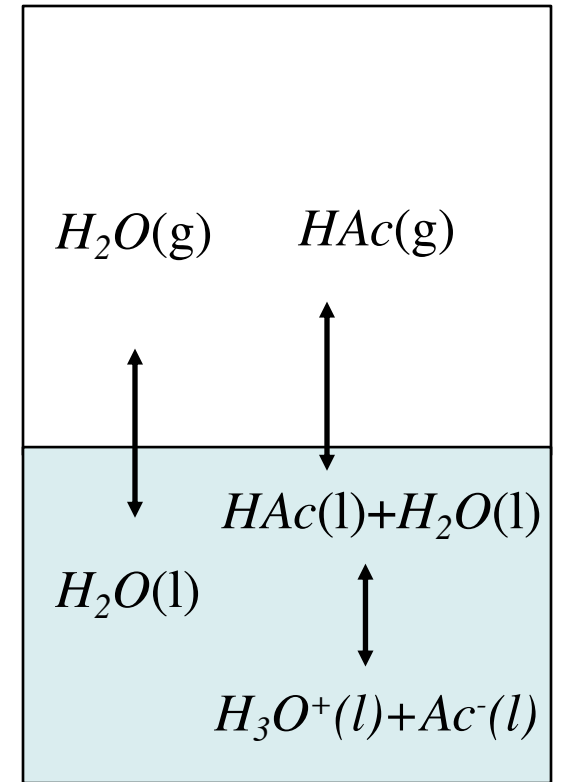
$$\mu_{H_2O}^g = \mu_{H_2O}^l$$



$$\mu_{HAc}^g = \mu_{HAc}^l$$



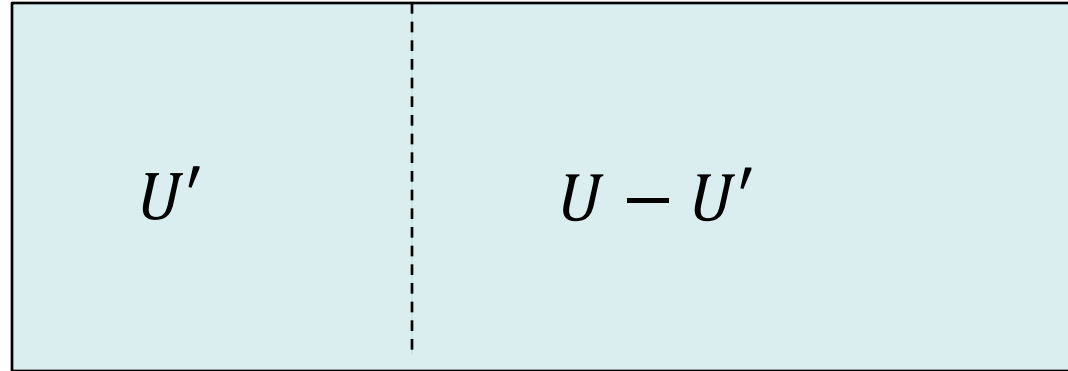
$$\mu_{HAc}^l + \mu_{H_2O}^l = \mu_{H_3O^+}^l + \mu_{Ac^-}^l$$



Phase equilibrium can be considered as chemical equilibrium

Direction of Change

If system is not
at equilibrium



$$\delta S = \delta S_1 + \delta S_2 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta U' > 0$$

$$T_1 > T_2 \quad \delta U' < 0 \quad T_1 < T_2 \quad \delta U' > 0$$

Energy always flows from Hi-T to lo-T

Questions to Think about

- Derive the equilibrium condition for a two-component system in a container with a diathermal partition wall that is fixed in position by a stopper. The wall is semipermeable, i.e., it only allows one species to diffuse through.
- What will happen to the wall if the stopper is removed?
- Derive the Gibbs free energy minimization principle from the Helmholtz free energy minimization principle, following similar idea as used in deriving the Helmholtz free energy minimization principle from the entropy maximization principle