

Lecture 8

Helmholtz and Gibbs energies

Concentrating on the system

- ✦ *Entropy is the basic concept for discussing the direction of natural change.*
- ✦ *To use the concept of entropy, we have to analyze changes in both the system and its surroundings.*
- ✦ *To simplify the discussion, we need to develop other relations concentrating in the system.*
- ✦ *These new formula will represent the foundation of all the applications of chemical thermodynamics.*

Concentrating on the system

✦ Consider a system in thermal equilibrium with its surroundings at a temperature T . When a change in the system occurs and there is a transfer of energy as heat between the system and the surroundings, the Clausius inequality requires;

$$\boxed{dS \geq \frac{dq}{T}} \quad \text{or} \quad \boxed{dS - \frac{dq}{T} \geq 0} \quad \text{Sys + Surr description}$$

dS : describes entropy change of system
 dq/T : describes entropy change of surroundings

► We can develop this inequality in two ways according to the conditions (of constant volume or constant pressure) under which the process occurs.

A: At constant volume

$$\boxed{dq_V = dU} \quad \text{and} \quad \boxed{dS - \frac{dU}{T} \geq 0} \quad \text{Sys description}$$

✦ The importance of the inequality in this form is that it expresses the criterion for spontaneous change solely in terms of the state functions of the system.

Rearrange $\boxed{TdS \geq dU}$ (constant V , no additional work other than PV work)

At constant U , $dU=0$ $\boxed{TdS_{U,V} \geq 0}$

► In a system at constant volume and constant internal energy (e.g., isolated systems), the entropy increases in a spontaneous change. 2nd Law

At constant S , $dS=0$

$$dU_{S,V} \leq 0$$

- If the entropy and volume of the system are constant, then the internal energy must decrease in a spontaneous change.

Interpretation

- ✦ If the entropy of the system is unchanged in a spontaneous process at constant volume, then there must be an increase in entropy of the surroundings, which can be achieved only if the energy of the system decreases as energy flows out as heat.

At constant volume

$$TdS \geq dU \quad \longrightarrow \quad dU - TdS \leq 0$$

- ✦ For a simple representation, a new property called Helmholtz energy, A , is defined as

$$A = U - TS$$

Helmholtz energy

All symbols in this definition refer to the system.
Arbeit is the German word for work; hence the symbol A .

- When the state of the system changes at constant temperature

$$dA = dU - TdS$$

Employing at constant V that

$$TdS \geq dU \quad \longrightarrow \quad dA_{T,V} \leq 0$$

Interpretation

$$\boxed{dA_{T,V} \leq 0}$$

- ▶ A change in a system at constant temperature and volume is spontaneous if $dA_{T,V} \leq 0$.
- ▶ A change under these conditions is spontaneous if it corresponds to a decrease in the Helmholtz energy.
- ▶ Such systems move spontaneously towards states of lower A if a path is available.

- ▶ The criterion of equilibrium, when neither the forward nor reverse process has a tendency to occur, is

$$\boxed{dA_{T,V} = 0}$$

$\Delta_r A_{T,V}$

}

< 0 , spontaneous

$= 0$, equilibrium

> 0 , non-spontaneous. Reverse is spontaneous

▶ When the state of the system changes but not isothermally

$$\boxed{dA = dU - TdS - SdT}$$

but

$dU = dq - pdV = TdS - pdV$

$dA = TdS - pdV - TdS - SdT$

$$\boxed{dA = -pdV - SdT}$$

Another Interpretation

$$dA = dU - TdS$$

$$dA_{T,v} \leq 0$$

- ⊕ *A negative value of dA is favored by a negative value of dU and a positive value of TdS .*
- ⊕ *This suggests that the tendency of a system to move to lower A is due to its tendency to move towards states of lower internal energy and higher entropy.*
- ⊕ *However, this is not true, because the tendency to lower A is solely a tendency towards states of greater overall entropy.*
- ⊕ *Systems change spontaneously if in doing so the total entropy of the system and its surroundings increases, not because they tend to lower internal energy.*

Misleading Interpretation

$$dA = dU - TdS$$

$$dA_{T,v} \leq 0$$

- ⊕ *The form of dA may give the impression that systems favor lower energy, but that is misleading.*
- ⊕ *dS is the entropy change of the system, $-dU/T$ is the entropy change of the surroundings (when the volume of the system is constant), and their total tends to a maximum.*

A is also called maximum free energy function or maximum work function

Helmholtz energy/Maximum expansion work function

From Clausius inequality $TdS \geq dq$ And 1st Law $dU = dq + dw$

$$dU \leq TdS + dw \quad \longrightarrow \quad dw \geq dU - TdS$$

► Considering a reversible pathway for a process, then the maximum work (most negative value of dw) is done by the system, and therefore the maximum energy can be obtained from the system as work, is given by

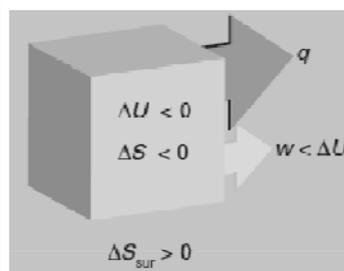
$$dw_{\max} = dU - TdS \quad \xrightarrow{\text{But at constant } T} \quad dA = dU - TdS$$

$$dw_{\max} = dA \quad \text{For isothermal processes, } dA \text{ equals to the maximum work done}$$

□ When a macroscopic isothermal change takes place in the system $w_{\max} = \Delta A$ and $\Delta A = \Delta U - T\Delta S$

Important understanding

⚡ If a change occurs with a decrease in entropy (of the system), i.e., $T\Delta S < 0$, then the right-hand side of this equation is not as negative as ΔU itself, and consequently the maximum work is less than ΔU .



⚡ For the change to be spontaneous, some of the energy must escape as heat in order to generate enough entropy in the surroundings to overcome the reduction in entropy in the system

Tax exemption is not allowed

$$\Delta A = \Delta U - T\Delta S$$

$$w_{\max} = \Delta A$$

- ⚡ *Nature is demanding a tax on the internal energy as it is converted into work.*
- ⚡ *This is the origin of the alternative name 'Helmholtz free energy' for A, because ΔA is that part of the change in internal energy that we are free to use to do work.*

Interpretation for A

- ⚡ *Work is energy transferred to the surroundings as the uniform motion of atoms.* $A = U - TS$
- ⚡ *Hence, A may represent the total internal energy of the system, U, less a contribution that is stored as energy of thermal motion (the quantity TS).*
- ⚡ *Because energy stored in random thermal motion cannot be used to achieve uniform motion in the surroundings, only the part of U that is not stored in that way, the quantity $U - TS$, is available for conversion into work.*

Nature may provide a tax refund

$$\Delta A = \Delta U - T\Delta S$$

$$w_{\max} = \Delta A$$

- ⚡ If the change occurs with an increase of entropy of the system (i.e., $T\Delta S > 0$), the right-hand side of the equation is more negative than ΔU .
- ⚡ In this case, the maximum work that can be obtained from the system is greater than ΔU . !!!!!!!!
- ⚡ This can be understood if the system is not isolated and energy may flow in ($S \uparrow$) as heat as work is done.
- ⚡ In this case (as S_{sys} increases), S_{surr} can decrease as long as ΔS_{t} is still positive.
- ⚡ Therefore, some energy (no more than the value of $T\Delta S$) may leave the surroundings as heat and contribute to the work the change is generating.

Exercise

- ⚡ When 1.000 mol $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) is oxidized to carbon dioxide and water at 25°C according to the equation $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$, calorimetric measurements give $\Delta_r U^0 = -2808 \text{ kJ mol}^{-1}$ and $\Delta_r S^0 = +259.1 \text{ J K}^{-1}\text{mol}^{-1}$ at 25°C. How much of this energy change can be extracted as (a) heat at constant pressure, (b) work? Assume ideal behavior for gases.

Answer

(a)

$$\begin{aligned} \Delta_r H^0 &= \Delta_r U^0 + RT\Delta n_g \\ &= \Delta U^0 = -2808 \text{ kJ mol}^{-1} \end{aligned}$$

(b)

$$\begin{aligned} \Delta A = \Delta U - T\Delta S &= (-2808 \text{ kJ mol}^{-1}) \\ &- (298 \text{ K})(+259.1 \text{ J K}^{-1}\text{mol}^{-1}) = -2885 \text{ kJ mol}^{-1} \end{aligned}$$

B: At constant pressure

$$dq_p = dH$$

and

$$dS - \frac{dH}{T} \geq 0$$

Rearrange

$$TdS \geq dH$$

(constant p , no additional work other than PV work)

At constant H , $dH=0$

$$TdS_{H,p} \geq 0$$

Interpretation

- The entropy of the system at constant pressure must increase if its enthalpy remains constant (for there can then be no change in entropy of the surroundings)

At constant S , $dS=0$

$$dH_{S,p} \leq 0$$

Interpretation

- The enthalpy must decrease if the entropy and pressure of the system is constant, for then it is essential to have an increase in entropy of the surroundings.

At constant pressure

$TdS \geq dH \longrightarrow dH - TdS \leq 0$

✦ For a simple representation, a new property called Gibbs energy, G , is defined as

$G = H - TS$ **Gibbs energy**

All symbols in this definition refer to the system.

▶ When the state of the system changes at constant temperature $dG = dH - TdS$

Employing at constant P that $TdS \geq dH \longrightarrow dG_{T,p} \leq 0$

Interpretation

$dG_{T,p} \leq 0$

▶ At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

▶ The criterion of equilibrium, when neither the forward nor reverse process has a tendency to occur, is $dG_{T,p} = 0$

$\Delta_r G_{T,p}$ $\left\{ \begin{array}{l} <0, \text{ spontaneous} \\ =0, \text{ equilibrium} \\ >0, \text{ non-spontaneous. Reverse is spontaneous} \end{array} \right.$

▶ *If state of the system changed but not isothermally*

$$G = H - TS \qquad G = U + pV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

but $dU = dq - pdV = TdS - pdV$

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT$$

$$dG = Vdp - SdT \quad \text{Compare with} \quad dA = -pdV - SdT$$

$$d(A + pV) = -pdV - SdT + pdV + Vdp$$

$$= Vdp - SdT = dG$$

$$G = A + pV$$

Spontaneous Endothermic reactions

$$dG = dH - TdS$$

- ▶ *For endothermic Rxs, H increases and $dH > 0$.*
- ▶ *Because the reaction is spontaneous, $dG < 0$ despite*
- ▶ *Hence, the entropy of the system must increase so much that TdS outweighs dH in $dG = dH - TdS$.*
- ▶ *Endothermic reactions are therefore driven by the increase of entropy of the system, and this entropy change overcomes the reduction of entropy brought about in the surroundings by the inflow of heat into the system ($dS_{sur} = -dH/T$ at constant pressure).*

Gibbs energy/Maximum non-expansion work function

$$H = U + PV$$

$$U = q + w$$

$$dH = dq + dw + d(pV)$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= dq + dw + d(pV) - TdS - SdT$$

At constant T $dG = dq + dw + d(pV) - TdS$

For a reversible, isothermal process, $d_w = d_{wrev}$ and $dq = dq_{rev} = TdS$, so

$$dG = dw_{rev} + d(pV)$$

dw_{rev} is defined as:

- Expansion, $-pdV$ for reversible change at const p
- non-expansion $dw_{add} = fdl + \gamma d\sigma + EdQ$

$$dG = -pdV + dw_{add} + d(pV)$$

$$dG = -pdV + dw_{add} + pdV + Vdp$$

At constant P, T $dG = dw_{add}$

► At constant T and p , the maximum additional (non-expansion) work, $w_{add,max}$ is given by the change in Gibbs energy.

Interpretation

$$\boxed{dw_{add,max} = dG} \xrightarrow[\text{change}]{\text{measurable}} \boxed{W_{add,max} = \Delta G}$$

- ▶ *This expression is particularly useful for assessing the electrical work that may be produced by fuel cells and electrochemical cells, and we shall see many applications of it.*
- ▶ *The free energy is sometimes called “net work function”*

Exercise

How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The standard entropy of reaction is +259.1 J K⁻¹ mol⁻¹ and the standard reaction enthalpy is -2808 kJ mol⁻¹.

Answer

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$

$$= (-2808 \text{ kJ mol}^{-1}) - [(310 \text{ K}) (259.1 \text{ J K}^{-1} \text{ mol}^{-1})]$$

$$= -2888 \text{ kJ mol}^{-1} \qquad W_{add,max} = -2888 \text{ kJ}$$

Consider that a person of mass 70 kg needs to do 2.1 kJ of work to climb vertically through 3.0 m;

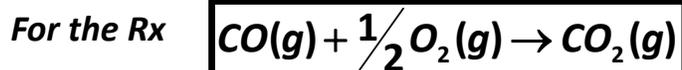
$$\frac{2.1 \text{ kJ} \times 180 \text{ g/mol}}{2888 \text{ kJ/mol}} = 0.13 \text{ g}$$

therefore, at least 0.13 g of glucose is needed to complete the task (and in practice significantly more).

Standard molar Gibbs energies

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$

$$\Delta_r G^0 = \sum_{\text{Products}} \nu \Delta_f G^0 - \sum_{\text{Reactants}} \nu \Delta_f G^0$$



$$\Delta_r G^0 = \Delta_f G^0(\text{CO}_2) - \Delta_f G^0(\text{CO}) - \frac{1}{2} \Delta_f G^0(\text{O}_2)$$

$$\begin{aligned} \Delta_r G^0 &= -394.4 \text{ kJ mol}^{-1} - \left(-137.2 - \frac{1}{2}(0) \right) \text{ kJ mol}^{-1} \\ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

Criteria for reversibility

For a change in a closed system of constant composition, and in the absence of any additional (non-expansion) work

Irreversible	Reversible
$(dS)_{V,U} > 0$	$(dS)_{V,U} = 0$
$(dU)_{V,S} < 0$	$(dU)_{V,S} = 0$
$(dH)_{p,S} < 0$	$(dH)_{p,S} = 0$
$(dA)_{T,V} < 0$	$(dA)_{T,V} = 0$
$(dG)_{T,p} < 0$	$(dG)_{T,p} = 0$

Combining the First and Second Laws

The fundamental equation

‡ For a reversible change in a closed system of constant composition, and in the absence of any additional (non-expansion) work

$$dU = dq + dw$$

$$dw_{rev} = -pdV$$

$$dq_{rev} = TdS$$

$$dU = TdS - pdV$$

The fundamental equation

‡ As dU is an exact differential and its value (ΔU) is path independent, the same value of dU is obtained whether the change is irreversible or reversible.

For reversible processes, $dq_{rev} = TdS$, and $dw_{rev} = -pdV$. However, for irreversible processes, $dq < TdS$, and $dw < -pdV$. Yet, $dw + dq = TdS - pdV$, provided the composition is constant.

Partial molal free energy

- As G is an extensive state property, thus for a system containing several components at constant T ,

$$G_{\text{sys}} = \sum G_{\text{components}} = n_1 \bar{G}_1 + n_2 \bar{G}_2 + \dots$$

\bar{G}_1

Partial molal free energy

- The increase in the total free energy of the system upon increasing n_1 by 1 mol while keeping other variables (n_2, n_3, \dots etc, p and T constant).

$$\bar{G}_1 = \left(\frac{\partial G_{\text{sys}}}{\partial n_1} \right)_{n_2, n_3, \dots, T, P}$$

Chemical Potential, μ

- For a pure substance (one component only), \bar{G}_1 is simply the free energy per mole.
- In solutions, \bar{G}_1 is called the chemical potential.

$$\mu_1 = \left(\frac{\partial G_{\text{sys}}}{\partial n_1} \right)_{n_2, n_3, \dots, T, P}$$

For an ideal gas

$$\mu = \mu_0 + RT \ln p$$

- Where μ_0 is the standard (1 atm, 298 K) chemical potential

For a real gas

$$\mu = \mu_0 + RT \ln f$$

f : fugacity or effective pressure

Free energy of solutions

$$dG = Vdp - SdT$$

✦ The above equation was derived for systems containing one component of fixed composition and assuming only PV work. If components and composition are changed during the process, then.

$$dG = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \dots$$

If other work is assumed

$$dG = Vdp + EdQ - SdT$$

or

$$dG = Vdp + \gamma d\sigma - SdT$$

Effect of T and p on G

$$dG = Vdp - SdT$$

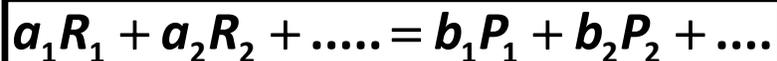
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

+ve quantity

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

-ve quantity

Consider this Rx



$$\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}}$$

$$\Delta G = [b_1 G_{P_1} + b_2 G_{P_2} + \dots] - [a_1 G_{R_1} + a_2 G_{R_2} + \dots]$$

$$\left(\frac{d\Delta G}{dp} \right)_T = \Delta V$$

$$\left(\frac{d\Delta G}{dT} \right)_p = -\Delta S$$

- ✦ If a reaction proceeds with no change in volume between reactants and products at constant T , ΔG will be independent of p .
- ✦ If a reaction proceeds with no change in entropy between reactants and products at constant p , ΔG will be independent of T .

Effect of T on G (another prospective)

Consider the differentiation of G/T with respect to T

Utilizing these formulas

$$\left(\frac{\partial G}{\partial T} \right)_p = -S$$

and

$$G = H - TS$$

$$\left(\frac{d(G/T)_p}{dT} \right) = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T^2}$$

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

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

Similarly, effect of T on A

$$dA = -pdV - SdT$$

Isochoric (const. V) processes

$$\left(\frac{dA}{dT}\right)_V = -S \quad \left(\frac{d\Delta A}{dT}\right)_V = -\Delta S$$

Isothermal Processes

$$\left(\frac{dA}{dV}\right)_T = -p \quad \left(\frac{d\Delta A}{dV}\right)_T = -\Delta p$$

$$\Delta A = \Delta U + T \left(\frac{d\Delta A}{dT}\right)_V$$

$$\left(\frac{d(\Delta A/T)}{dT}\right)_V = -\frac{\Delta U}{T^2}$$

Gibbs-Helmholtz equation

For isothermal processes

$$\Delta G = \Delta H - T\Delta S$$

Utilizing this formula

$$\left(\frac{d\Delta G}{dT}\right)_p = -\Delta S$$

$$\Delta G = \Delta H + T \left(\frac{d\Delta G}{dT}\right)_p$$

Gibbs-Helmholtz equation

Kinetic limited/controlled RX

- ✦ *Are those reactions having a negative ΔG , yet they do not proceed spontaneously unless a barrier is overcome (energy is provided to initiate the Rx) by adding a catalyst.*

Example,



- ✦ *Just mixing of $H_2(g)$ and $O_2(g)$ do not produce unless a catalyst (electric spark, platinied asbestos) is added.*
- ✦ *A $-Ve \Delta G$ measures the driving force of reactions when these reactions occur.*
- ✦ *The catalyst does not affect ΔG (path independent).*