Physical Chemistry for Energy Engineering

(11th: 2018/10/17)

Takuji Oda

Associate Professor, Department of Nuclear Engineering
Seoul National University

*The class follows the text book: D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (tentative)

Lecture #	Date	Contents
1	3-Sep	Introduction
2	5-Sep	1. Thermodynamics: Basic concepts of thermodynamics
3	10-Sep	1. Thermodynamics: The first law of thermodynamics
4	12-Sep	1. Thermodynamics: Thermodynamic process and cycle
5	17-Sep	1. Thermodynamics: The second and third laws of thermodynamics-1
6	19-Sep	1. Thermodynamics: The second and third laws of thermodynamics-2
	24-Sep	No lecture (holiday)
	26-Sep	No lecture (holiday)
7	1-Oct	1. Thermodynamics: The second and third laws of thermodynamics-3 (1. Equation of state of gas will be covered in future)
	3-Oct	No lecture (holiday)
8	8-Oct	Answer of homework-1
9	10-Oct	Exam-01 (2 hour)
10	15-Oct	2. Introduction to equilibrium theory
11	17-Oct	2. Free energy-1
12	22-Oct	2. Free energy-2
13	24-Oct	2. Calculation of thermodynamic quantities
	29-Oct	No lecture
	31-Oct	

Contents of today

<Last class>

- 2.1. Equilibrium theory: Introduction
  - #. Short introduction on what we are learning
  - 2.1.1. Direction of system evolution
  - 2.1.2. Meaning of entropy in microscopic scale
  - 2.1.3. Summary of processes

<Today's class>

- 2.2. Equilibrium theory: free energy
  - **2.2.1. Helmholtz energy**
  - 2.2.2. Gibbs energy
  - 2.2.3. Maxwell relations and some useful formula

(Review) 2.1.1. Direction of spontaneous system evolution

- $20.2: Non-equilibrium isolated systems evolve in a direction that increases their disorder -

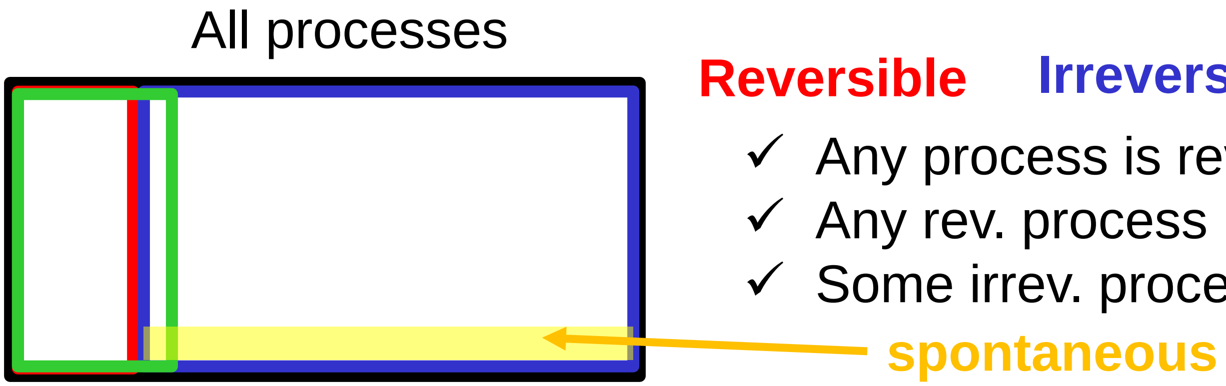
<A statement of the Second Law of Thermodynamics>
There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the (closed) system,

$$dS \geq \frac{\delta q}{T}$$

where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.

<Another statement of the Second Law of Thermodynamics)
The entropy of an isolated system never decreases, because isolated systems always evolve toward thermodynamic equilibrium—the state with the maximum possible entropy.”

- ✓ $dS > 0$ for a spontaneous process (irreversible process)
- ✓ $dS = 0$ for an equilibrium state (reversible process)



- ✓ Any process is rev. or irrev.
- ✓ Any rev. process is quasi-static.
- ✓ Some irrev. process is quasi-static.

- ✓ <Reversible process> process from one equilibrium state to another equilibrium state. During the process, the system is always at some equilibrium state.
  - ➢ For an isolated system, $dS = 0$
- ✓ <Quasi-static process> process from a state to another state. During the process, the system or all sub-systems in the system are always at some equilibrium state.
- ✓ <Spontaneous process> process from a non-equilibrium state to an equilibrium or to a non-equilibrium state. We may / may not define thermodynamic quantities during the process. (*the initial state of spontaneous process must be a non-equilibrium state.)
  - ➢ For an isolated system, if quasi-static (we can define dS), $dS > 0$.
- ✓ <Irreversible process> processes other than reversible processes. We may / may not define thermodynamic quantities during the process.
  - ➢ For an isolated system , if quasi-static (we can define dS), $dS > 0$
    - ➢ Someone may think the condition as $dS \neq 0$. However, in reality, processes of $dS < 0$ violates the condition “isolated”.

2.2. Equilibrium theory: free energy

- Introduction ($22)-

- ✓ The following criteria just work for an isolated system; hence it is not so practical. (Isolated systems are rare, e.g. universe)
  - ✓ $\mathrm{dS} > 0$ for a spontaneous process (irreversible process)
  - ✓ $\mathrm{dS} = 0$ for an equilibrium state (reversible process)

- ✓ To applied it to a practical case, the total entropy change, which is equal to the sum of entropies of system and surroundings ($\Delta S_{total} = \Delta S_{system} + \Delta S_{sur.}$), needs to be checked, where we re-define "system + surroundings" as an isolated system to use the criteria for isolated systems.

- ✓ $dS \geq \frac{\delta q}{T}$ works in any systems and processes, but evaluating δq is often difficult as q is not a state function.

- ✓ In this chapter ($22), two state functions are introduced, which indicates the direction of a spontaneous process in systems that are not isolated. These state functions are Helmholtz and Gibbs (free) energies.

2.2.1. Helmholtz energy

- definition ($22-1) -

A new state function, called Helmholtz energy, is introduced as:

$$\mathrm{A} \equiv U - TS$$

Its differential is given as:

$$dA = d(U - TS) = dU - TdS - SdT$$

Here we consider the 1st law of a reversible constant-volume process:

$$dU = TdS - PdV = TdS \quad \text{then} \quad dU - TdS = 0 \quad \textit{[rev. const.-V]}$$

We additionally assume the process is constant-temperature:

$$d(U - TS) = dU - TdS - SdT = dU - TdS = 0 \quad \textit{[rev. const.-T const.-V]}$$

Hence, we have the following condition for reversible constant-T constant-V process.

$$dA = d(U - TS) = 0 \quad \textit{[rev. const.-T const.-V]}$$

*If we only assume reversible constant-T or constant-V, Helmholtz energy can be written as follows:

- ✓ *[Rev. const-V]* $dA = \cdots$
- ✓ *[Rev. const-T]* $dA = \cdots$

2.2.1. Helmholtz energy

- definition ($22-1) -

A new state function, called Helmholtz energy, is introduced as:

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Hence, we have the following condition for reversible constant-T constant-V process.

$$dA = d(U - TS) = 0 \quad \textit{[rev. const.-T const.-V]}$$

*If we only assume reversible constant-T or constant-V, Helmholtz energy can be written as follows:

- ✓ *[Rev. const-V]* $dA = dU - TdS - SdT = (TdS - PdV) - TdS - SdT = -SdT$
- ✓ *[Rev. const-T]* $dA = dU - TdS - SdT = (TdS - PdV) - TdS - SdT = -PdV$

2.2.1. Helmholtz energy

- criterion of reaction direction for const.-T const.-V system ($22-1) -

We consider a process in a constant-temperature constant-volume.

- ✓ This system often appears in a real chemistry, but the criterion "$dS \geq 0$" does not work in this system because a “constant-temperature” system is not isolated (heat transfer can happen to keep the temperature constant).
- ✓ Hence, we need a criterion other than "$dS \geq 0$“.

As the first law: $dU = \delta q + \delta w$, And $\delta w = -P_{external} dV$

As a constant-volume system: $dV = 0$, then $\delta w = 0$. Hence, $dU = \delta q$

Here, we apply the equation above into a version of the second law ($dS \geq \delta q/T$ for closed systems) as

$$dS \geq \delta q/T = dU/T$$

Then, finally we obtain the following equation, where the equality holds for a reversible process and the inequality for an irreversible process.

$dU \leq TdS$ then $dU - TdS \leq 0$ *[const.-V]*

*Be sure that $dS \geq \delta q/T$ is true for any change in the thermodynamic state of closed systems, not only for isolated systems. (This is much easily achieved than $dS \geq 0$, which is only for isolated systems).

2.2.1. Helmholtz energy

- criterion of reaction direction for const.-T const.-V system ($22-1) -

We consider a process in a constant-volume constant-temperature system.

Helmholtz energy is defined as:

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$dU - TdS \leq 0 \quad \text{[const.-V]}$$

where the equality holds for a reversible process and the inequality for an irreversible process.

In the constant-T condition, the differential of Helmholtz energy is written as:

$$dA = d(U - TS) = dU - TdS - SdT = dU - TdS \quad \text{[quasi-static const.-T]}$$

If we introduce this relation into the equation to judge whether the process is reversible or irreversible:

$$dU - TdS = dA \leq 0 \quad \text{[quasi-static const.-T const.-V]}$$

$$dA = d(U - TS) = 0 \quad \text{[rev. const.-T const.-V]}$$

Consequently, we have a criterion for const.-T const.-V system.

- ✓ $\mathrm{dA} < 0$ for a spontaneous process (irreversible process)
- ✓ $\mathrm{dA} = 0$ for an equilibrium state (reversible process)

2.2.1. Helmholtz energy

-criterion of reaction direction for const.-T const.-V system ($22-1)-

Consequently, we have a criterion for const.-V const.-T system.

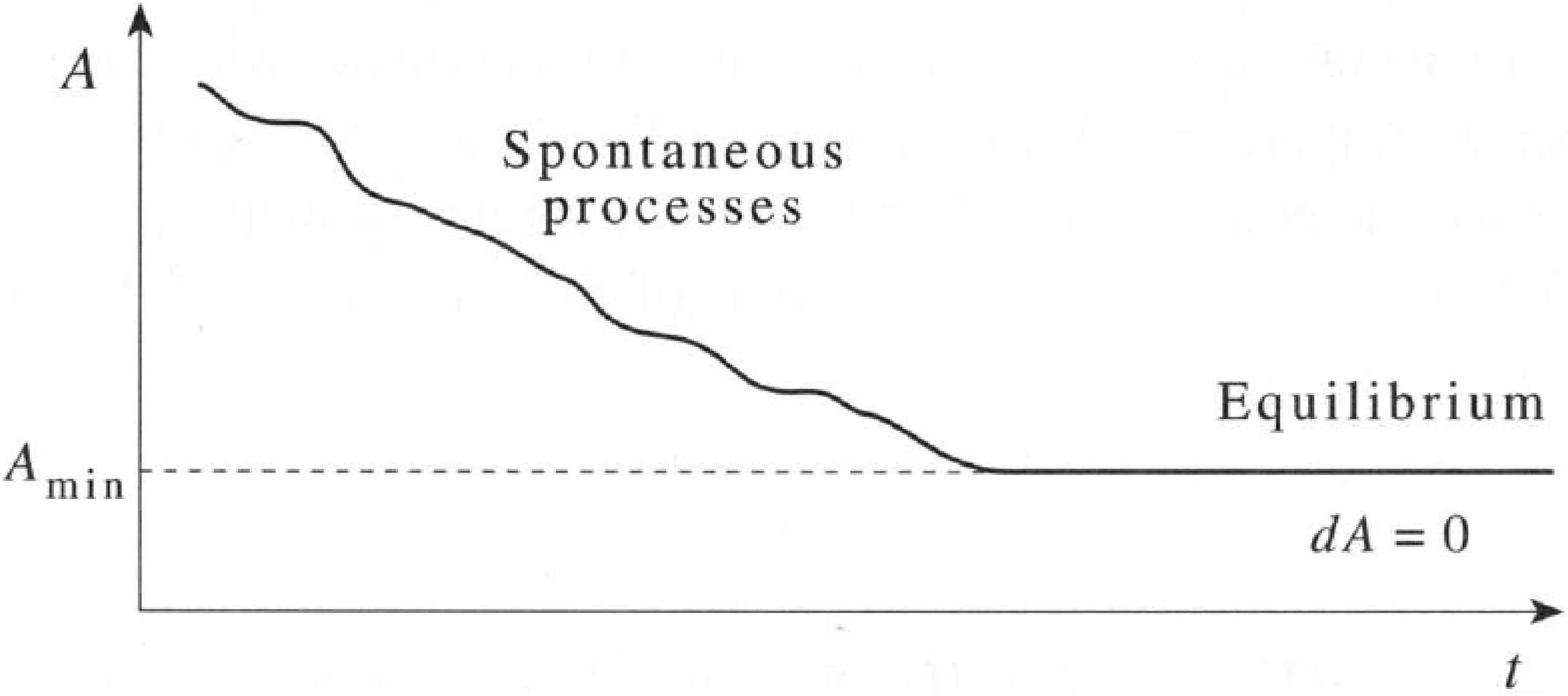
- ✓ $\mathrm{dA} < 0$ for a spontaneous process (irreversible process)
  - ✓ (Integral form) $\Delta\mathrm{A} = \Delta U - T\Delta S < 0$
- ✓ $\mathrm{dA} = 0$ for an equilibrium state (reversible process)
  - ✓ (Integral form) $\Delta\mathrm{A} = \Delta U - T\Delta S = 0$

This result means that

- ➢ "a process of "$\Delta\mathrm{A} < 0$" takes place spontaneously in a system at constant T and V until it becomes "$\Delta\mathrm{A} = 0$" (thus, until *A* will be a minimum).
  - ➢ Ex-1) when $\Delta U < 0$ (some energy will be gained by the process) and $\Delta S > 0$ (the system will be more disordered by the process), $\Delta\mathrm{A}$ is clearly less than 0, and thus this process spontaneously takes place.
  - ➢ Ex-2) a process where ΔU and ΔS have the same signs, $\Delta\mathrm{A}$ gives a quantitative measure of whether is process is spontaneous or not. Basically, because of the factor of T in $\mathrm{T}\Delta S$ term, ΔU dominates at low temperatures while $\mathrm{T}\Delta S$ dominates at high temperatures.
    - ➢ We say "entropy effect becomes stronger at a higher temperature".

2.2.1. Helmholtz energy

- criterion of reaction direction for const.-T const.-V system ($22-1) -



*textbook, figure 22.1

*This is for const.-T const.-V system.

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

2.2.1. Helmholtz energy

- criterion of reaction direction for const.-T const.-V system ($22-1) -

A state function, Helmholtz energy $(\mathrm{A} = U - TS)$ behaves as below for a spontaneous process in a constant-T constant-V system (not isolated):

“$dA \leq 0$ (for constant T and V)”

As the differential is “$dA = dU - TdS - SdT$”, if const.-T const.-V are achieved,

$$\Delta A = \int dA = \int dU - \int TdS - \int SdT = \int dU - T\int dS = \Delta U - T\Delta S \leq 0$$

Hence, “$\Delta A = \Delta U - T\Delta S \leq 0$ (for const.-T const.-V)” is the condition of integral form.

This criteria also means that

- “a process of "$\Delta\mathrm{A} > 0$" does not take place spontaneously in a system at constant T constant V”. To advance a process of "$\Delta\mathrm{A} > 0$“, something such as work must be added to the system.

(Appendix) differential expression and integral expression

A new state function, called Helmholtz energy, is introduced as:

$$\mathrm{A} \equiv U - TS$$

$$dA = d(U - TS) = dU - TdS - SdT$$

Be careful that

$$\Delta A = \Delta(U - TS)$$

is always true, but

$$\Delta(U - TS) = \int \{d(U - TS)\} = \int dU - \int TdS - \int SdT = \Delta U - \int TdS - \int SdT$$

Here, if T and S are constants

$$\Delta U - \int TdS - \int SdT = \Delta U - T\int dS - S\int dT = \Delta U - T\Delta S - S\Delta T$$

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

However, it T and S are not constants,

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

2.2.1. Helmholtz energy

- criterion of reaction direction for const.-T const.-V system ($22-1) -

Here we consider a reversible isothermal process, then

$$\Delta A = \int dA = \int dU - \int TdS - \int SdT = \int dU - T\int dS = \Delta U - T\Delta S$$

Because the process is reversible,

$$\Delta S = \int dS = \int \frac{\delta q_{rev}}{T} = \frac{q_{rev}}{T}$$

Thus, $\Delta\mathrm{A} = \Delta U - T\Delta S = \Delta U - q_{rev}$ (reversible isothermal)

According to the first law, $\Delta U - q_{rev} = w_{rev}$, we obtain

$\Delta\mathrm{A} = w_{rev}$ (reversible isothermal)

Then, if we consider P-V work and non-P-V work with further assuming constant-V process,

$$\Delta\mathrm{A} = w_{rev} = w_{rev-PV} + w_{rev-non-PV} = w_{rev-non-PV}$$

(reversible cosnt-T const-V)

2.2.1. Helmholtz energy

- criterion of reaction direction for const.-T const.-V system ($22-1) -

$\Delta\mathrm{A} = w_{rev}$ (reversible const.-T)

$\Delta\mathrm{A} = w_{rev} = w_{rev-non-PV}$ (reversible const.-T const.-V)

If $\Delta\mathrm{A} < 0$ and the process is of const.-T and const.-V,

- The process will occur spontaneously and w_{rev} represents the work that can be done by the system if this change is carried out reversibly.
  - This is why we often call the Helmholtz energy “free energy”.
- If any irreversible process (like friction) is involved, the quantity of work will be less than w_{rev}. Thus, this w_{rev} and $\Delta\mathrm{A}$ represent the maximum work that could be obtained.

If $\Delta\mathrm{A} > 0$ and the process is of const-T and const-V,

- The process will not occur spontaneously and w_{rev} represents the work that must be added to the system to make this change in a reversible manner.
- If any irreversible processes are involved, more work is needed. Thus this w_{rev} and $\Delta\mathrm{A}$ represent the minimum work that are needed to make this change progress.

2.2.2. Gibbs Energy

- criterion of reaction direction for const.-T const.-P system ($22-2) -

- ✓ Most reaction occur at constant pressure rather than at constant volume: for example, reactions occur when they are open to atmosphere.
- ✓ As we can expect, *U* (internal energy) for a constant volume process/system is replaced with *H* (enthalpy) for a constant pressure ones.

A process in a const.-V system. ⇨ A process in a const.-P system.

As the first law: $dU = \delta q + \delta w$,
And $\delta w = -P_{external} dV$

As a const.-V system:
$dV = 0$ *, then* $\delta w = 0$
Hence, $dU = \delta q$

⇨

As a const.-P system, if the process is static, it is OK to assume that $P_{ext}=P_{sys}$.
Thus, $\delta w = -PdV$
Hence, $dU + PdV = d(U + PV) = \delta q$
$$dH = \delta q$$

Here, we apply the equation above into the second law ($dS \geq \delta q / T$)

$dU \leq TdS$ (for const.-V) ⇨ $dH \leq TdS$ (for const.-P)

2.2.2. Gibbs energy

- definition ($22-2) -

A new state function, called Gibbs energy, is introduced as:

$$G \equiv H - TS = U + PV - TS = A + PV$$

Its differential is given as:

$$dG = d(H - TS) = dH - TdS - SdT$$

Here we consider the 1st law of a reversible const.-P process: $dU = TdS - PdV$

then $dH - TdS = (dU + PdV + VdP) - TdS = VdP = 0$ *[rev. const.-P]*

We additionally assume the process is constant-T:

$d(H - TS) = dH - TdS - SdT = dH - TdS = 0$ *[rev. const.-T const.-P]*

Hence, we have the following condition for reversible constant-T constant-P process.

$dG = d(H - TS) = 0$ *[rev. const.-T const.-P]*

*If we only assume constant-T or constant-P, Gibbs energy can be written as follows:

- ✓ *[Rev. const-P]* $dG = \cdots$
- ✓ *[Rev. const-T]* $dG = \cdots$

2.2.2. Gibbs energy

- definition ($22-2) -

A new state function, called Gibbs energy, is introduced as:

$$G \equiv H - TS = U + PV - TS = A + PV$$

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We additionally assume the process is constant-T:

$d(H - TS) = dH - TdS - SdT = dH - TdS = 0$ *[rev. const.-T const.-P]*

Hence, we have the following condition for reversible constant-T constant-P process.

$dG = d(H - TS) = 0$ *[rev. const.-T const.-P]*

*If we only assume constant-T or constant-P, Gibbs energy can be written as follows:

- ✓ *[Rev. const-P]* $dG = dH - TdS - SdT = (TdS + VdP) - TdS - SdT = -SdT$
- ✓ *[Rev. const-T]* $dG = dH - TdS - SdT = (TdS + VdP) - TdS - SdT = -PdV$

2.2.2. Gibbs energy

- criterion of reaction direction for const.-T const.-P system ($22-2) -

We consider a process in a const.-T const.-P system.

Gibbs energy is defined as:

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dH - TdS \leq 0 \quad \textit{[const.-P]}$$

where the equality holds for a reversible process and the inequality for an irreversible process.

In constant-T condition, the differential of Gibbs energy is written as:

$$dG = dH - TdS - SdT = dH - TdS \quad \textit{[quasi-static const.-T]}$$

If we introduce this relation into the equation to judge whether the process is reversible or irreversible:

$$dH - TdS = dG \leq 0 \quad \textit{[quasi-static const.-T const.-P]}$$

$$dG = d(H - TS) = 0 \quad \textit{[rev. const-T const.-P]}$$

Consequently, we have a criterion for const.-T const.-P system.

- ✓ $\mathrm{dG} < 0$ for a spontaneous process (irreversible process)
- ✓ $\mathrm{dG} = 0$ for an equilibrium state (reversible process)

2.2.2. Gibbs energy

-criterion of reaction direction for const.-T const.-P system ($22-2)-

Consequently, we have a criterion for const.-T const.-P system.

- ✓ $\mathrm{dG} < 0$ for a spontaneous process (irreversible process)
  - ✓ (Integral form) $\Delta\mathrm{G} = \Delta H - T\Delta S < 0$
- ✓ $\mathrm{dG} = 0$ for an equilibrium state (reversible process)
  - ✓ (Integral form) $\Delta\mathrm{G} = \Delta H - T\Delta S = 0$

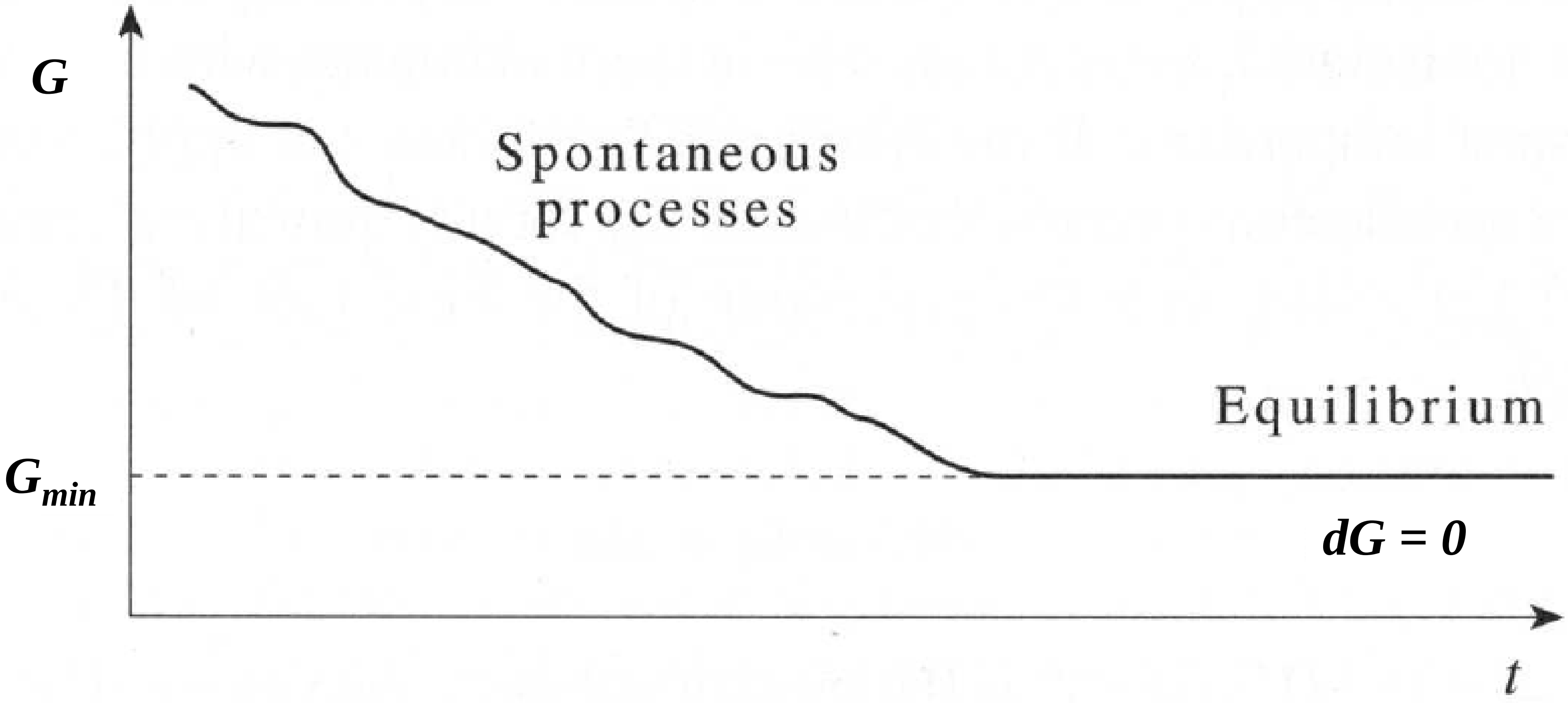
This result means that

- “a process of "$\Delta\mathrm{G} < 0$" takes place spontaneously in a system at constant T and P until it becomes "$\Delta\mathrm{G} = 0$" (thus, until *G* will be a minimum).
  - Ex-1) when $\Delta H < 0$ (some energy will be gained) and $\Delta S > 0$ (the system will be more disordered), $\Delta\mathrm{G}$ is clearly less than 0, and thus this process spontaneously takes place.
  - Ex-2) a process where ΔH and ΔS have the same signs, $\Delta\mathrm{G}$ gives a quantitative measure of whether is process is spontaneous or not. Basically, because of the factor of T in $\mathrm{T}\Delta S$ term, ΔH dominates at low temperatures while $\mathrm{T}\Delta S$ dominates at high temperatures.

***Be sure on the analogy between “U, A” for constant-volume and “H, G” for constant-pressure system/process.**

2.2.2. Gibbs energy

- criterion of reaction direction for const.-T const.-P system ($22-1) -



*textbook, figure 22.2

*This is for const.-T const.-P system.

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

2.2.2. Gibbs energy

- criterion of reaction direction for const.-T const.-P system ($22-2) -

A state function, Gibbs energy $(G = H - TS)$ behaves as below for a spontaneous process in a constant-pressure constant-temperature system: "$dG \leq 0$ (for constant T and P)"

As the differential is "$dG = dH - TdS - SdT$", if const.-T and const.-P are achieved, $\Delta G = \int dG = \int dH - \int TdS - \int SdT = \int dH - T\int dS = \Delta H - T\Delta S \leq 0$.
Hence, "$\Delta G = \Delta H - T\Delta S \leq 0$ (for constant T and P)" is the condition of integral form.

This criteria also means that

- "a process of "$\Delta G > 0$" does not take place spontaneously in a system at constant T and P". To advance a process of "$\Delta G > 0$", something such as work must be added to the system.

2.2.2. Gibbs energy

- criterion of reaction direction for const.-T const.-P system ($22-1) -

Here we consider a reversible isothermal process, then

$$\Delta G = \int dG = \int dH - \int TdS - \int SdT = \int dH - T\int dS = \Delta H - T\Delta S$$

Because the process is reversible,

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Thus, $\Delta \mathrm{G} = \Delta H - T\Delta S = \Delta H - q_{rev}$ (reversible isothermal)

According to the first law, we obtain

$\Delta \mathrm{G} = \Delta \mathrm{H} - q_{rev} = \Delta U + \Delta(PV) - q_{rev} = \Delta(PV) + w_{rev}$(reversible isothermal)

Then, if we consider P-V work and non-P-V with further assuming constant-P process,

$$\Delta \mathrm{G} = \Delta(PV) + w_{rev} = P\Delta V + w_{rev-PV} + w_{rev-non-PV} = w_{rev-non-PV}$$

(reversible cosnt-T const-P)

2.2.2. Gibbs energy

- criterion of reaction direction for const.-T const.-P system ($22-1) -

$\Delta G = w_{rev-non-PV}$ (reversible const.-T const.-P)

If $\Delta\mathrm{G} < 0$ and the process is of const.-T and const.-P,

- The process will occur spontaneously and $w_{rev-non-PV}$ represents the work that can be done by the system if this change is carried out reversibly.
  - This is, again, why we often call the Gibbs energy "free energy".
- If any irreversible process (like friction) is involved, the quantity of work will be less than $w_{rev-non-PV}$. Thus, this $w_{rev-non-PV}$ and ΔG represent the maximum work that could be obtained.

If $\Delta\mathrm{G} > 0$ and the process is of const.-T and const.-P,

- The process will not occur spontaneously and $w_{rev-non-PV}$ represents the work that must be done on the system to make this change in a reversible manner.
- If any irreversible processes are involved, more work is needed. Thus this $w_{rev-non-PV}$ and $\Delta\mathrm{G}$ represent the minimum work that are needed to make this change progress.

2.2.2. Gibbs energy
- examples for how to determine the reaction direction-

(Example-1) A chemical reaction "NH_3 (g) + HCl (g) NH_4Cl (s)"

- ✓ We consider this reaction under constant-T (298.15 K) and constant-P (1 bar = $1\text{x}10^5$ Pa) condition.

- ✓ In this reaction at 298.15 K and 1 bar,

$$\Delta_r H = -176.2 \text{ kJ} \qquad\qquad \Delta_r S = -0.285 \text{ kJ } K^{-1}.$$

- ✓ Hence, this reaction at 298.15 K holds

$$\Delta_r G = \Delta_r H - T\Delta_r S = -91.21 \text{ kJ}.$$

- ✓ Therefore, …..

Quiz

(Example-1) A chemical reaction “NH_3 (g) + HCl (g) NH_4Cl (s)”

- ✓ We consider this reaction under constant-T (298.15 K) and constant-P (1 bar = 1x10^5 Pa) condition.

- ✓ In this reaction at 298.15 K and 1 bar,

$$\Delta_r H = -176.2\ \mathrm{kJ} \qquad\qquad \Delta_r S = -0.285\ \mathrm{kJ}\ K^{-1}.$$

<Quiz-1> At which temperature, the reaction proceeds from right to left under constant-T and constant-P (1x10^5 Pa) condition?

<Quiz-2> If the system is isolated, which direction the reaction should proceed?

Quiz

(Example-1) A chemical reaction "NH_3 (g) + HCl (g) NH_4Cl (s)"

✓ We consider this reaction under constant-T (298.15 K) and constant-P (1 bar = $1\text{x}10^5$ Pa) condition.

✓ In this reaction at 298.15 K and 1 bar,

$$\Delta_r H = -176.2\ \text{kJ} \qquad \Delta_r S = -0.285\ \text{kJ}\ K^{-1}.$$

<Quiz-1> At which temperature, the reaction proceeds from right to left?

✓ To make it, $\Delta_r G > 0$ need to be achieved.

✓ Then,

$$\Delta_r G = \Delta_r H - T\Delta_r S = -176.2\ + 0.285 \times \mathrm{T} < 0$$

$$\mathrm{T} > 618\ \mathrm{K}$$

<Quiz-2> If the system is isolated, which direction the reaction should proceed?

✓ Because $dS > 0$ is the criteria, the process spontaneously proceeds from the right to the left.

2.2.2. Gibbs energy
- examples for how to determine the reaction direction-

(Example-2) A vaporization "H_2O (l) → H_2O (g)"

- ✓ The molar Gibbs energy of vaporization ($\Delta_{vap}\bar{G}$) is:

$$\Delta_{vap}\bar{G} = \bar{G}[H_2O(g)] - \bar{G}[H_2O(l)] = \Delta_{vap}\bar{H} - T\Delta_{vap}\bar{S}$$

- ✓ $\Delta_{vap}\bar{H} = 40.65\ kJ\ mol^{-1}$ and $\Delta_{vap}\bar{S} = 108.9\ J\ K^{-1}\ mol^{-1}$ at 1 bar (1x10^5 Pa) near 373.15 K (100ºC). Thus,

$$\Delta_{vap}\bar{G} = 40.65 - T \times 0.1089\ \ \mathrm{k}J\ mol^{-1}$$

  - ➢ If $\mathrm{T} = 373.15\ K$,

$$\Delta_{vap}\bar{G} = \cdots$$

  - ➢ If $\mathrm{T} = 363\ K$ (slightly lower than the normal melting point),

$$\Delta_{vap}\bar{G} = \cdots$$

  - ➢ If $\mathrm{T} = 383\ K$ (slightly higher than the normal melting point),

$$\Delta_{vap}\bar{G} = \cdots$$

2.2.2. Gibbs energy
- examples for how to determine the reaction direction-

(Example-2) A vaporization "H_2O (l) → H_2O (g)"

- ✓ The molar Gibbs energy of vaporization ($\Delta_{vap}\bar{G}$) is:

$$\Delta_{vap}\bar{G} = \bar{G}[H_2O(g)] - \bar{G}[H_2O(l)] = \Delta_{vap}\bar{H} - T\Delta_{vap}\bar{S}$$

- ✓ $\Delta_{vap}\bar{H} = 40.65\ kJ\ mol^{-1}$ and $\Delta_{vap}\bar{S} = 108.9\ J\ K^{-1}\ mol^{-1}$ at 1 bar (1x10^5 Pa) near 373.15 K (100ºC). Thus,

$$\Delta_{vap}\bar{G} = 40.65 - T \times 0.1089\ \ \mathrm{k}J\ mol^{-1}$$

- ➢ If $\mathrm{T} = 373.15\ K$,

$$\Delta_{vap}\bar{G} = 40.65 - 373.15 \times 108.9 = 0\ kJ\ mol^{-1}$$

which means the transfer of 1 mole liquid water to water vapor is a reversible process at 373.15 K at 1x10^5 Pa.

- ➢ If $\mathrm{T} = 363\ K$ (slightly lower than the normal melting point),

$$\Delta_{vap}\bar{G} = 40.65 - 363.15 \times 0.1089 = +1.12\ kJ\ mol^{-1}$$

which means the water vaporization is not spontaneous at 363 K at 1x10^5 Pa.

- ➢ If $\mathrm{T} = 383\ K$ (slightly higher than the normal melting point),

$$\Delta_{vap}\bar{G} = 40.65 - 383.15 \times 0.1089 = -1.06\ kJ\ mol^{-1}$$

which means the vaporization is spontaneous at 383 K at 1x10^5 Pa.

2.2.2. Gibbs energy
- examples for how to determine the work to be obtained/required-

(Example-3: a case of "$\Delta G < 0$“) Combustion of H_2

H_2 (g) + ½ O_2 (g)→ H_2O (l) @298.15 K and 1 bar (1×10^5 Pa)

- ✓ $\Delta_r G = -237.1\ kJ\ mol^{-1}$ at 298.15 K and 1×10^5 Pa.
- ✓ Thus, a maximum of -237.1 kJ mol^{-1} of usual work (excluding reversible P-V work) can be obtained from this spontaneous reaction.
- ✓ If some energies are irreversibly transferred and thus causing temperature increase (e.g. friction), we cannot reconvert some of it to “usual work”, due to the second law.

(Example-4: a case of "$\Delta G > 0$“) Decomposition of H_2O

H_2O (l) → H_2 (g) + ½ O_2 (g) @298.15 K and 1 bar (1×10^5 Pa)

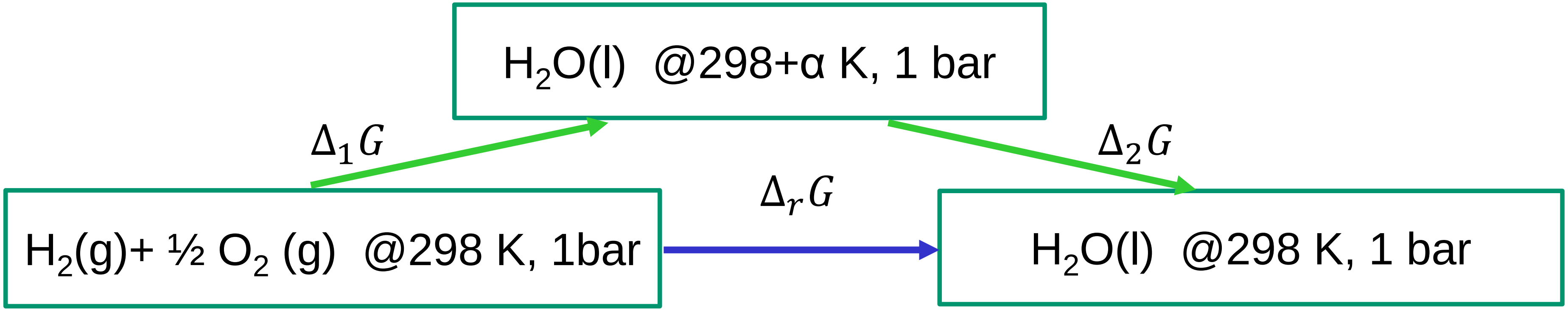
- ✓ As the opposite reaction of H_2 combustion, $\Delta_r G = 237.1\ kJ\ mol^{-1}$ at 298.15 K and 1×10^5 Pa.
- ✓ Thus, it would require at least 237.1 kJ mol^{-1} of energy to drive this (nonspontaneous) reaction.
- ✓ If some non-reversible processes are involved (certainly involved in practice), some additional energy to 237.1 kJ mol^{-1} have to be put on the system.

2.2.2. Gibbs energy
- examples for how to determine the work to be obtained/required-

(Example-3: a case of "$\Delta G < 0$") Combustion of H_2

H_2 (g) + ½ O_2 (g)→ H_2O (l) @298.15 K and 1 bar (1x10^5 Pa)

- ✓ $\Delta_r G = -237.1\ kJ\ mol^{-1}$ at 298.15 K and 1x10^5 Pa.
- ✓ Thus, a maximum of -237.1 kJ mol^{-1} of usual work (excluding the reversible P-V work) can be obtained from this spontaneous reaction.



H_2O(l) @298+α K, 1 bar

$\Delta_1 G$

$\Delta_2 G$

$\Delta_r G$

H_2(g)+ ½ O_2 (g) @298 K, 1bar

H_2O(l) @298 K, 1 bar

- ✓ As the Gibbs energy is a state function, $\Delta_r G = \Delta_1 G + \Delta_2 G$
- ✓ We cannot take $\Delta_r G$ work from this reaction, because some irreversible processes should be involved.
  - ✓ Combustion explosively occurs in general, which is far away from reversible process where process should go slowly and the system is always at some equilibrium state.

2.2.2. Gibbs energy

- examples for how to determine the work to be obtained/required-

(Example-1: a case of "$\Delta G < 0$") Combustion of H_2

H_2 (g) + ½ O_2 (g)→ H_2O (l)   @298.15 K and 1 bar (1x10^5 Pa)

- ✓ $\Delta_r G = -237.1\ kJ\ mol^{-1}$ at 298.15 K and 1x10^5 Pa.

✓ We may take some electrical energy out of the chemical energy by

- ➢ [(2) directly to electrical energy] using a fuel cell.

  "$H_2 \rightarrow 2H^+ + 2e^-$" (anode)   &   "$2H^+ + ½\ O_2 + 2e^- \rightarrow H_2O$ (cathode)

  *theoretical efficiency = $\Delta G/\Delta H$ = $(\Delta H - T\Delta S)/\Delta H$

Contents of today

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2.1. Equilibrium theory: Introduction

- #. Short introduction on what we are learning
- 2.1.1. Direction of system evolution
- 2.1.2. Meaning of entropy in microscopic scale
- 2.1.3. Summary of processes

<Today's class>

2.2. Equilibrium theory: free energy

- 2.2.1. Helmholtz energy
- 2.2.2. Gibbs energy
- **2.2.3. Maxwell relations and some useful formula**

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Helmholtz energy ($22.2)-

As an example, a “Maxwell relation” for Helmholtz energy (A) is given here.

Differential equation of Helmholtz energy ($\mathrm{A} = U - TS$) is:

$$dA = dU - TdS - SdT$$

Considering a process along a reversible path, the first and second laws are:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Hence,

$$dA = -PdV - SdT$$

Here, we can compare it with the total differential of $\mathrm{A} = A(V,T)$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \text{ , then}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \text{ and } \left(\frac{\partial A}{\partial T}\right)_V = -S$$

Since, the cross derivatives are equal as:

$$\left(\frac{\partial^2 A}{\partial T \partial V}\right) = \left(\frac{\partial^2 A}{\partial V \partial T}\right) \text{ , then}$$

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

(Appendix) cross derivatives -

We consider a case of F for “F is a function of x and y, namely $F = F(x, y)$”

$$
\begin{aligned}
\left(\frac{\partial^2 F}{\partial y \partial x}\right) &= \frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right) = \frac{\partial}{\partial y}\left[\frac{F(x+\Delta x, y) - F(x, y)}{\Delta x}\right] \\
&= \left\{\left[\frac{F(x+\Delta x, y+\Delta y) - F(x, y+\Delta y)}{\Delta x}\right] - \left[\frac{F(x+\Delta x, y) - F(x, y)}{\Delta x}\right]\right\} / \Delta y \\
&= \left\{\left[\frac{F(x+\Delta x, y+\Delta y) - F(x+\Delta x, y)}{\Delta y}\right] - \left[\frac{F(x, y+\Delta y) - F(x, y)}{\Delta y}\right]\right\} / \Delta x \\
&= \frac{\partial}{\partial x}\left[\frac{F(x, y+\Delta y) - F(x, y)}{\Delta y}\right] = \frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right) = \left(\frac{\partial^2 F}{\partial x \partial y}\right)
\end{aligned}
$$

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Helmholtz energy ($22.2)-

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

This kind of equation, which is obtained by the second cross partial derivatives of A (U, H, and G, as well) is called a Maxwell relation.

Indeed, Maxwell relation give us a useful equations.
For example, here, we assume a constant temperature process, then:

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{(constant T)}$$

- If we know a P-V-T data, such as the equation of state, this is easily utilized to determine *S*.
    - For an ideal gas, for example,

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)\right)_V dV = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR\ln\frac{V_2}{V_1}$$

(*constant T)

- If V_1 is very large, a gas behaves as an ideal gas. So, we can evaluate ΔS in reference to $S^{ideal\text{-}gas}$ value.

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Gibbs energy ($22.2)-

Here, we consider the Maxwell relation for Gibbs energy (G).

Differential equation of Gibbs energy ($G = U - TS + PV$) is:

$$dG = dU - TdS - SdT + PdV + VdP$$

Considering a process along a reversible path, the first and second laws are:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Hence,

$$dG = -SdT + VdP$$

Here, we can compare it with the total derivative of $G = G(T, P)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \quad , \quad \text{then}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

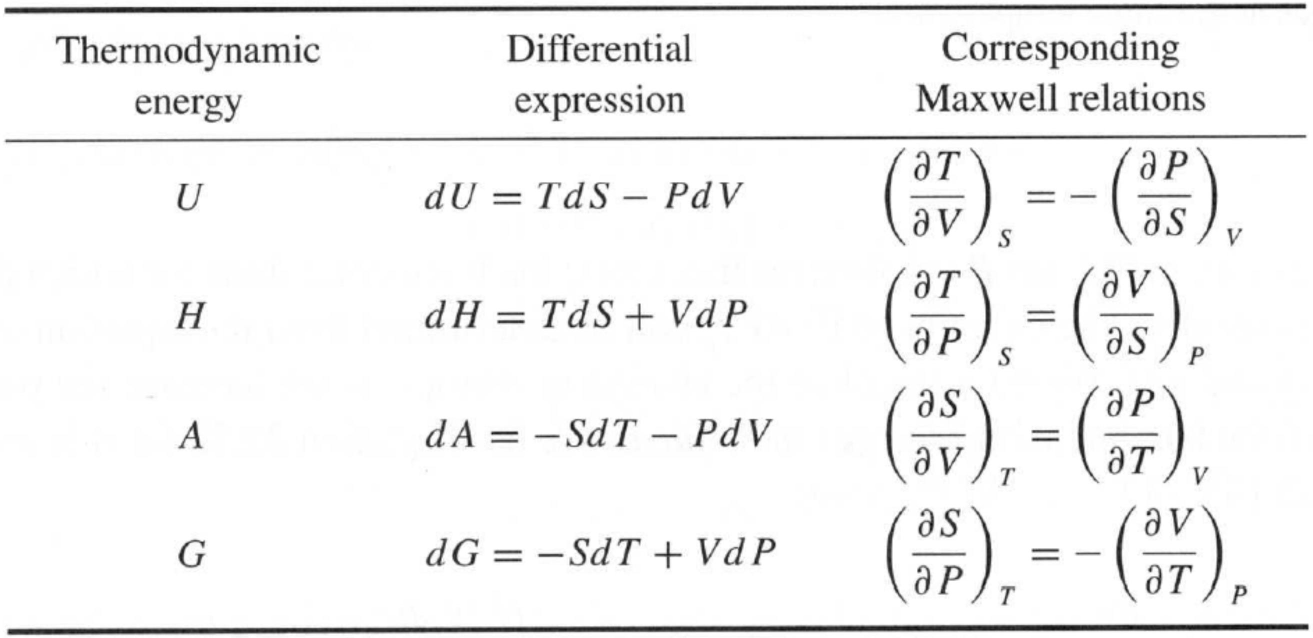
Since, the cross derivatives are equal as:

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

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

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations ($22.2)-

- ✓ Likewise, the four principal thermodynamic energies (*U, H, A, G*), have natural independent variables and then Maxwell relations as follows.
- ✓ These differential expression were derived only according to the first & second laws and considering a reversible path.
  - ✓ Even for non-equilibrium states and/or for irreversible processes, as far as thermodynamic quantities are definitely determined at around the concerned state, these relations are applicable because they are about state functions.



Thermodynamic energy	Differential expression	Corresponding Maxwell relations
U	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
H	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
A	$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
G	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

2.2.3. Maxwell relations and some useful formulas
- Maxwell relations for Gibbs energy ($22.2)-

The meaning of “natural independent variables” is given for U as example.

Considering a process along a reversible path, the first and second laws are:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Here, the variables of U are S and V.

However, if we wish, we can use T and V as the variables of U, for example:

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

In comparison,

$$dU = TdS - PdV$$

is apparently more simple. Thus we consider S and V are “natural independent variables” for U.

2.2.3. Maxwell relations and some useful formulas
- some useful formulas from Maxwell relations ($22.7)-

Similarly, we can derive several useful equations.

(1) A equation which plays a central role in chemical equilibria involving gas-phase reactions.

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{then} \quad \Delta G = \int_{P_1}^{P_2} V dP \quad \text{(constant T)}$$

For 1 mole of an ideal gas (constant T),

$$\Delta\bar{G} = RT\int_{P_1}^{P_2} \frac{dP}{P} = RT\ln\frac{P_2}{P_1}$$

$$\bar{G} = G°(T) + RT\ln\left(\frac{P}{1\ bar}\right)$$

Here, $G°(T)$ is called the standard molar Gibbs energy.

It is the Gibbs energy of 1 mole of the ideal gas at a pressure of 1 bar at T K, which is called "standard state".

*1 bar = 1x10^5 Pa

2.2.3. Maxwell relations and some useful formulas
- some useful formulas from Maxwell relations ($22.7)--

Similarly, we can derive several useful equations.

(2) A equation (called Gibbs-Helmholtz equation) which is used to derive an equation for the temperature dependence of an equilibrium constant.

$G = H - TS$ then $\frac{G}{T} = \frac{H}{T} - S$

By differentiating partially with respect to T keeping P fixed:

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

As $C_P(T) = (\partial H/\partial T)_P = T(\partial S/\partial T)_P$,

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$$

This equation can be directly applied to any process, in which case it is:

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$