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LECTURE-SECOND & THIRD LAW OF THERMODYNAMICS  
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## Second Law of thermodynamics

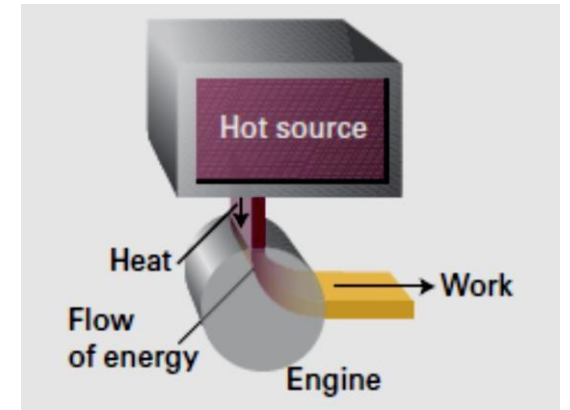
The recognition of two classes of process, **spontaneous and non-spontaneous**, is summarized by the **Second Law of thermodynamics**. This law may be expressed in a variety of equivalent ways. One statement was formulated by Kelvin:

*No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.*

- The First Law uses the **internal energy** to identify *permissible* changes;
- the Second Law uses the **entropy** to identify the *spontaneous changes* among those permissible changes.
- The Second Law of thermodynamics can be expressed in terms of the entropy as follows:
- *The entropy of an isolated system increases in the course of a spontaneous change:*

$$\Delta S_{tot} > 0$$

where  $S_{tot}$  is the total entropy of the system and its surroundings. Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy.



**Fig 1:** The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change.

### (a) The thermodynamic definition of entropy

The thermodynamic definition of entropy is based on the expression

$$dS = \frac{dq_{rev}}{T} \longrightarrow (1)$$

where  $q_{rev}$  is the heat supplied reversibly. For a measurable change between two states i and f this expression integrates to

$$\Delta S = 1/T \int_i^f dq_{rev} \longrightarrow (2)$$

According to eqn (2), when the energy transferred as heat is expressed in joules and the temperature is in kelvins, the **units of entropy are joules per kelvin ( $J K^{-1}$ )**. Entropy is an **extensive** property. Molar entropy, the entropy divided by the amount of substance, is expressed in joules per kelvin per mole ( $J K^{-1} mol^{-1}$ ). Molar entropy is an **intensive** property.

#### *Calculation of entropy change for the isothermal expansion of a perfect gas:*

Suppose we have to calculate the entropy change of a sample of perfect gas when it expands **isothermally** from a volume  $V_i$  to a volume  $V_f$ .

The energy absorbed as heat during a reversible isothermal expansion of a perfect gas can be calculated from  $\Delta U = q + w$  and  $\Delta U = 0$ , which implies that  $q = -w$  in general and therefore that  $q_{rev} = -w_{rev}$  for a reversible change.

Because the temperature is constant, eqn (2) becomes

$$\Delta S = 1/T \int_i^f dq_{rev} = q_{rev}/T \longrightarrow (3)$$

$$q_{rev} = -w_{rev} = nRT \ln V_f/V_i \longrightarrow (4)$$

It follows that

$$\boxed{\Delta S = nR \ln \frac{V_f}{V_i}} \longrightarrow (5)$$

When the volume occupied by 1.00 mol of any perfect gas molecules is doubled at any constant temperature,  $V_f/V_i = 2$  and  $\Delta S = (1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln 2 = +5.76 \text{ J K}^{-1}$ .

**Example 3:** Calculate the change in entropy when the pressure of a fixed amount of perfect gas is changed isothermally from  $p_i$  to  $p_f$ . What is this change due to?

**(b) Entropy change of the surroundings**

$$dS_{sur} = \frac{dq_{sur}}{T_{sur}}$$

Furthermore, because the temperature of the surroundings is constant whatever the change, for a measurable change

$$\Delta S_{sur} = \frac{q_{sur}}{T_{sur}}$$

Since for any adiabatic change,  $q_{sur} = 0$ ;

*Hence, for an adiabatic change:  $\Delta S_{sur} = 0$*

**Example 4:** Calculate the entropy change in the surroundings when 1.00 mol  $\text{H}_2\text{O}(\text{l})$  is formed from its elements under standard conditions at 298 K, we use  $\Delta H^\circ = -286 \text{ kJ/mol}$ .

**Ans :** The energy released as heat is supplied to the surroundings, now regarded as being at constant pressure, so  $q_{sur} = +286 \text{ kJ}$ .  $\Delta S_{sur} = 2.86 \times 10^5 \text{ J/298 K} = 960 \text{ JK}^{-1}$ .

**Example 5:** Calculate the entropy change in the surroundings when 1.00 mol  $\text{N}_2\text{O}_4(\text{g})$  is formed from 2.00 mol  $\text{NO}_2(\text{g})$  under standard conditions at 298 K. ( $\Delta H^\circ = -9.16 \text{ kJ/mol}$ ).

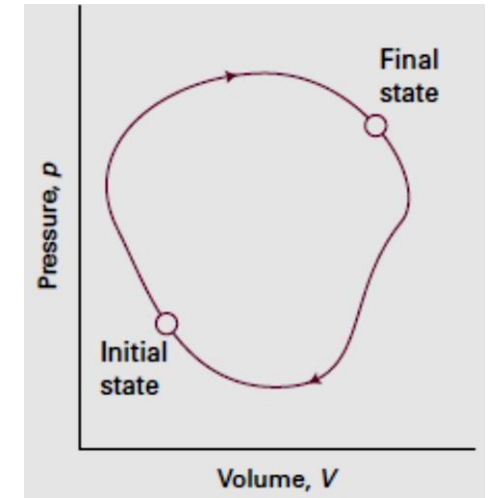
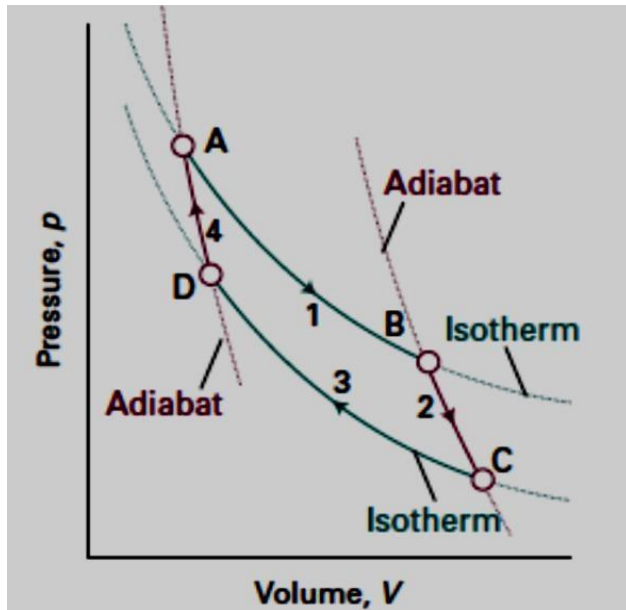
### (c) The entropy as a state function

Entropy is a state function. To prove this, we need to show that the integral of  $dS$  is independent of path.

$$\oint \frac{dq_{rev}}{T_{surr}} = 0 \longrightarrow (6)$$

where the symbol  $\oint$  denotes integration around a closed path. There are three steps in the argument:

A **Carnot cycle**, which is named after the French engineer Sadi Carnot, consists of **four reversible stages**.



**Fig. 2:** In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.

**Fig. 3:** The basic structure of a Carnot cycle: In **Step 1**, there is an **isothermal reversible expansion** at the temperature  $T_h$ . **Step 2** is a **reversible adiabatic expansion** in which the temperature falls from  $T_h$  to  $T_c$ . In **Step 3** there is an **isothermal reversible compression** at  $T_c$ , and that isothermal step is followed by an **adiabatic reversible compression**, which restores the system to its initial state.

1. **Reversible isothermal expansion** from A to B at  $T_h$ ; the entropy change is  $q_h/T_h$ , where  $q_h$  is the energy supplied to the system as heat from the hot source.

$$q_h = nRT_h \ln V_B/V_A \longrightarrow (7)$$

2. **Reversible adiabatic expansion** from B to C. No energy leaves the system as heat, so the change in entropy is zero.

In the course of this expansion, the temperature falls from  $T_h$  to  $T_c$ , the temperature of the cold sink.

$$V_C T_c^c = V_B T_h^c \longrightarrow (8)$$

3. **Reversible isothermal compression** from C to D at  $T_c$ . Energy is released as heat to the cold sink; the change in entropy of the system is  $q_c/T_c$ ; in this expression  $q_c$  is negative.

$$q_c = nRT_c \ln V_D/V_C \longrightarrow (9)$$

4. **Reversible adiabatic compression** from D to A. No energy enters the system as heat, so the change in entropy is zero. The temperature rises from  $T_c$  to  $T_h$ .

$$V_A T_h^c = V_D T_c^c \longrightarrow (10)$$

Multiplying equations (8) and (10)

$$V_C V_A T_h^c T_c^c = V_B V_D T_c^c T_h^c$$

which, on cancellation of the temperatures, simplifies to

$$V_A/V_B = V_D/V_C$$

With this relation established, we can write

$$q_c = nRT_c \ln V_D/V_C = nRT_c \ln V_A/V_B = -nRT_c \ln V_B/V_A$$

Thus,

$$\frac{q_h}{q_c} = - \frac{nRT_h \ln \frac{V_B}{V_A}}{nRT_c \ln \frac{V_B}{V_A}}$$

$$\frac{q_h}{q_c} = - \frac{T_h}{T_c} \longrightarrow (11)$$

The total change in entropy around the cycle is the sum of the changes in each of these four steps:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0 \longrightarrow (12)$$

(as  $\frac{q_h}{T_h} = -\frac{q_c}{T_c}$  and change in entropy is zero in both Step-2 and Step-4).



the **efficiency**,  $\eta$  (eta), of a heat engine:

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from hot source}} = |w|/|q|_h \longrightarrow (13)$$

The energy supplied as work by the engine is the **difference** between the energy supplied as heat by the hot reservoir and returned to the cold reservoir:

$$\eta = \frac{|q_h| - |q_c|}{|q_h|} = 1 - \frac{|q_c|}{|q_h|} \longrightarrow (14)$$

It follows from eqn (11),

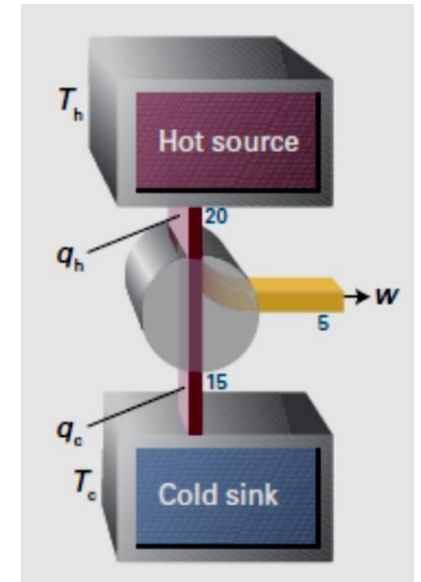
$$\eta = 1 - \frac{T_c}{T_h} \quad \boxed{\text{Carnot efficiency}} \longrightarrow (15)$$

**The second law of thermodynamics implies that *all reversible engines have the same efficiency regardless of their construction.***

#### (d) The thermodynamic temperature

Suppose we have an engine that is working reversibly between a hot source at a temperature  $T_h$  and a cold sink at a temperature  $T$ , then we know from eqn (15) that

$$T = (1 - \eta)T_h \longrightarrow (16)$$



**Fig 4:** Suppose an energy  $q_h$  is supplied to the engine and  $q_c$  is lost from the engine and discarded into the cold reservoir. The work done by the engine is equal to  $q_h + q_c$ . The efficiency is the work done divided by the energy supplied as heat from the hot source.

### (e) Entropy Changes Accompanying Specific Processes

The change in entropy of a perfect gas that expands isothermally from  $V_i$  to  $V_f$  is

$$\Delta S = nR \ln V_f/V_i$$

Because  $S$  is a **state function**, the value of  $\Delta S$  of the system is **independent of the path** between the initial and final states, so this expression applies whether the change of state occurs **reversibly or irreversibly**.

The **total change in entropy**, however, does depend on how the expansion takes place. For any process, the energy lost as heat from the system is acquired by the surroundings, so  $dq_{\text{sur}} = -dq$ . For a reversible change ( $q_{\text{rev}} = nRT \ln(V_f/V_i)$ ); consequently, from eqn (3)

$$\Delta S_{\text{sur}} = q_{\text{sur}}/T = -q_{\text{rev}}/T = -nR \ln V_f/V_i \longrightarrow (17)$$

$$\Delta S_{\text{tot}} = 0 \text{ (for a reversible process)}$$

If, on the other hand, the isothermal expansion occurs freely ( $w = 0$ ), then  $q = 0$  (because  $\Delta U = 0$ ).

Consequently,

$\Delta S_{\text{sur}} = 0$ , and the total entropy change is given by eqn itself:

$$\Delta S_{\text{tot}} = nR \ln V_f/V_i \longrightarrow (18)$$

$$\Delta S_{\text{tot}} > 0 \text{ (for an irreversible process)}$$

## (f) Phase transition

Consider a system and its surroundings at the **normal transition temperature**,  $T_{\text{trs}}$ , the temperature at which two phases are in equilibrium at 1 atm.

At the **transition temperature**, any transfer of energy as heat between the system and its surroundings is **reversible** because the two phases in the system are in **equilibrium**. Because at constant pressure  $q = \Delta_{\text{trs}}H$ , the change in molar entropy *of the system* is

$$\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}}$$

Entropy of  
phase transition

 $\longrightarrow$  (19)

- If the phase transition is **exothermic** ( $\Delta_{\text{trs}}H < 0$ , as in freezing or condensing), then the entropy change of the system is **negative**.
- If the transition is **endothermic** ( $\Delta_{\text{trs}}H > 0$ , as in melting and vaporization), then the entropy change of the system is **positive**.

## Third Law of thermodynamics

- The **Nernst heat theorem** implies the Third Law of thermodynamics.
- The Third Law allows us to define **absolute entropies** of substances and the **standard entropy** of a reaction. At  $T = 0$ , all energy of thermal motion is **quenched**, and in a perfect crystal all the atoms or ions are in a regular, uniform array. **The localization of matter and the absence of thermal motion** suggest that such materials also have zero entropy. The observation that the entropy of a regular array of molecules is zero at  $T = 0$  is summarized by the **Nernst heat theorem**:

*The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero:  $\Delta S \rightarrow 0$  as  $T \rightarrow 0$  provided all the substances involved are perfectly ordered.*

It follows from the Nernst theorem that, if we ascribe the value zero to the entropies of elements in their perfect crystalline form at  $T = 0$ , then all perfect crystalline compounds also have zero entropy at  $T = 0$ . This conclusion is summarized by the **Third Law of thermodynamics**:

*The entropy of all perfect crystalline substances is zero at  $T = 0$ .*

If  $S > 0$  at  $T = 0$ , we say that the substance has a **residual entropy**. Ice has a residual entropy of  $3.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . It arises from the **arrangement of the hydrogen bonds between neighbouring water molecules**: a given  $-\text{O}-$  atom has two short  $\text{O}-\text{H}$  bonds and two long  $\text{O}-\text{H}$  bonds to its neighbours, but there is a degree of randomness in which two bonds are short and two are long.

### **Third-Law entropies**

Entropies reported on the basis that  $S(0) = 0$  are called **Third-Law entropies**. When the substance is in its standard state at the temperature  $T$ , the **standard (Third-Law) entropy** is denoted  $S^\theta(T)$ .

The **standard reaction entropy**,  $S^\ominus(T)$ , is defined as the difference between the molar entropies of the pure, separated products and the pure, separated reactants; all substances being in their standard states at the specified temperature:

$$\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus \longrightarrow (20)$$

**Example 6 :** Calculate the standard reaction entropy of  $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$  at  $25^\circ\text{C}$ .

$$\begin{aligned} \Delta_r S^\ominus &= S_m^\ominus(\text{H}_2\text{O}, \text{l}) - \{S_m^\ominus(\text{H}_2, \text{g}) + 1/2 S_m^\ominus(\text{O}_2, \text{g})\} = 69.9 \text{ J K}^{-1} \text{ mol}^{-1} - \{130.7 + 1/2(205.0)\} \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -163.4 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

**Example 7 :** Calculate the standard reaction entropy for the combustion of methane to carbon dioxide and liquid water at  $25^\circ\text{C}$ .

Compound	$S_m^\ominus / (\text{J K}^{-1} \text{ mol}^{-1})$
Water, $\text{H}_2\text{O}(\text{l})$	69.9
Methane, $\text{CH}_4(\text{g})$	186.3
Carbon dioxide, $\text{CO}_2(\text{g})$	213.7
Hydrogen, $\text{H}_2(\text{g})$	130.7
Oxygen, $\text{O}_2(\text{g})$	205.0

## The Clausius inequality

More work is done when a change is **reversible than when it is irreversible**. That is,  $|dw_{\text{rev}}| \geq |dw|$ . Because  $dw$  and  $dw_{\text{rev}}$  are negative when energy leaves the system as work, this expression is the same as  $-dw_{\text{rev}} \geq -dw$ , and hence  **$dw - dw_{\text{rev}} \geq 0$** .

$$dU = dq + dw = dq_{\text{rev}} + dw_{\text{rev}}$$

It follows that  **$dq_{\text{rev}} - dq = dw - dw_{\text{rev}} \geq 0$** , or  **$dq_{\text{rev}} \geq dq$** , and therefore that  **$dq_{\text{rev}}/T \geq dq/T$** . Now using the thermodynamic definition of the entropy ( $dS = dq_{\text{rev}}/T$ )

$$\boxed{dS \geq dq/T}$$

—————→ (21)

This expression is known as the **Clausius inequality**.

## Criteria for spontaneity

If we consider heating at constant volume, then **in the absence of non-expansion work**, we can write  $dq_V = dU$  and placing that in eqn (21) we get,

$$dS - dU/T \geq 0 \quad \text{—————→ (22)}$$

$$\mathbf{TdS \geq dU} \text{ (constant } V, \text{ no additional work)} \quad \text{—————→ (23)}$$

This is the criterion for **spontaneous change in terms of the state functions** of the system.

At either constant internal energy ( $dU = 0$ ) or constant entropy ( $dS = 0$ ), this expression becomes, respectively,

$$\mathbf{dS_{U,V} \geq 0} \quad \mathbf{dU_{S,V} \leq 0} \quad \text{—————→ (24)}$$

When energy is transferred as heat at constant pressure, and there is no work other than expansion work, we can write  $dq_p = dH$  and obtain

$$TdS \geq dH \text{ (constant } p, \text{ no additional work)} \longrightarrow (25)$$

(because,  $dH = dq + Vdp$ )

At either constant enthalpy or constant entropy this inequality becomes, respectively,

$$dS_{H,p} \geq 0 \qquad dH_{S,p} \leq 0 \longrightarrow (26)$$

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). Alternatively, the enthalpy must decrease if the entropy of the system is constant.

Because eqns (23) and (25) have the forms  $dU - TdS \leq 0$  and  $dH - TdS \leq 0$ , respectively, they can be expressed more simply by introducing two more thermodynamic quantities. One is the **Helmholtz energy**,  $A$ , which is defined as

$$A = U - TS$$

The other is the **Gibbs energy**,  $G$ :

$$G = H - TS$$



## Criteria for spontaneity

$$A = U - TS$$

$$G = H - TS$$

Definition of Helmholtz energy	→ (27)
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Definition of Gibbs energy	→ (28)
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When the state of the system changes at constant temperature, the two properties change as follows:

(a) $dA = dU - TdS$	(b) $dG = dH - TdS$	→ (29)
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When we introduce eqns (23) and (25), respectively, we obtain the criteria of spontaneous change as

$$TdS \geq dU \text{ (constant } V, \text{ no additional work)}$$

$$TdS \geq dH \text{ (constant } p, \text{ no additional work)}$$

(a) $dA_{T,V} \leq 0$	(b) $dG_{T,p} \leq 0$	→ (30)
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- A spontaneous process at **constant temperature and volume** is accompanied by a **decrease** in the **Helmholtz energy**.
- The change in the Helmholtz energy is equal to the maximum work accompanying a process at constant temperature.
- A spontaneous process at **constant temperature and pressure** is accompanied by a **decrease** in the **Gibbs energy**.
- The change in the Gibbs energy is equal to the maximum non-expansion work accompanying a process at constant temperature and pressure.

## Remarks on the Helmholtz energy

- A change in a system at constant temperature and volume is spontaneous, if  $dA_{T,V} \leq 0$  i.e., a change under these conditions is **spontaneous** if it corresponds to a **decrease** in the **Helmholtz energy**.
- The criterion of equilibrium, when neither the forward nor reverse process has a tendency to occur, is

$$dA_{T,V} = 0 \longrightarrow (31)$$

The expressions  $dA = dU - TdS$  and  $dA < 0$  are sometimes interpreted as follows:

- **A negative value of  $dA$  is favoured by a negative value of  $dU$  and a positive value of  $TdS$ .**
- **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.**

## Maximum work

*The change in the Helmholtz function is equal to the maximum work accompanying a process at constant temperature:*

$$dw_{\max} = dA \longrightarrow (32)$$

From the Clausius inequality  $dS \geq dq/T$ , we can write  $TdS \geq dq$

And with the First Law,  $dU = dq + dw$ , and obtain

$$dU \leq TdS + dw \quad (dU \text{ is smaller than the term of the right because we are replacing } dq \text{ by } TdS, \text{ which in general is larger.})$$

This expression rearranges to

$$dw \geq dU - TdS$$

It follows that the most negative value of  $dw$ , and therefore the maximum energy that can be obtained from the system as work, is given by

$$dw_{\max} = dU - TdS$$

Because at constant temperature  $dA = dU - TdS$ , we conclude that,  **$dw_{\max} = dA$ .**

When a macroscopic isothermal change takes place in the system

$$w_{\max} = \Delta A \quad \text{with} \quad \Delta A = \Delta U - T\Delta S.$$

## Remarks on the Gibbs energy

The criterion  $dG_{T,p} \leq 0$  i.e *at constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy* is most common in chemistry.

- Thus, **if  $G$  decreases** as the reaction proceeds, then the reaction has a **spontaneous tendency to convert the reactants** into products. If  $G$  increases, then the reverse reaction is spontaneous.
- For spontaneous **endothermic reactions**  $H$  increases,  $dH > 0$ . Because the reaction is spontaneous we know that  $dG < 0$  despite  $dH > 0$ ; it follows that **the entropy of the system increases 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 ( $dS_{\text{sur}} = -dH/T$  at constant pressure).

## Maximum non-expansion work

At constant temperature and pressure, the maximum additional (non-expansion) work,  $w_{\text{add,max}}$ , is given by the change in Gibbs energy:

$$dw_{\text{add,max}} = dG$$

$$w_{\text{add,max}} = \Delta G$$

—————→ (33)

Relation between  $G$  and  
maximum non-expansion work

### *Maximum non-expansion work*

Because  $H = U + pV$ , for a general change in conditions, the change in enthalpy is

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

The corresponding change in Gibbs energy ( $G = H - TS$ ) is

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

When the **change is isothermal we can set  $dT = 0$** ; then

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

When **the change is reversible,  $dw = dw_{\text{rev}}$  and  $dq = dq_{\text{rev}} = TdS$** , so for a reversible isothermal process

$$dG = TdS + dw_{\text{rev}} + d(pV) - TdS = dw_{\text{rev}} + d(pV)$$

The work consists of **expansion work, which for a reversible change is given by  $-pdV$** , and possibly some **other kind** of work (for instance, the electrical work of pushing electrons through a circuit or of raising a column of liquid); this additional work we denote  $dw_{\text{add}}$ . Therefore, with  $d(pV) = pdV + Vdp$ ,

$$dG = (-pdV + dw_{\text{add,rev}}) + pdV + Vdp = dw_{\text{add,rev}} + Vdp$$

If the change occurs **at constant pressure (as well as constant temperature)**, we can set  $dp = 0$  and obtain  $dG = dw_{\text{add,rev}}$ .

Therefore, at constant temperature and pressure,  **$dw_{\text{add,rev}} = dG$** .

Problem 1: 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<sup>-1</sup> mol<sup>-1</sup>. Glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(s)  $\Delta_r H^\circ$  (−2808 kJ mol<sup>-1</sup> )

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ .$$

**Answer:** Because the standard reaction enthalpy is −2808 kJ mol<sup>-1</sup>, it follows that the standard reaction Gibbs energy is

$$\Delta_r G^\circ = -2808 \text{ kJ mol}^{-1} - (310 \text{ K}) \times (259.1 \text{ J K}^{-1} \text{ mol}^{-1}) = -2888 \text{ kJ mol}^{-1}$$

Therefore,  $w_{\text{add,max}} = -2888 \text{ kJ}$  for the combustion of 1 mol glucose molecules, and the reaction can be used to do up to 2888 kJ of non-expansion work.

Problem 2: How much non-expansion work can be obtained from the combustion of 1.00 mol CH<sub>4</sub>(g) under standard conditions at 298 K? Use  $\Delta_r S^\circ = -243 \text{ J K}^{-1} \text{ mol}^{-1}$ . Methane CH<sub>4</sub>(g)  $\Delta_r H^\circ$  ( −890 kJ mol<sup>-1</sup> )

## Standard Molar Gibbs energies

Standard Gibbs energies of formation are used to calculate the **standard Gibbs energies of reactions**.

Standard entropies and enthalpies of reaction can be combined to obtain the **standard Gibbs energy of reaction** (or ‘standard reaction Gibbs energy’),  $\Delta_r G^\ominus$ :

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus \longrightarrow (34)$$

Procedure for calculating the standard Gibbs energy of reaction

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus \longrightarrow (35)$$

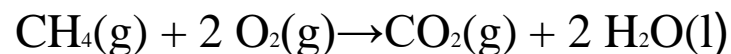
To calculate the standard Gibbs energy of the reaction  $\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$  at 25°C, we write  $\Delta_r G^\ominus = \Delta_f G^\ominus$

$$(\text{CO}_2, \text{g}) - \{\Delta_f G^\ominus(\text{CO}, \text{g}) + \Delta_f G^\ominus(\text{O}_2, \text{g})\}$$

$$= -394.4 \text{ kJ mol}^{-1} - \{(-137.2) + (0)\} \text{ kJ mol}^{-1}$$

$$= -257.2 \text{ kJ mol}^{-1}$$

Problem 3: Calculate the standard reaction Gibbs energy for the combustion of  $\text{CH}_4\text{(g)}$  at 298 K.



Compound	$\Delta_f G^\ominus / (\text{kJ mol}^{-1})$
Methane, $\text{CH}_4\text{(g)}$	-50.7
Carbon dioxide, $\text{CO}_2\text{(g)}$	-394.4
Water, $\text{H}_2\text{O(l)}$	-237.1
$\text{CO(g)}$	-137.17
$\text{O}_2\text{(g)}$	0

## Combination of the First and Second Laws

The fundamental equation, a **combination** of the First and Second Laws, is an expression for the change in internal energy that accompanies **changes in the volume and entropy** of a system.

The First Law of thermodynamics may be written  $dU = dq + dw$ .

For a **reversible change in a closed system** of constant composition, and in the absence of any additional (non-expansion) work,  $dw_{\text{rev}} = -pdV$  and (from the definition of entropy)  $dq_{\text{rev}} = TdS$ , where  $p$  is the pressure of the system and  $T$  its temperature.

Therefore, for a **reversible change in a closed system**,

$$dU = TdS - pdV$$

The fundamental equation  $\longrightarrow (36)$

*Eqn (36) applies to any change—reversible or irreversible—of a closed system that does no additional (non-expansion) work.* This combination of the First and Second Laws is called the **fundamental equation**.



## Properties of Gibbs Energy

(a) The Gibbs energy of a system is given by  $G = H - TS$

For infinitesimal changes in each property, we can write,

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

Because  $H = U + pV$ , we know that

$$dH = dU + d(pV) = dU + pdV + Vdp$$

and therefore

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

For a closed system doing no non-expansion work, we can replace  $dU$  by the **fundamental equation**  $dU = TdS - pdV$

and obtain

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

$$\mathbf{dG = Vdp - SdT} \longrightarrow (37)$$

This expression, which shows that a change in  $G$  is proportional to a change in  $p$  or  $T$ , suggests that  $G$  may be best regarded as a function of  $p$  and  $T$ . It may be regarded as the **fundamental equation of chemical thermodynamics**.

## The variation of the Gibbs energy with temperature

With the first relation,  $(\partial G/\partial T)_p = -S$ ,

If we can express it in terms of the enthalpy by using the definition of  $G$  to write  $S = (H - G)/T$ . Then

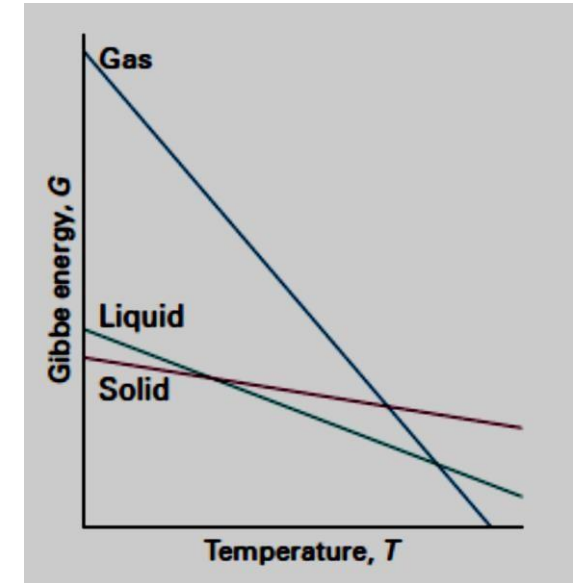
$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T}$$

→ (38)

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

→ (39)

This expression is called the **Gibbs–Helmholtz equation**.



The variation of the Gibbs energy with the temperature is determined by the entropy. Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is the smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

## The variation of $G$ with $T$ and $p$

$dG = Vdp - SdT$ , now gives

$$(\partial G / \partial T)_p = -S \quad \longrightarrow \quad (40)$$

$$(\partial G / \partial P)_T = V \quad \longrightarrow \quad (41)$$

These relations show how the **Gibbs energy varies with temperature and pressure**. The first implies that:

- Because  $S > 0$  for all substances,  **$G$  always decreases when the temperature is raised** (at constant pressure and composition).
- Because  $(\partial G / \partial T)_p$  becomes more negative as  $S$  increases,  **$G$  decreases most sharply when the entropy of the system is large. Therefore, the Gibbs energy of the gaseous phase of a substance, which has a high molar entropy, is more sensitive to temperature than its liquid and solid phases.**

Similarly, the second relation implies that:

- Because  $V > 0$  for all substances,  **$G$  always increases when the pressure of the system is increased** (at constant temperature and composition).
- Because  $(\partial G / \partial p)_T$  increases with  $V$ ,  **$G$  is more sensitive to pressure when the volume of the system is large.**

## The variation of the Gibbs energy with pressure

To find the Gibbs energy at one pressure in terms of its value at another pressure, the temperature being constant, we set  $dT = 0$  in eqn (37)\*, which gives  $dG = Vdp$ , and integrate:

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$$

For molar quantities

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m dp$$

Substituting  $V_m = RT/p$  into the integral, treat  $RT$  as the constant,

$$G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{1}{p} dp$$

$$G_m(p_f) = G_m(p_i) + RT \ln p_f/p_i \longrightarrow (42)$$

\* [eqn (37) is  $dG = Vdp - SdT$ ]

# Chemical potential

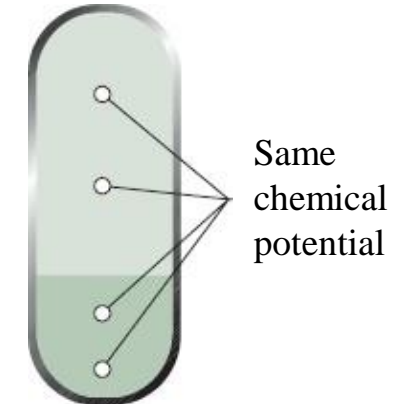
For a one-component system, ‘molar Gibbs energy’ and ‘chemical potential’ are synonyms, so  $\mu = G_m$ .  $\mu$  is a measure of the potential that a substance has for undergoing change in a system.

*At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.*

Criterion of  
Phase equilibrium

Consider a system in which the chemical potential of a substance is  $\mu_1$  at one location and  $\mu_2$  at another location. When an infinitesimal amount  $dn$  of the substance is transferred from one location to the other, the Gibbs energy of the system changes by  $-\mu_1 dn$  when material is removed from location 1, and it changes by  $+\mu_2 dn$  when that material is added to location 2. The overall change is therefore  $dG = (\mu_2 - \mu_1)dn$ .

If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in  $G$ , and so has a spontaneous tendency to occur. If  $\mu_1 = \mu_2$  then is the system at equilibrium.



When two or more phases are in equilibrium, the chemical Potential of a substance (and, in a mixture, a component) is the same in each phase and is the same at all points in each phase.

## Partial molar Gibbs energies

For a substance in a mixture, the chemical potential is *defined* as the partial molar Gibbs energy:

$$\mu_J = \left( \frac{\partial G}{\partial n_J} \right)_{p, T, n} \longrightarrow (1)$$

It follows that the total Gibbs energy of a binary mixture is

$$G = n_A \mu_A + n_B \mu_B \longrightarrow (2)$$

where  $\mu_A$  and  $\mu_B$  are the chemical potentials at the composition of the mixture. That is, **the chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture**. Because the chemical potentials depend on composition (and the pressure and temperature), the Gibbs energy of a mixture may change when these variables change, and, for a system of components A, B, etc., the equation  $dG = Vdp - SdT$  becomes

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots \longrightarrow (3)$$

This expression is the **fundamental equation of chemical thermodynamics**. At constant pressure and temperature, eqn simplifies to

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots \longrightarrow (4)$$

## The Gibbs–Duhem equation

Because the total Gibbs energy of a binary mixture is given by eqn (2) and the chemical potentials depend on the composition, when the compositions are changed infinitesimally we might expect  $G$  of a binary system to change by

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B \longrightarrow (5)$$

However, we have seen that at constant pressure and temperature, a change in Gibbs energy is given by eqn (4). Because  $G$  is a **state function**, these two equations must be **equal**, which implies that at constant temperature and pressure

$$n_A d\mu_A + n_B d\mu_B = 0 \longrightarrow (6)$$

This equation is a special case of the **Gibbs–Duhem equation**:

$$\sum_J n_J d\mu_J = 0$$

The significance of the Gibbs–Duhem equation is that **the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.**

Example 1: Calculate the expansion work done when 50 g of water is electrolyzed under constant pressure at 25°C.

2H<sub>2</sub>O → 2H<sub>2</sub> + O<sub>2</sub>

Total moles of H<sub>2</sub>O =  $\frac{50 \text{ g}}{18 \text{ g/mol}} = 2.7 \text{ moles}$

So, no. of moles of O<sub>2</sub> = 1.35  
" " " " H<sub>2</sub> = 2.7

Now, work done =  $-nRT$

$w(\text{O}_2) = -1.35 \times R \times 298$   
 $w(\text{H}_2) = -2.7 \times R \times 298$

Total work done =  $w(\text{O}_2) + w(\text{H}_2)$   
 $= -(4 \times 8.314 \times 298) \text{ J}$   
 $= -10.03 \text{ kJ}$



Example 2: Calculate the enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane.

	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	$\Delta_c H^\ominus / (\text{kJ mol}^{-1})$
Benzene, $\text{C}_6\text{H}_6(\text{l})$	+49.0	-3268
Cyclohexane		-3920

