

# **2nd Law of Thermodynamics**

## Ist Law of Thermodynamics:

- The different forms of energy are inter convertible.
- When one form of energy disappears an equivalent of another kind must appear. Conversion of energy.
- Energy can be transferred / transformed, keeping the total energy fixed.

$$q_{\text{sys}} = - q_{\text{surr}}$$

$$w_{\text{sys}} = - w_{\text{surr}}$$

$$\Delta U = q + w (= - p_{\text{ex}} dV)$$

$$\Delta U = q - p_{\text{ex}} dV$$

Incompleteness of Ist Law: **It Does not say anything about:**

- Whether any transfer / transformation of energy would **occur at all?**
- If it does, then in **which direction would the change occur?**
- If any transfer / transformation of energy occurs in a particular direction, then **how long will it be sustained?**
- If any transfer / transformation of energy occurs in a particular direction, then **how fast will it proceed?**

## First Law of Thermodynamics

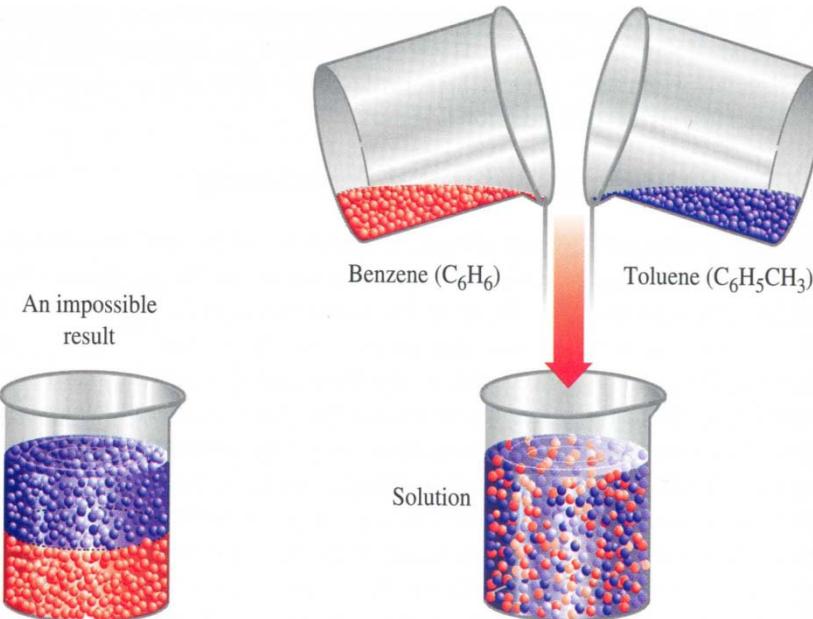
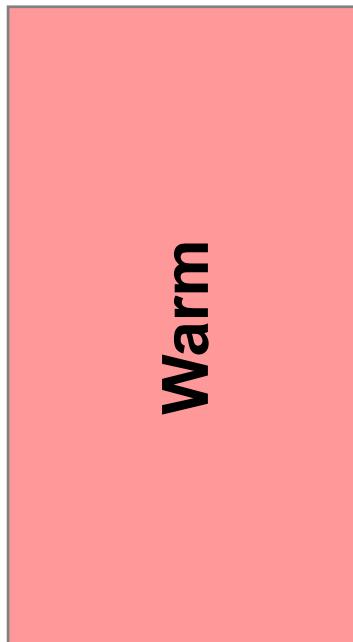
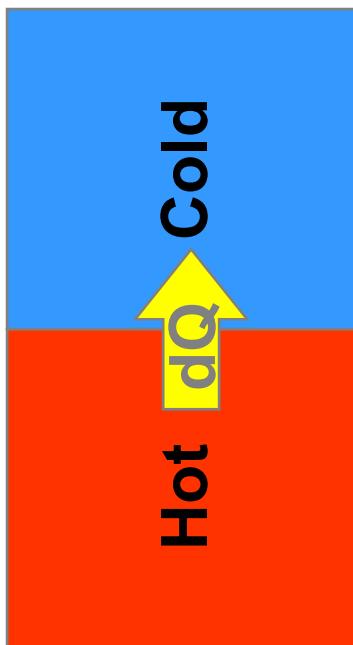
- Conservation of Energy
- Says Nothing About Direction of Energy Transfer

## Second Law of Thermodynamics

- Preferred (or Natural) Direction of Energy Transfer
- Determines Whether a Process Can Occur
- Thermodynamic Processes can be classified into Three Types :
  - Natural (or Irreversible)
  - Impossible
  - Reversible

# Second Law of Thermodynamics

## Thermal Conduction

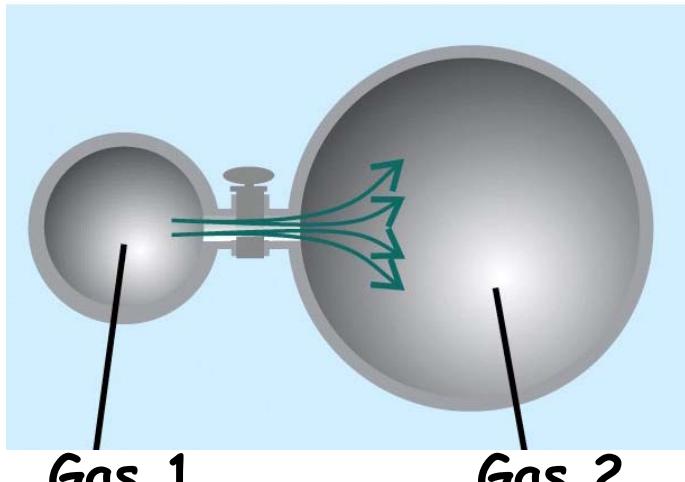


The two liquids (with very similar molecules) form an ideal solution ( $\Delta H \approx 0$ ), in which the molecules are randomly and uniformly mixed.

Suppose two bodies are brought in contact. Then from the 1st law, we ONLY know if  $q$  heat was lost by one, exactly  $q$  heat would be gained by the other. The law does not specify if the 1st one will lose heat or, the other one. To know the direction of flow of heat, we need another information, namely the temp of the two bodies.

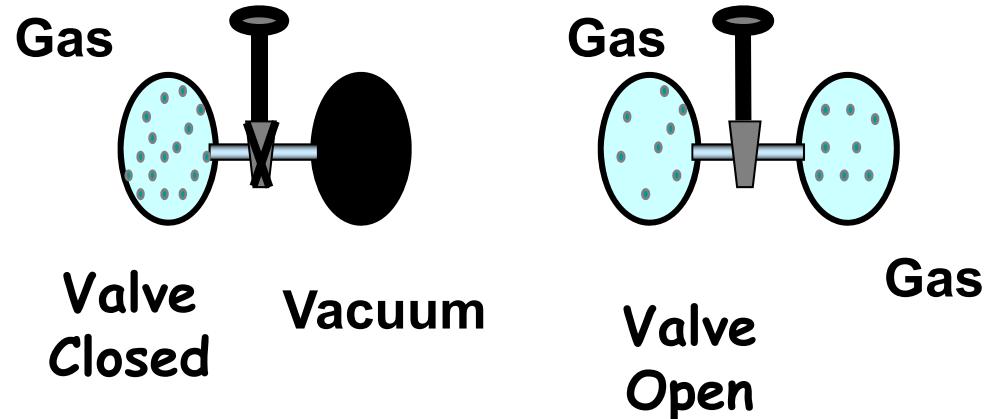
# Second Law of Thermodynamics

What happens when ?



Ideal gas mixture  $\Delta H=0$

## Free Expansion of Gas



Gases tend to occupy the whole available volume of the container.

### Two questions:

- 1) Does the enthalpy of the system increase or decrease and how much ?
- 2) Does the system become more or less disordered and by how much?

The driving force of such a process is the increase of the disorder in the system.

## Second Law of Thermodynamics

**Disorder increase for the following processes:**

- Solids melt to liquids
- Solids or liquids vaporize to form gases
- Solids or liquids dissolve in a solvent to form non-electrolyte solution
- A substance is heated (increased temperature increases the molecular motions and the disorder)
- A chemical reaction produces an increase in the number of molecules of gases
- The 2<sup>nd</sup> Law puts forward the criteria for the direction of the spontaneous chemical/ physical change of a thermodynamic system.
- The historical roots of the second law stems from the **invention of heat engine (namely, the steam engine)**. It is known that **work can be fully converted to heat (joule's expt)**, the question is can **heat be converted to work???**

# Carnot Engine: Introduction to Heat Engines

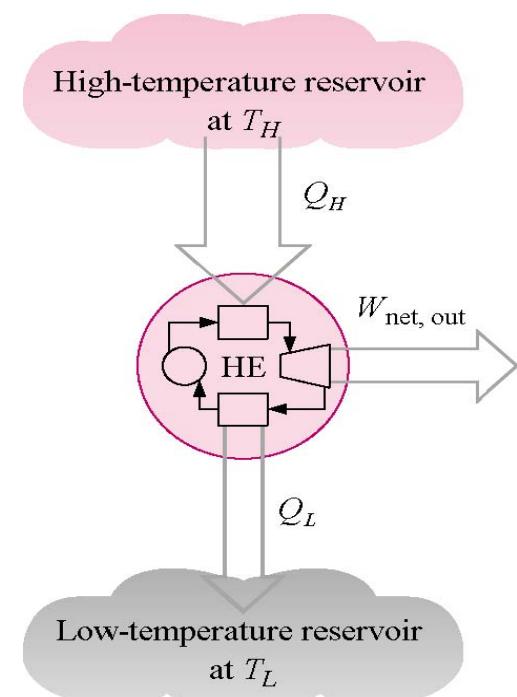
- One of the primary applications of thermodynamics is to turn **heat into work**

Let us consider a **CYCLIC** Process where a series of transformations brings the system back to its initial state where,  $Q_H$  = amount heat absorbed by the system;  $Q_L$  = amount heat released by the system;  $w$  = amount of work done by the system.

If  $|Q_H| > |Q_L|$  and  $w < 0$ , then the **mechanical device** by which the system is made to undergo the cyclic process is called a **HEAT ENGINE** and the system is termed as the **working substance**.

- The standard heat engine works on a **reversible cyclic process**:
  1. extract heat from a hot reservoir,
  2. perform work,
  3. dump excess heat into a cold reservoir (often the environment).

A “**reservoir**” is a large body whose temperature doesn’t change when it absorbs or gives up heat



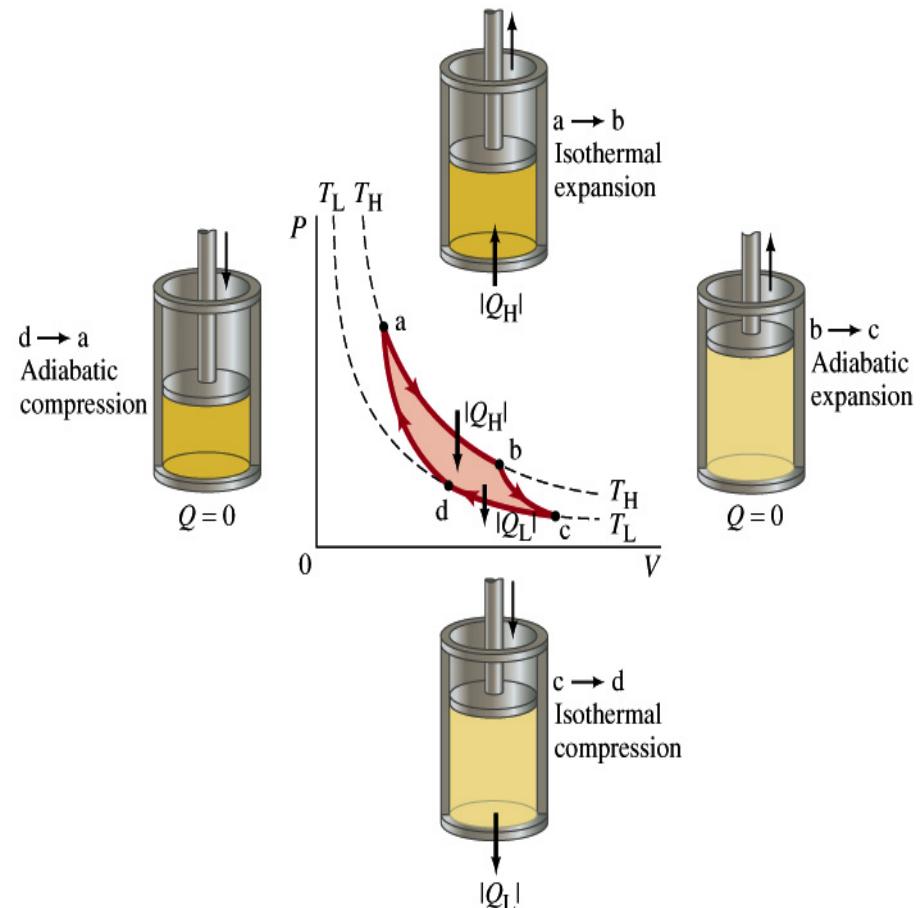
# Heat Engines

- By conservation of energy:  $|Q_H| = |W| + |Q_L|$ .
- The high and low temperatures  $T_H$  and  $T_L$  are called the operating temperatures of the engine.
- We will consider only engines that run in a repeating *cycle*, that is, the system returns repeatedly to its starting point, and thus can run continuously. **The engine operates in cycles and delivers work continuously by performing the same cycle over and over again.**
- Absolute value signs are used because we are interested only in the magnitudes.
- **Input in the cycle is the heat absorbed by the working substance and output is the net work in the cycle.**
- **Thermal efficiency of the engine will thus be defined as**

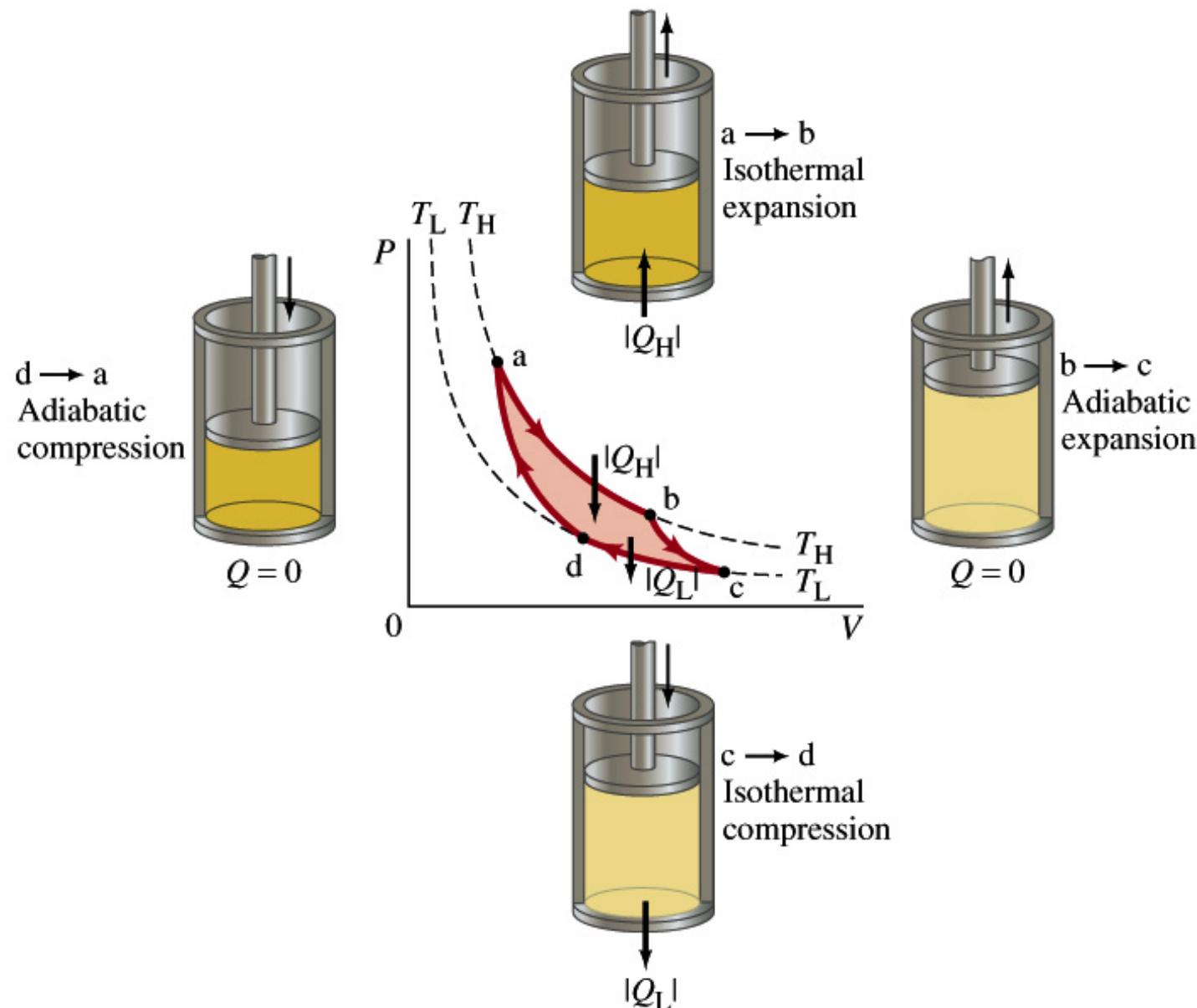
$$\varepsilon = \frac{(-W)}{Q_H}$$

## Second Law of Thermodynamics: The Carnot Cycle.

- The Carnot cycle is an example of a reversible process, which is a process that can be done in reverse.
- A reversible process requires that any changes are made infinitely slowly.
- Real processes are not reversible due to friction , turbulence in the gas, etc.



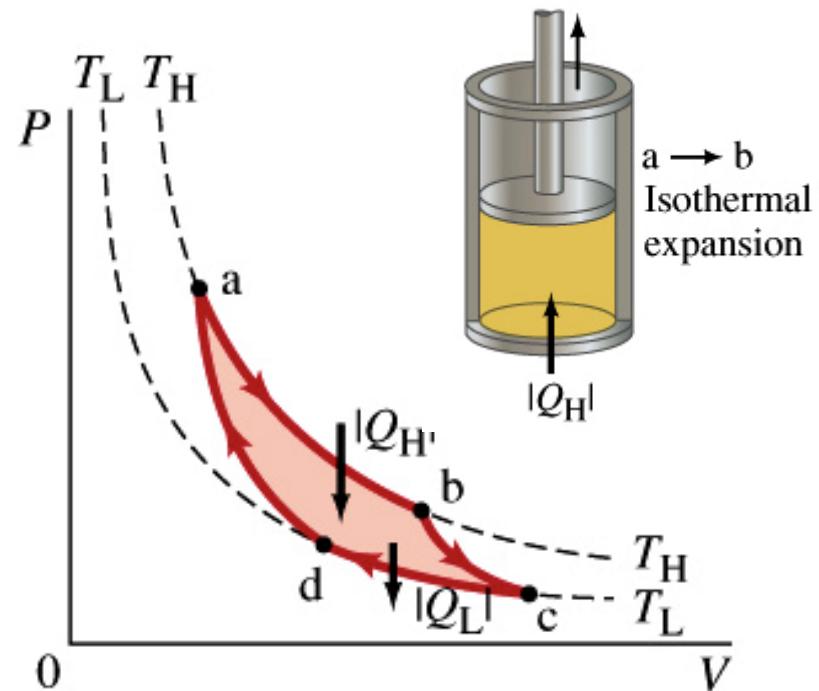
# Second Law of Thermodynamics: The Carnot Cycle



# Second Law of Thermodynamics

## The Carnot Cycle

- Step 1: a to b.
  - The gas is in contact with a heat bath at temperature  $T_H$  and weight is removed from the piston.
  - The gas expands, while maintaining a constant temperature, isothermal
  - the change in the internal energy is thus equal to zero



$$w_1 = -nRT_H \ln \frac{V_b}{V_a}$$

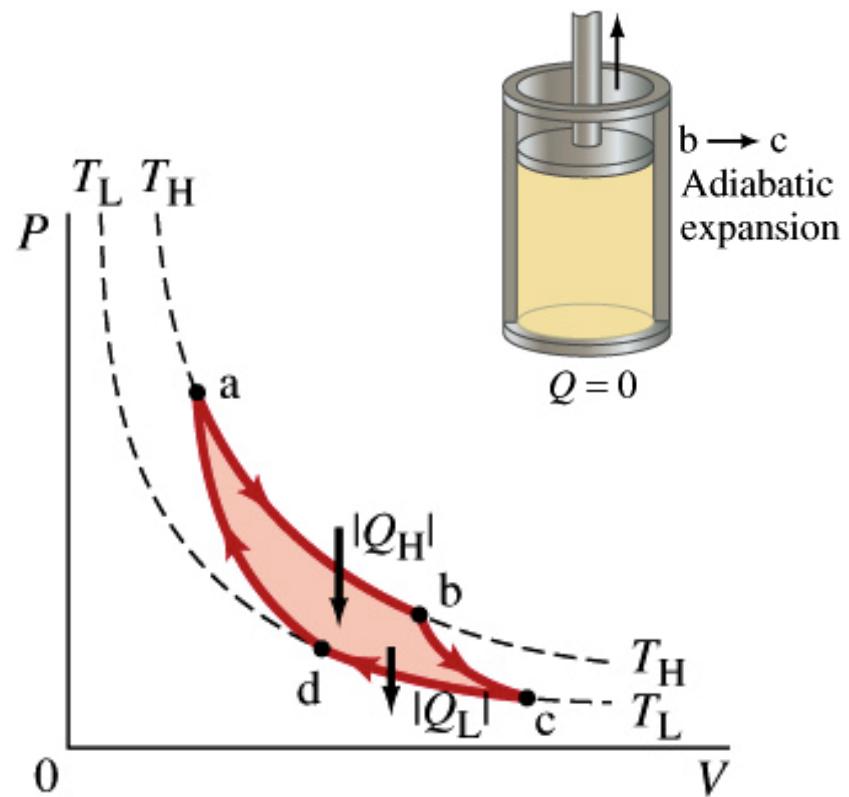
$$dU = 0$$

$$w_1 = -q_1 \equiv -q_H = nRT_H \ln \frac{V_b}{V_a} \equiv -nRT_H \ln \frac{V_a}{V_b}$$

# Second Law of Thermodynamics

## The Carnot Cycle

- Step 2: b to c.
  - The gas is isolated from the environment and some more weight is removed from the piston.
  - The gas expands and during the **adiabatic expansion**, the temperature of the gas will decrease.
  - For adiabatic expansion  $pV^\gamma$  is constant, and we can thus relate state b to state c:



$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1}$$

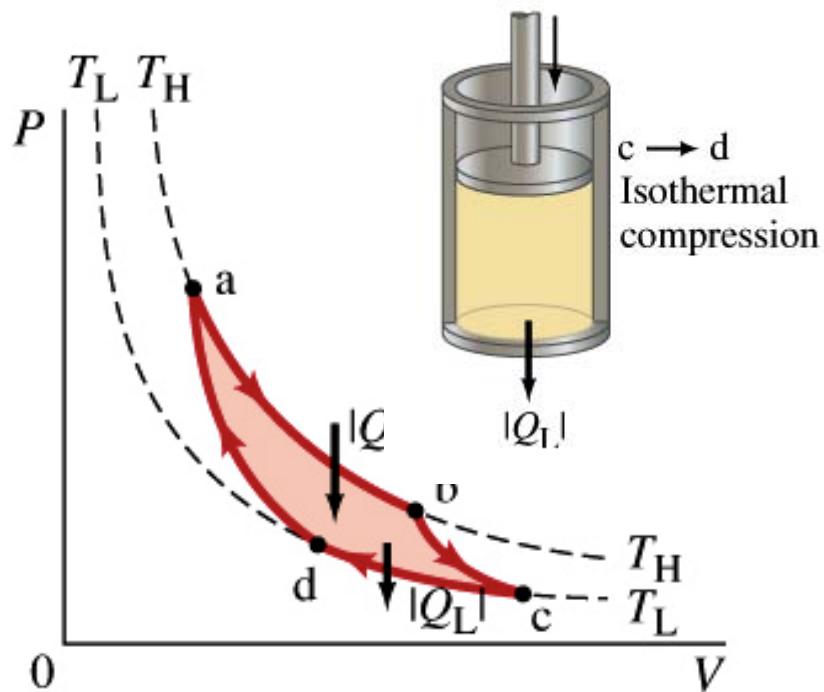
$$w_2 = nC_V(T_L - T_H)$$

$$q_2 = 0$$

# Second Law of Thermodynamics

## The Carnot Cycle

- Step 3: c to d.
  - The gas is in contact with a heat bath at temperature  $T_c$  and weight is added to the piston.
  - The gas is compressed, while **maintaining a constant temperature**, isothermal
  - the change in the internal energy is thus **equal to zero**



$$w_3 = -nRT_L \ln \frac{V_d}{V_c}$$

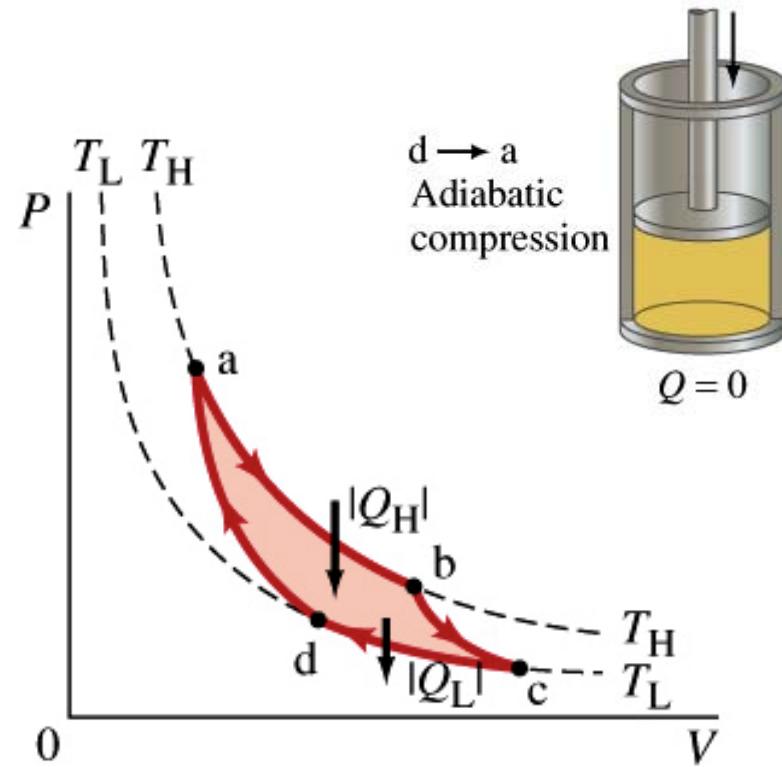
$$dU = 0$$

$$w_3 = -q_3 \equiv -q_L = nRT_L \ln \frac{V_d}{V_c}$$

# Second Law of Thermodynamics

## The Carnot Cycle

- Step 4: d to a.
  - The gas is isolated from the environment and some more weight is added to the piston.
  - The gas is compressed and during the adiabatic compression, the temperature of the gas will **increase**.



$$T_H V_a^{\gamma-1} = T_L V_d^{\gamma-1}$$

$$w_4 = nC_V(T_H - T_L)$$

$$q_4 = 0$$

## 2nd Law of Thermodynamics: The Carnot Cycle

- Four steps
- Isothermal expansion: a to b
- Adiabatic expansion: b to c
- Isothermal compression: c to d
- Adiabatic compression: d to a

Define the efficiency  $\varepsilon$

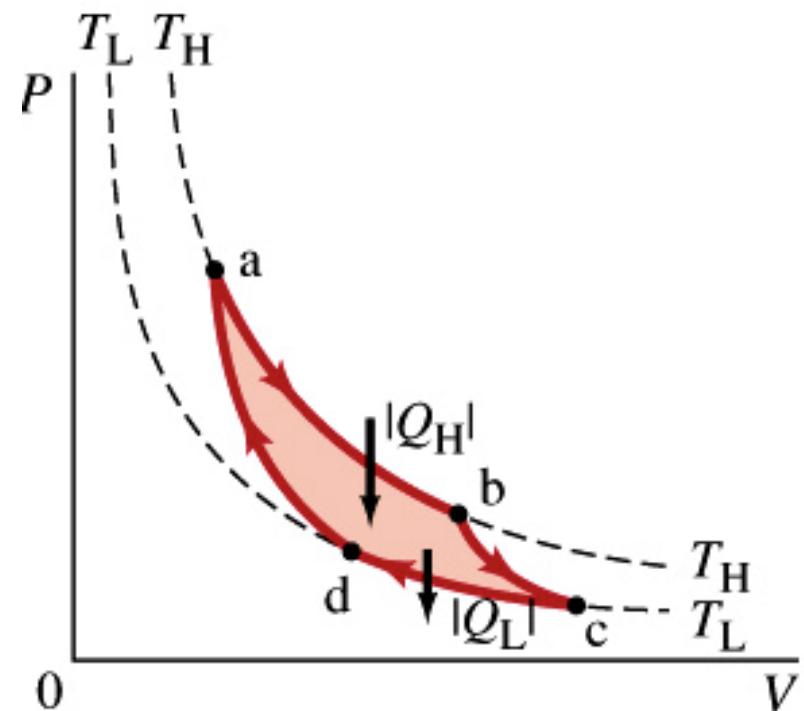
$$\varepsilon \equiv \frac{\text{work done by system}}{\text{heat extracted from reservoir}} = \frac{\text{"work"}}{\text{"cost"}}$$

$Q_H$  = amount heat absorbed by the system;

$Q_L$  = amount heat released by the system;

w = amount of work done by the system.

$$\varepsilon(\text{efficiency}) = \frac{|w|}{Q_H} = \frac{(Q_H - Q_L)}{Q_H} = 1 - \frac{|Q_L|}{|Q_H|}$$



Valid for all heat engines.

( $\Delta U = 0$  for closed cycle)

where,  $|w| = |Q_H| - |Q_L|$ ; following conservation of energy

# Second Law of Thermodynamics

## The Carnot Cycle: Four steps

- Isothermal expansion: a to b
- Adiabatic expansion: b to c
- Isothermal compression: c to d
- Adiabatic compression: d to a

$$w_1 = -nRT_H \ln \frac{V_b}{V_a}$$

$$dU = 0$$

$$w_1 = -q_1$$

$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1}$$

$$w_2 = nC_V(T_L - T_H)$$

$$q_2 = 0$$

$$w_3 = -nRT_L \ln \frac{V_d}{V_c}$$

$$dU = 0$$

$$w_3 = -q_3$$

$$T_H V_a^{\gamma-1} = T_L V_d^{\gamma-1}$$

$$w_4 = nC_V(T_H - T_L)$$

$$q_4 = 0$$

# The Carnot Cycle

$$w_{cycle} = w_1 + w_2 + w_3 + w_4$$

$$w_{cycle} = -nRT_H \ln \frac{V_b}{V_a} + nC_v(T_L - T_H) - nRT_L \ln \frac{V_d}{V_c} + nC_v(T_H - T_L)$$

$$w_{cycle} = -nRT_H \ln \frac{V_b}{V_a} - nRT_L \ln \frac{V_d}{V_c}$$

$$\oint dU = 0 \quad \text{So, } w_{cycle} = -q_{cycle}$$

$$q_{cycle} = nRT_H \ln \frac{V_b}{V_a} + nRT_H \ln \frac{V_d}{V_c}$$

$$w_{cycle} = nRT_H \ln \frac{V_a}{V_b} - nRT_L \ln \frac{V_d}{V_c}$$

$$w_{cycle} = nR(T_H - T_L) \ln \frac{V_a}{V_b}$$

$$\begin{aligned} T_H V_b^{\gamma-1} &= T_L V_c^{\gamma-1} \\ T_L V_d^{\gamma-1} &= T_H V_a^{\gamma-1} \\ \frac{T_H}{T_L} &= \frac{V_c^{\gamma-1}}{V_b^{\gamma-1}} = \frac{V_d^{\gamma-1}}{V_a^{\gamma-1}} \quad \therefore \quad \frac{V_c}{V_b} = \frac{V_d}{V_a} \end{aligned}$$

$$(V_D/V_C) = (V_A/V_B)$$

$$\ln(V_D/V_C) = -\ln(V_B/V_A)$$

# The Carnot Cycle

$$\varepsilon \equiv \frac{\text{work done by system}}{\text{heat extracted from reservoir}} = \frac{\text{"work"}}{\text{"cost"}}$$

$$\text{efficiency} = \varepsilon = \frac{W}{Q_H}$$

But,  $Q_H = q_1 = -w_1$

And,  $Q_L = q_3 = -w_3$

$$w_1 = -nRT_H \ln \frac{V_b}{V_a}$$

$$w_3 = -nRT_L \ln \frac{V_d}{V_c}$$

$$dU = 0$$

$$dU = 0$$

$$w_1 = -q_1$$

$$w_3 = -q_3$$

$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1}$$

$$T_L V_d^{\gamma-1} = T_H V_a^{\gamma-1}$$

$$\frac{T_H}{T_L} = \frac{V_c^{\gamma-1}}{V_b^{\gamma-1}} = \frac{V_d^{\gamma-1}}{V_a^{\gamma-1}} \quad \therefore \quad \frac{V_c}{V_b} = \frac{V_d}{V_a}$$

$$\varepsilon = \frac{w}{Q_H} = \frac{(Q_H - Q_L)}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L \ln \left( \frac{V_d}{V_c} \right)}{T_H \ln \left( \frac{V_b}{V_a} \right)}$$

$$\varepsilon = \left(1 - \frac{Q_L}{Q_H}\right) = \left(1 - \frac{T_L}{T_H}\right)$$

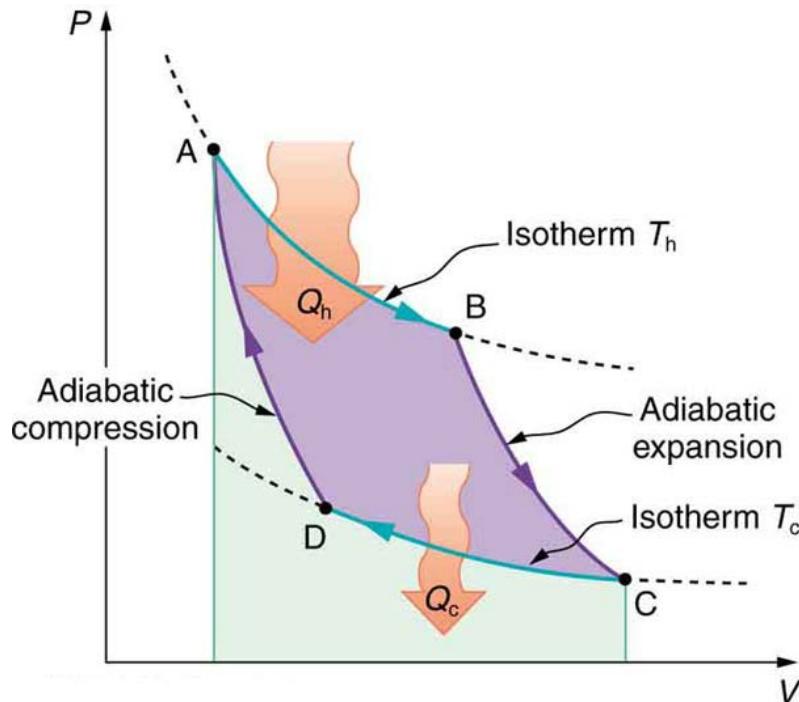
$$\Rightarrow \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \Rightarrow \left(\frac{Q_L}{T_L}\right) = \left(\frac{Q_H}{T_H}\right)$$

$$\Rightarrow \left(\frac{Q_L}{T_L}\right) - \left(\frac{Q_H}{T_H}\right) = 0$$

$$\sum \frac{q_i}{T_i} = 0 \Rightarrow \oint \frac{\partial q}{T} = 0$$

Thus, the term  $\delta q/T$  is a state function

# Summary: Carnot Cycle (Ideal gas, All the steps are reversible)



$$TV^{\gamma-1} = \text{const.};$$

$$T_h V_B^{\gamma-1} = T_C V_C^{\gamma-1} \quad T_h V_A^{\gamma-1} = T_C V_D^{\gamma-1}$$

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \quad \left(\frac{V_B}{V_A}\right) = \left(\frac{V_C}{V_D}\right)$$

$$\ln(V_D/V_C) = -\ln(V_B/V_A)$$

Step	1 (A → B)	2 (B → C)	3 (C → D)	4 (D → A)	Total (A → B → C → D → A)
w	$-nRT_h \ln\left(\frac{V_B}{V_A}\right)$	$C_V(T_c - T_h)$	$-nRT_c \ln\left(\frac{V_D}{V_C}\right)$	$C_V(T_h - T_c)$	$-nR(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)$
q	$nRT_h \ln\left(\frac{V_B}{V_A}\right)$	0	$nRT_c \ln\left(\frac{V_D}{V_C}\right)$	0	$nR(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)$
$\Delta U$	0	$C_V(T_c - T_h)$	0	$C_V(T_h - T_c)$	0
$\frac{q_{rev}}{T}$	$nR \ln\left(\frac{V_B}{V_A}\right)$	0	$nR \ln\left(\frac{V_D}{V_C}\right)$	0	0

## Summary: Efficiency of Carnot Cycle

### Efficiency of Carnot Engine

For any cyclic engine,  $\Delta U = 0 \Rightarrow |w| = |Q| = |Q_h + Q_c|$

when taken  $\rightarrow w = Q = Q_h - Q_c$

Thus, by definition  $\epsilon = \frac{|w|}{Q_h} = \frac{Q_h + Q_c}{Q_h}$  i.e.

$$\epsilon = 1 - \frac{Q_c}{Q_h}$$

As the Carnot engine works **reversibly** and employs **an ideal gas**,

$$Q_H = nRT_h \ln\left(\frac{V_B}{V_A}\right) \text{ and } |w| = nR(T_h - T_c) \ln\left(\frac{V_B}{V_A}\right)$$

$$\therefore \epsilon = \frac{|w|}{Q_H} = \frac{T_h - T_c}{T_h} \text{ i.e.}$$

$$\epsilon = 1 - \frac{T_c}{T_h}$$

Note:  $T_C$  and  $T_L$  represents the same,  
i.e., the Temp. of the cold/low  
temperature reservoir

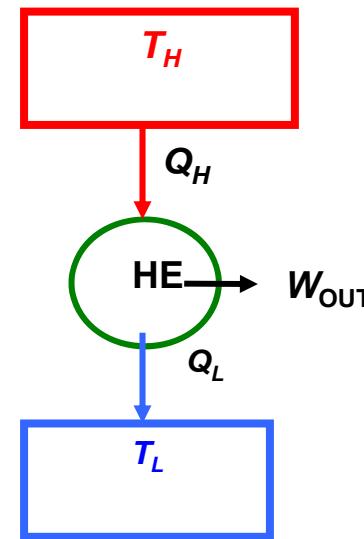
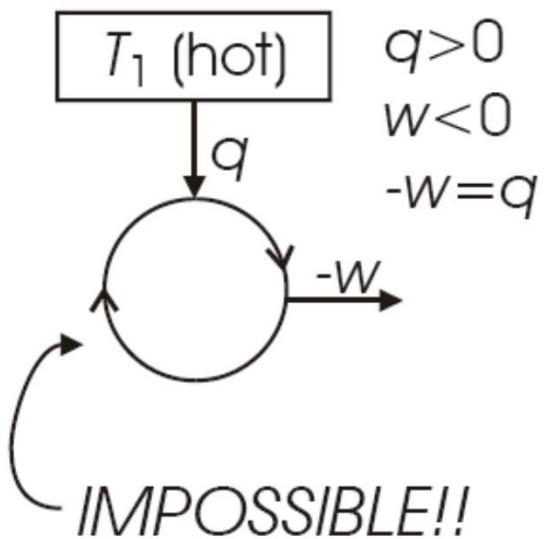
Note:  $1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \Rightarrow \frac{Q_h}{T_h} - \frac{Q_c}{T_c} = 0$

Isothermal, absorption of heat at  $T_h$

Isothermal, release of heat at  $T_c$

## Kelvin's Statement of Second Law of Thermodynamics

**Kelvin:** It is impossible for any system to operate in a cycle that takes heat from a **hot reservoir** and converts it to work in the surroundings without at the same time transferring some heat to a **colder reservoir**.



**Thermal efficiency**

$$\varepsilon = \frac{-W}{Q_H} = \frac{|w_{cycle}|}{Q_H}$$

For a complete cycle:  $dU = 0$

$$\therefore Q_{cy} = -W_{cy}$$

$$Q_{cy} = Q_H - Q_L$$

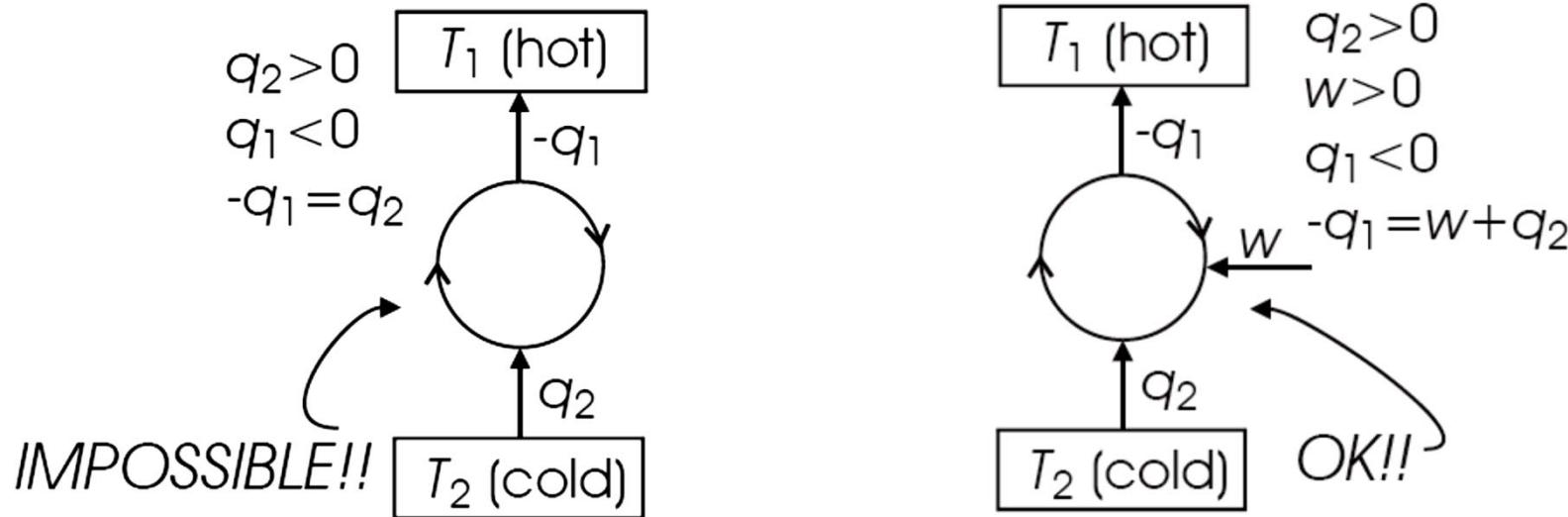
$$\therefore \varepsilon_{cyc} = \frac{|w_{cycle}|}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$Q_H$  = amount heat absorbed by the system;  
 $Q_L$  = amount heat released by the system;  
 $w$  = amount of work done by the system.

The engine will have 100% efficiency only when  $Q_L$  (heat absorbed by the low temp reservoir) = 0

## Clausius's Statement of Second Law of Thermodynamics

Clausius: It is impossible for any system to operate in a cycle that takes **heat from a cold reservoir** and **transfers it to a hot reservoir** without at the same time converting some work into heat.



**Alternative Clausius statement:** All spontaneous processes are irreversible.  
(e.g. heat flows from hot to cold spontaneously and irreversibly)

**Mathematical statement:**

$$\oint \frac{\partial q_{rev}}{T} = 0 \quad \text{and} \quad \oint \frac{\partial q_{irrev}}{T} < 0$$

$$\oint \frac{\partial q}{T} \leq 0$$

Leads to Clausius inequality

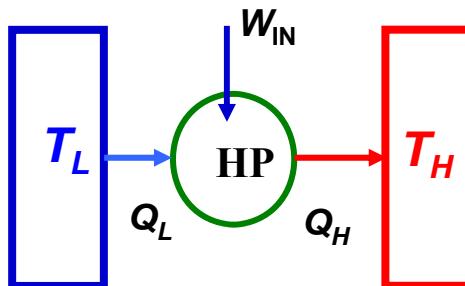
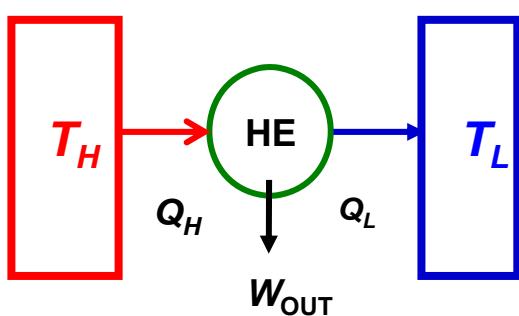
$$\oint \frac{\partial q}{T} \leq 0$$

contains

$$\begin{cases} \oint \frac{\partial q_{rev}}{T} = 0 \\ \oint \frac{\partial q_{irrev}}{T} < 0 \end{cases}$$

# Refrigerator and Heat Pump

"Refrigerator" if the objective is to cool the heat source (as in the normal operation of a freezer).



A "Heat pump" is a machine or device that moves heat from one location (the 'source') at a lower temperature to another location (the 'sink' or 'heat sink') at a higher temperature using mechanical work or a high-temperature heat source.

	output	input	efficiency
heat engine	W	$Q_h$	$W/Q_h$
refrigerator	$Q_c$	W	$Q_c/W$
heat pump	$Q_h$	W	$Q_h/W$

Thus a heat pump may be thought of a "heater" if the objective is to warm the heat sink or a "refrigerator" if the objective is to cool the heat source (as in the normal operation of a freezer)

In HP and R, in both cases, the operating principles are identical. Heat is moved from a cold place to a warm place.

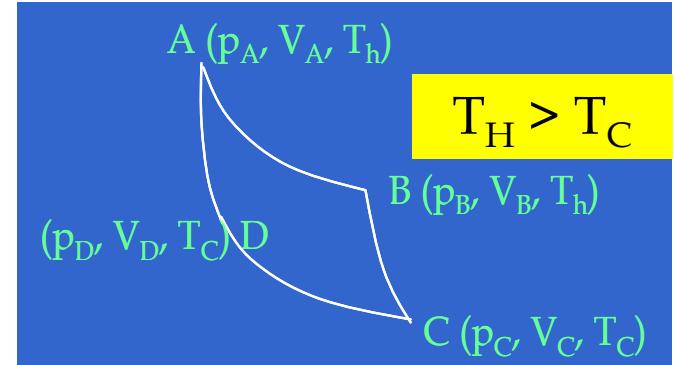
The efficiency of a refrigerator or heat pump is given by a parameter called the coefficient of performance (COP).

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$$w_{cycle} = nR(T_H - T_C) \ln \frac{V_a}{V_b}$$

$$Efficiency, \epsilon \text{ or } \eta = \frac{-w_{cycle}}{q_1} = \frac{|w_{cycle}|}{q_1}$$

$$\eta = \frac{-nR(T_H - T_C) \ln \frac{V_a}{V_b}}{nRT_H \ln \frac{V_b}{V_a}} = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H}$$



### Note:

$T_H > T_C$  and  $Q_H > Q_C$   
 And  $T_C$  and  $Q_C$  and  $T_L$  and  $Q_L$  represent the temp and the heat transfer to the low temp. reservoir respectively

### Carnot's theorem:

- Efficiency of Carnot engine  $< 1$
- No cycle can have an efficiency greater than a Carnot cycle
- All reversible engines operates between same 2 temperatures have same efficiency

- Carnot's theorem tells us that **no real engine can have an efficiency more than that of the Carnot engine.**

**Carnot's theorem:** No engine operating between two reservoirs can be more efficient than a reversible engine operating between the same two reservoirs

Efficiency of a reversible ideal gas Carnot cycle is given by:

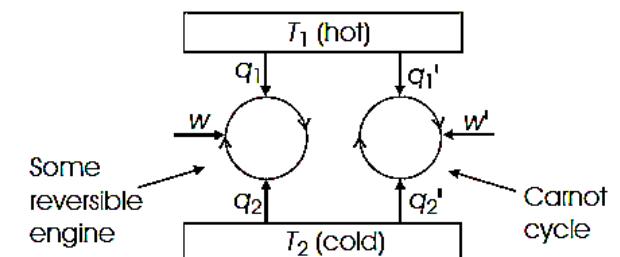
$$\epsilon = \frac{-w}{Q_H} = \frac{(q_H^{rev} + q_C^{rev})}{q_H^{rev}} \Rightarrow 1 - \frac{q_C^{rev}}{q_H^{rev}} = 1 - \frac{T_C}{T_H} \Rightarrow \frac{q_C^{rev}}{T_C} - \frac{q_H^{rev}}{T_H} = 0$$

$$\Rightarrow \oint \frac{\partial q^{rev}}{T} = 0$$

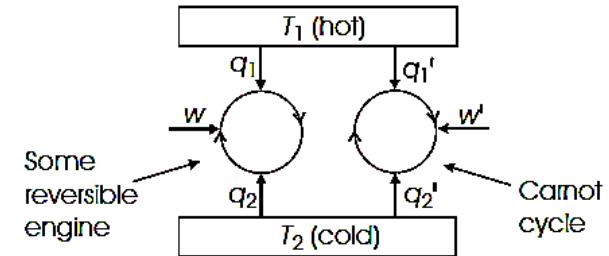
**To prove the Carnot's Theorem:** Consider any reversible engine that has a efficiency of  $\epsilon$  and another is the Carnot Engine with efficiency of  $\epsilon'$ :

Assume  $\epsilon' > \epsilon$  (left engine less efficient cycle than Carnot Cycle)

$$\text{where, } \epsilon = \frac{|w|}{q_1} \text{ and } \epsilon' = \frac{|w'|}{q'_1}$$



Since the engine is reversible, we can run it backwards. Use the work ( $-w'$ ) out of the Carnot engine as work input ( $w$ ) to run the left engine backwards.



$$\therefore \text{Total work out} = 0 \quad (-w' = w > 0)$$

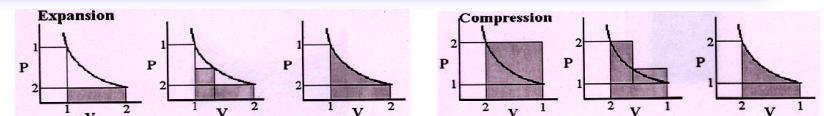
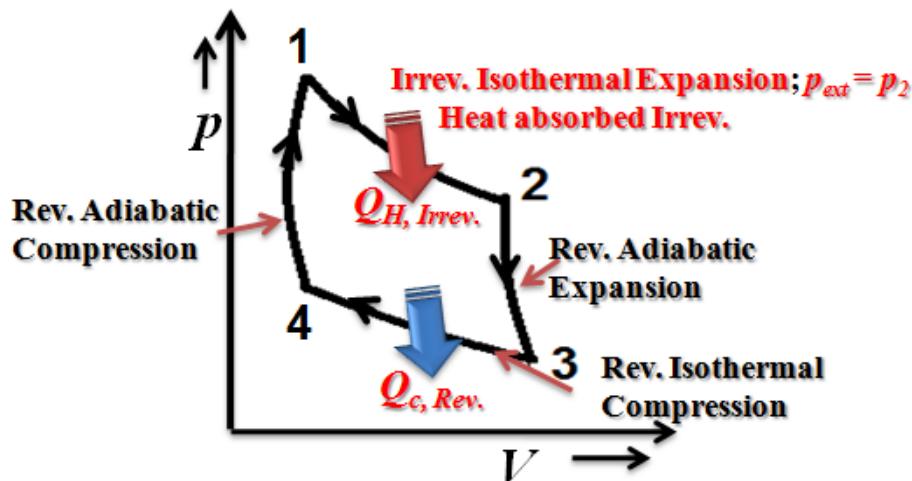
$$\text{But } \varepsilon' > \varepsilon \Rightarrow \frac{-w'}{q'_1} > \frac{-w}{q_1} \Rightarrow \frac{w}{q'_1} > \frac{-w}{q_1} = \frac{w}{-q_1} \Rightarrow q_1 < -q'_1 \text{ since } q_1 < 0, q'_1 > 0$$

$$\Rightarrow -(q'_1 + q_1) > 0$$

$\therefore$  The efficiency of any reversible engine is  $\varepsilon = 1 - \frac{T_2}{T_1}$

- Entropy is a state function, but to calculate  $\Delta S$  requires a reversible path.
- If **any step in a cycle is irreversible** then the **entire cycle will be considered an Irreversible cycle** and will NOT REMAIN A CARNOT ENGINE, which ONLY if all steps are reversible)

And an engine operating through an IRREVERSIBLE cycle is always LESS efficient than a reversible one.



Step:  $1 \rightarrow 2$  : Heat absorbed Irreversibly in this Isothermal Expansion

$$(-w)_{irrev} < (-w)_{rev}$$

$$\Delta U_{1 \rightarrow 2, irrev} = \Delta U_{1 \rightarrow 2, rev} \quad (\text{State function})$$

$$\Leftrightarrow (q_{H, irrev} + w_{irrev}) = (q_{H, rev} + w_{rev})$$

since,  $(-w)_{irrev} < (-w)_{rev}$  for Isothermal Expansion

$$\therefore q_{H, rev} > q_{H, irrev}$$

\*\* An irreversible isothermal expansion requires less heat than a reversible one. \*\*

$$\varepsilon_{irrev} = 1 - \frac{Q_c^{rev}}{Q_H^{irrev}} \quad \text{and} \quad \varepsilon_{rev} = 1 - \frac{Q_c^{rev}}{Q_H^{rev}}; \quad \text{Since, } q_{H, rev} > q_{H, irrev}$$

$$\therefore \varepsilon_{rev} > \varepsilon_{irrev}$$

also  $\frac{dq_{irrev}}{T} < \frac{dq_{rev}}{T} \Rightarrow \oint \frac{dq_{irrev}}{T} < 0$

# Entropy

- Carnot Engine showed that :

*Heat adsorbed in Rev.  
Iso. Expansion at Th*

$$\text{Over a cycle: } \oint \frac{\partial q_{rev}}{T} = \left( \frac{Q_h}{T_h} - \frac{Q_c}{T_c} \right) = 0$$

*Heat released in Rev.  
Iso compression at Tc*

Since,  $Q_c$  is the heat evolved so we ALSO write it as:

$$\text{Over a cycle: } \oint \frac{\partial q_{rev}}{T} = \frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$$

- By Definition:

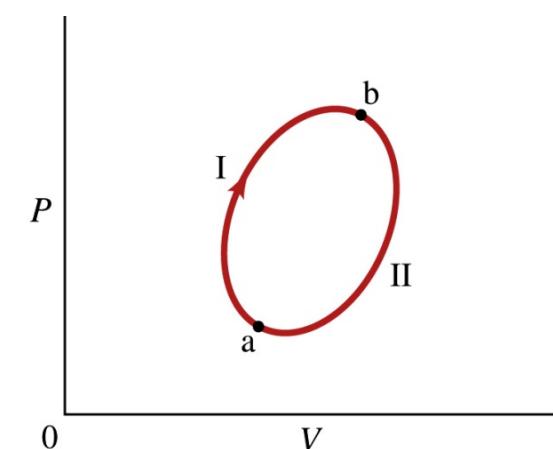
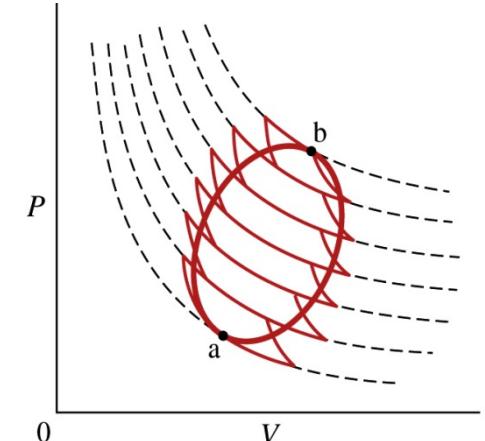
$$dS \text{ (Entropy Change)} = \frac{\partial q_{rev}}{T}$$

- Entropy is a state variable

$$dS = \frac{\partial q_{rev}}{T} \text{ is an exact differential}$$

- Since any reversible cycle can be approximated by a series of Carnot cycles, we expect that the  $\int dS$  along the closed path of the cycle = 0.

$$\sum_i \frac{q_i}{T_i} = 0 \quad \text{or, } \oint \frac{\partial q_i}{T_i} = 0; \quad \text{hence, } \sum_i dS_i = 0 \quad \text{or, } \oint dS = 0$$



# Entropy

- Entropy ( $\Delta S$ ) is a **state variable**, but  $Q$  and  $W$  are **not state variables** since they depend on the path used to get from  $a$  to  $b$ . One consequence :

$$\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{\partial q_{rev}}{T}$$

is **independent of the path**.

- Thus, for a **REVERSIBLE PROCESS**, the **change in entropy ( $\Delta S_{sys}$ ) of the engine is equal and opposite to the change in entropy of the environment ( $\Delta S_{surr}$ ) that provides the heat required (or, absorbs the heat generated)**. The **net change in Total Entropy ( $\Delta S_{univ}$ ) = 0**.

$$dS_{net} = \oint \frac{\partial q_{rev}}{T} = 0$$

**NOTE:**  $\oint \frac{\partial q_{irrev}}{T} \neq \Delta S$  (entropy change)

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

- For an **IRREVERSIBLE PROCESS**, the **net change in the total entropy ( $\Delta S_{univ}$ ) will be larger than 0 (For ISOLATED SYSTEM)**

$$dS_{net} > 0 \quad \text{or,} \quad dS_{univ} > 0$$

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

# Entropy

- **S** reflects of the disorderliness of a system
- In a reversible thermodynamic process, entropy of a system is related to the extent to which energy is dispersed in a disorderly manner, which in turn depends on the amount of energy transferred as heat (as heat stimulates motion) to the surroundings.
- $\Delta S$  is the measure of the energy in a system or process that is unavailable to do work
- For a process occurring at constant temperature (an isothermal process):

$$\frac{\partial q_{rev}}{T} = \Delta S \quad \text{where,}$$

$q_{rev}$  = heat that is transferred when the process is carried out reversibly at constant  $T$   
 $T$  = temperature at which the heat is transferred (in Kelvin)

- The change in the thermodynamic function, entropy,  $S$ , and is defined such that:
  - $dS = \frac{\partial q_{rev}}{T}$  is an exact differential
  - $\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{\partial q_{rev}}{T}$  is independent of the path
- $\Delta S$  can be measured for reversible and irreversible process

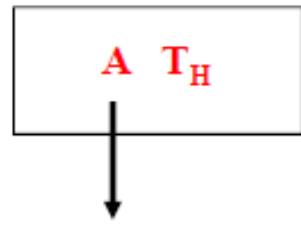
# Entropy

- The thermodynamic property of a system that is related to its degree of randomness or disorder is called entropy ( $S$ ).
- The entropy,  $S$ , and the entropy change  $\Delta S = S_2 - S_1$  are **state functions**
- The **entropy** is an **extensive property**, i.e. increases with the amount of matter in the system
- When **heat is absorbed** by the system,  $dq_{rev} > 0$ ,  $T$  is always **+ive**, therefore entropy change is  $dS > 0$ . In other words, **absorption of heat increases the entropy** of the system, hence **rejection of heat**,  $dq_{rev} < 0$ , will lead to a **decrease in the entropy** of the system,  $dS < 0$
- For a Reversible Adiabatic change,  $dq_{rev} = 0$  the process is Isoentropic,  $dS = 0$
- The entropy,  $S$ , has a **unique value**, once the pressure ( $p$ ), the temperature ( $T$ ) and the composition  $n$  moles of the system are specified,  $S = S(p, T, n)$
- Absolute value of  $S$  can be estimated using the **Third Law of Thermodynamics**

## How do you calculate entropy change?

In a process, where a given quantity of heat  $q$  is transferred to the system from a cold body and hot body, the Entropy change when it is TRANSFERRED to a colder body will be always greater.

$$dS \propto \frac{1}{T \text{ (temp at which heat is supplied)}}$$



For  $dq$  amount of heat leaving A reversibly, entropy change:  $-\left(\frac{dq}{T_H}\right)$



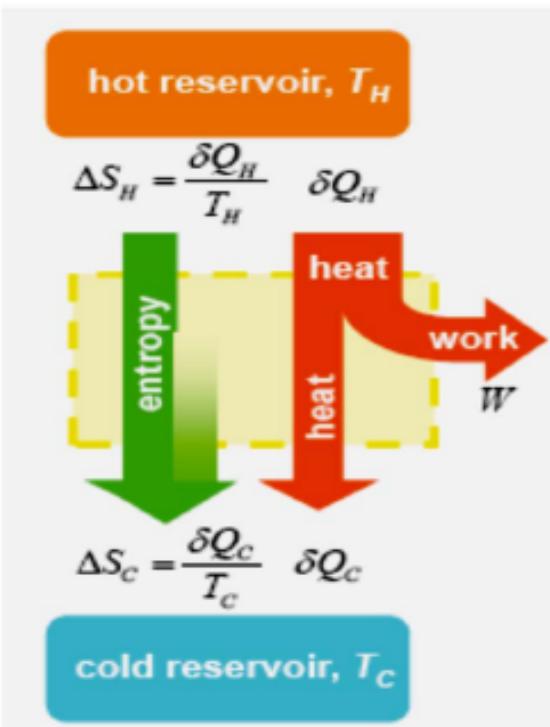
For  $dq$  amount of heat enters B reversibly, entropy change:  $\left(\frac{dq}{T_C}\right)$

Overall change in Entropy  $-\left(\frac{dq}{T_H}\right) + \left(\frac{dq}{T_C}\right)$   $dS = dq \left[ \frac{1}{T_C} - \frac{1}{T_H} \right]$

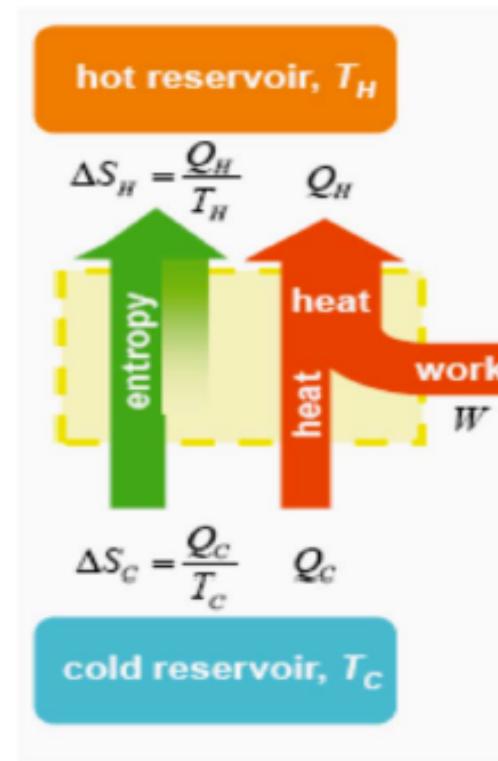
- when  $T_H > T_C$  then  $dS > 0$ ; which means transfer of heat from a hot body to cold body is a the direction of spontaneous flow of heat i.e., a spontaneous process
- when  $T_H = T_C$  (i.e., the temp of the two bodies are equal); then  $dS = 0$ ; the system is supposed to have reached thermal equilibrium

# How do you calculate entropy change?

## Heat Engines



## Refrigerators



For same quantity of heat absorbed,  $dS$  is higher for lower  $T$ . Therefore, refrigerator is NOT spontaneous .

$$\Delta S_{Total} = q \left( \frac{1}{T_L} - \frac{1}{T_H} \right)$$

$T_H$  very High  $\Leftrightarrow \Delta S_{Total} > 0$

$T_H$  very Low  $\Leftrightarrow \Delta S_{Total} < 0$

Spontaneous process

NOT Spontaneous process

## How do you calculate Entropy change of Surrounding?

### For surrounding: A reservoir of large constant Volume

When heat of  $q$  quantity is transferred to the Surrounding in a process, then

- The change in internal of the Surrounding,  $\Delta U_{surr}$ , is Independent of whether it is carried out Reversibly or, Irreversibly, since  $\Delta U$  is a state function
- Reservoir is considered to be of large constant Volume; so,  $dV = 0$  so,  $w = 0$ ; Therefore,  $\Delta U_{surr} = dq_{rev}$

$$\therefore dS_{surr} = \frac{-dq_{rev}}{T_{surr}} \text{ or, } \Delta S_{surr} = \frac{-q_{rev}}{T_{surr}}$$

- So, regardless of how the change was carried out, the change of entropy of the surrounding will also be given by amount of heat transferred reversibly divided by the temp at which heat is transferred
- In Reversible adiabatic process, the entropy change of surrounding is zero

$$dS_{surr} = 0 \text{ and } dq_{surr} = 0 \text{ (ISENTROPIC)}$$

## How do you calculate Entropy Change Real Gas undergoing a process?

### Entropy Change

$$dS = \frac{dq_{rev}}{T} = \frac{dU - w_{rev}}{T}$$

$$= \frac{\left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT + p dV}{T}$$

substitute the value of  $dU$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T dV + C_V \frac{dT}{T} + \frac{p}{T} dV$$

where,  $C_V$  and  $C_P$  are molar specific heat values

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T dV + C_V \frac{dT}{T} + \frac{p}{T} dV$$

## How do you calculate Entropy Change Ideal Gas undergoing a process?

$$dS = \frac{1}{T} \cancel{\left(\frac{\partial U}{\partial V}\right)}^0_T dV + C_V \frac{dT}{T} + \frac{p}{T} dV = C_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$\Delta S = S_2 - S_1 = \int_1^2 dS = \int_1^2 C_V \frac{dT}{T} + \int_1^2 nR \frac{dV}{V}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{p_1}{p_2} + C_P \ln \frac{T_2}{T_1}$$

# Calculation of Entropy Change for Ideal Gas undergoing various processes

By definition:

$$dS = \frac{\partial q_{rev}}{T} \quad \text{and} \quad \Delta S = \int_1^2 \frac{\partial q_{rev}}{T}$$

For an adiabatic process

$$\partial q_{rev} = 0 \Rightarrow dS = 0 \text{ for non-zero temperatures}$$

$$\therefore \int_1^2 dS = S_2 - S_1 = \Delta S = 0 \Rightarrow S_2 = S_1$$

For any isothermal process

$$\Delta S = \int_1^2 \frac{\partial q_{rev}}{T} = \frac{1}{T} \int_1^2 \partial q_{rev} \quad \therefore \Delta S = \frac{Q_{rev}}{T}$$

For an isothermal expansion of an ideal gas

$$\Delta U = 0 \Rightarrow Q_{rev} = -w_{rev} = nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$\therefore \Delta S = nR \ln \left( \frac{V_2}{V_1} \right)$$

For an isochoric reversible process

$$\partial w_{rev} = 0 \Rightarrow dU = \partial q_V = C_V dT \quad \therefore \Delta S = \int_1^2 \frac{\partial q_V}{T} = C_V \int_1^2 \frac{dT}{T} \quad \therefore \Delta S_V = C_V \ln \left( \frac{T_2}{T_1} \right)$$

# Calculation of Entropy Change for Ideal Gas undergoing various processes

For Reversible heating at constant volume

$$\partial q_{rev} = \partial q_V = C_V dT \Rightarrow \Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} \therefore \Delta S_v = C_V \ln\left(\frac{T_2}{T_1}\right)$$

For Reversible Expansion at constant temperature

$$\partial q_{rev} = dU + pdV \Rightarrow \frac{\partial q_{rev}}{T} = \frac{dU}{T} + \frac{p}{T} dV$$

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) \Rightarrow \therefore \Delta S_r = R \ln\left(\frac{p_1}{p_2}\right) \text{ or, } \Delta S_r = R \ln\left(\frac{V_2}{V_1}\right)$$

Reversible heating at constant pressure (with phase change)

$$\Delta S = \frac{Q_{rev}}{T} = \frac{\Delta H}{T}$$

Here,  $\Delta H$  is the enthalpy of phase change (latent heat) at the transition temperature  $T$

Measurement of Entropy at any Temperature

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta H_{fus}}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^T \frac{C_p(g)}{T} dT$$

## Calculation of Entropy change with Phase Transition

As degree of disorder changes at phase transition, so entropy change is associated with phase transition

$$\Delta_{trs} S_{sys} = \frac{q_p}{T_{trs}} = \frac{\Delta_{trs} H}{T_{trs}}$$

$$\Delta_{trs} S_{surr} = -\frac{q_p}{T_{trs}} = -\frac{\Delta_{trs} H}{T_{trs}}$$

where,  $T_{trs}$  is the Normal Transition Temp. at 1 atm

- At phase transition temperature ( $T_{trs}$ ) two phases are in equilibrium  
e.g.,  $\text{H}_2\text{O} (\text{l}, 0^\circ\text{C}, 1 \text{ atm}) \xrightleftharpoons{fusion} \text{H}_2\text{O} (\text{s}, 0^\circ\text{C}, 1 \text{ atm})$

- Transition occurs at constant  $p$  and  $T$

$$q_{trs} = \Delta H_{trs} \quad (\text{reversible})$$

- It is thus an Isothermal Reversible Process

Transition	Vaporization	Melting	Freezing
$\Delta H_{trs}$	> 0	> 0	< 0
$\Delta S_{trs}$	> 0	> 0	< 0

### Trouton's Rule

A wide range of liquid give approx. the same standard entropy of vaporization

$\Delta S^0_{vap} \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$  (unless there are strong molecular interactions in the liquid)

$$\Delta H^0_{vap} = T_b \Delta S^0_{vap}$$

Standard Enthalpy of Vaporization where,  $T_b$  is the boiling point

# Calculation of Entropy at any Temperature

The entropy of a system at a temperature  $T_f$  [i.e.,  $S(T_f)$ ] from the entropy value at a temperature  $T_i$  and the heat supplied to change its temperature

- On heating of an Ideal gas at constant pressure (such as from the atmosphere):

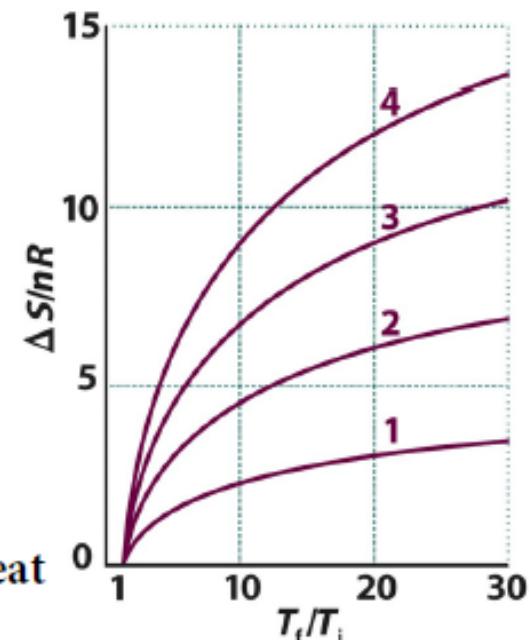
$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + Cp \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + Cp \ln\left(\frac{T_f}{T_i}\right)$$

- \*  $C_p$  is assumed to be independent of temperature in the temperature range of interest
- \* The logarithmic increase in entropy of a substance as it is heated at constant pressure

- On heating of an Ideal Gas at constant volume:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + C_V \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_V \ln\left(\frac{T_f}{T_i}\right)$$

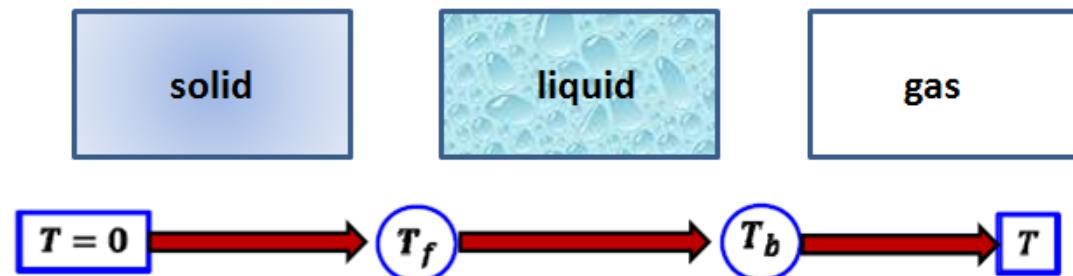
- \*  $C_V$  is assumed to be independent of  $T$  in the temp. range
- \* The logarithmic increase in entropy of a substance as it is heated at constant  $V$
- \* Different curves correspond to different values of the constant-volume heat capacity expressed as  $C_{v,m}/R$



# Calculation of Entropy Change at any Temperature

The entropy of a system at a temperature  $T$  is related to its entropy at  $T = 0$ . To determine, we need the heat capacity  $C_p$  at different temperatures (under constant pressure)

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta H_{fus}}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^T \frac{C_p(g)}{T} dT$$

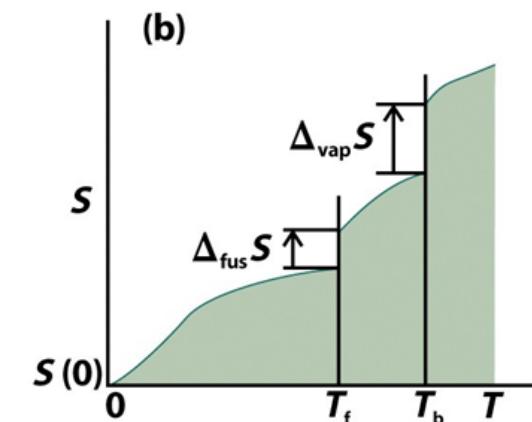
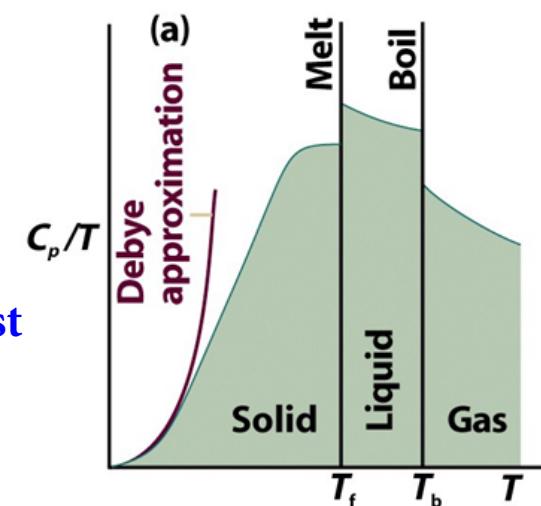


- Using heat capacity  $C_p$  at different  $T$ ; the area under the curve of  $C_p/T$  against  $T$  (alternatively, area under a plot of  $C_p$  against  $\ln T$ ) and Entropy of transition ( $\Delta_{trs}H/T_{trs}$ ) for each phase transition

- Difficulty in measuring  $C_p$  at LOW TEMP (near  $T = 0$ ).  
 $C_p$  is proportional to  $T^3$  at LOW  $T$ : the basis of Debye extrapolation.  
Expression  $C_p = aT^3$  is valid down to  $T = 0$

**At low  $T$  for the solid,  $C_p(s) = aT^3$  Debye Law**

- Entropy at very LOW TEMPERATURES : The Nernst Heat Theorem  
The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero:  $S \rightarrow 0$  as  $T \rightarrow 0$  provided all the substances involved are perfectly crystalline



# Calculation of Entropy at any Temperature

The entropy of a system at a temperature  $T_f$  [i.e.,  $S(T_f)$ ] from the entropy value at a temperature  $T_i$  and the heat supplied to change its temperature

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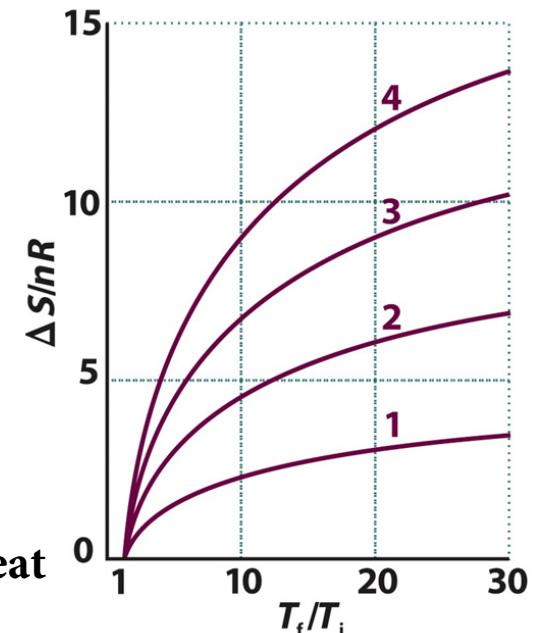
$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + Cp \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + Cp \ln\left(\frac{T_f}{T_i}\right)$$

- \*  $C_p$  is assumed to be independent of temperature in the temperature range of interest
- \* The logarithmic increase in entropy of a substance as it is heated at constant pressure

- On heating of an Ideal Gas at constant volume:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + C_v \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_v \ln\left(\frac{T_f}{T_i}\right)$$

- \*  $C_v$  is assumed to be independent of  $T$  in the temp. range
- \* The logarithmic increase in entropy of a substance as it is heated at constant  $V$
- \* Different curves correspond to different values of the constant-volume heat capacity expressed as  $C_{v,m}/R$



# Calculation of Entropy at any Temperature

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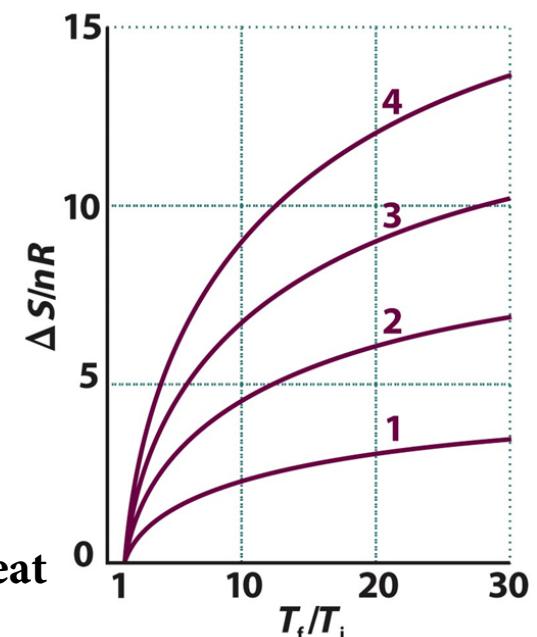
$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + Cp \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + Cp \ln\left(\frac{T_f}{T_i}\right)$$

- \*  $C_p$  is assumed to be independent of temperature in the temperature range of interest
- \* The logarithmic increase in entropy of a substance as it is heated at constant pressure

- On heating of an Ideal Gas at constant volume:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + C_V \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_V \ln\left(\frac{T_f}{T_i}\right)$$

- \*  $C_V$  is assumed to be independent of  $T$  in the temp. range
- \* The logarithmic increase in entropy of a substance as it is heated at constant  $V$
- \* Different curves correspond to different values of the constant-volume heat capacity expressed as  $C_{v,m}/R$



## Entropy Change for Ideal Gas under Reversible and Irreversible Process

- For a reversible process  $(T_1 \ V_1 \ n) \rightarrow (T_2 \ V_2 \ n)$

$$\Delta S = C_V \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right)$$

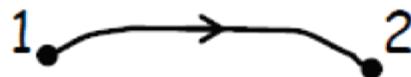
- For an irreversible process between  $(T_1 \ V_1 \ n) \rightarrow (T_2 \ V_2 \ n)$

$$\Delta S = C_V \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right)$$

This is because

- ✓ entropy  $S$  is a state function and
- ✓  $\Delta S$  is independent of the path connecting the two states

# Entropy Change for Ideal Gas under Reversible and Irreversible Process



$$\Delta S = S_2 - S_1$$

independent of path

But!

$\Delta S_{\text{surroundings}}$  depends on whether the process is reversible or irreversible

- (a) Irreversible: Consider the universe as an isolated system containing our initial system and its surroundings.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$
$$\therefore \Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$$

- (b) Reversible:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S'_{\text{surr}} = 0$$
$$\therefore \Delta S'_{\text{surr}} = -\Delta S_{\text{sys}}$$

# Entropy and Clausius Inequality

- For any **reversible** engine, operating in cycle between two temperatures  $T_h$  and  $T_c$ ,

$$\varepsilon_{rev} = \frac{|w_{rev}|}{Q_h} = 1 - \frac{T_c}{T_h}$$

$$\oint \frac{\partial q}{T} = 0$$

- For any arbitrary engine (**NOT** reversible) operating in cycle between the **same two temperatures**  $T_h$  and  $T_c$ , with the **same input of  $Q_h$**

$$\varepsilon_{irrev.engine} < \varepsilon_{rev.engine} \quad \text{as } (-w)_{\text{Rev. Iso. Expansion}} > (-w)_{\text{Irrev. Iso. Expansion}}$$

$$(q_H)_{\text{Heat absorbed Iso. Rev.Expansion}} < (q_H)_{\text{Heat absorbed Iso. Rev.Expansion}}$$

Heat absorbed at  $T_h$  under Irrev. Isothermal expansion      Heat released at  $T_c$  under Rev. Isothermal compression

$$\therefore 1 - \frac{Q_c}{Q_h} < 1 - \frac{T_c}{T_h} \quad \Rightarrow \quad \frac{Q_h}{T_h} - \frac{Q_c}{T_c} < 0$$

$$\oint \frac{\partial q}{T} < 0$$

# Entropy and Clausius Inequality

To show that the definition of Entropy is consistent with the Second Law

We know that **MORE** energy flows out of the system as **WORK** under **REVERSIBLE CONDITION** than under **IRREVERSIBLE** condition...

So, we can write:

$$(-\partial w_{rev}) \geq (-\partial w) \Rightarrow (\partial w - \partial w_{rev}) \geq 0$$
$$dU_{irrev} = (\partial q + \partial w) \quad \text{and} \quad dU_{rev} = (\partial q_{rev} + \partial w_{rev})$$

But, as **internal energy is a state function**, its change is the same for irreversible and reversible paths between the same two states, so we can also write:

$$dU_{irrev} = dU_{rev} = (\partial q + \partial w) = (\partial q_{rev} + \partial w_{rev})$$
$$\therefore (\partial w - \partial w_{rev}) = (\partial q_{rev} - \partial q); \text{ however, we know: } (\partial w - \partial w_{rev}) \geq 0$$
$$\therefore (\partial q_{rev} - \partial q) \geq 0$$

Thus,  $\partial q_{rev} \geq \partial q \Rightarrow \left(\frac{\partial q_{rev}}{T}\right) \geq \left(\frac{\partial q}{T}\right)$

And by definition:  $dS = \left(\frac{\partial q_{rev}}{T}\right);$

$$\therefore dS \geq \left(\frac{\partial q}{T}\right) \Leftrightarrow dS - \left(\frac{\partial q}{T}\right) \geq 0 \Leftrightarrow \left(\frac{\partial q}{T}\right) \leq 0$$

Clausius Inequality

Important in determining the direction and extent of change in a spontaneous process

# Entropy and Clausius Inequality

To Show the Clausius Inequality for Irreversible Cyclic Process:  $\oint \left( \frac{\partial q}{T} \right) \leq 0$

Consider for any **irreversible cycle** for which:

$$\oint \frac{\partial q}{T} \leq 0$$



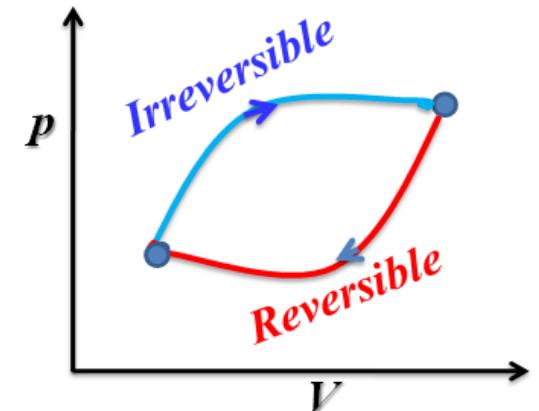
$\therefore$  we can rewrite as,  $\int_1^2 \frac{\partial q_{irr}}{T} + \int_2^1 \frac{\partial q_{rev}}{T} \leq 0$

$$\int_1^2 \frac{\partial q_{irr}}{T} - \int_1^2 dS \leq 0 \quad \because \int_2^1 \frac{\partial q_{rev}}{T} = \int_2^1 dS \quad \text{By definition}$$

$$\Delta S = S_2 - S_1 \geq \int_1^2 \frac{\partial q_{irr}}{T}$$

$\because \oint dS = 0$ ; as entropy is a state function

$$\therefore \oint \frac{\partial q_{irrev}}{T} < 0 \quad \equiv \quad \oint \frac{\partial q}{T} \leq 0$$



# Entropy and Clausius Inequality

For an irreversible change in state from state 1 to state 2

$$\int_1^2 dS > \int_1^2 \frac{\partial q_{irr}}{T} \Rightarrow dS > \frac{\partial q_{irr}}{T}$$

Mathematical statement of 2<sup>nd</sup> law of thermodynamics

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

$dS > \frac{\partial q}{T}$	Irreversible and spontaneous change in state
$dS = \frac{\partial q}{T}$	Reversible process
$dS < \frac{\partial q}{T}$	Process associated with the change in state is NOT permitted

## Second Law of Thermodynamics: ISOLATED SYSTEM

Entropy of the Universe (i.e., **ISOLATED SYSTEM**):

- Does not change for reversible processes
- Increases for spontaneous processes.
- But, entropy can decrease for individual systems

**Reversible (ideal):**

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

**Irreversible (real, spontaneous):**

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

## Entropy Change in an Isolated System

ISOLATED SYSTEM : for irreversible change state

We know:  $dS - dq/T \geq 0$  (Clausius inequality) where,  $dS = dq_{rev}/T$

In Isolate system:

1. Surrounding is NOT affected,  $dS_{surr} = 0$
2.  $dq = 0$  (for both Rev. and Irrev. change)  
So,  $dS > 0$  (from Clausius inequality)

Therefore,

- For any process occurring in an ISOLATED system, the ENTROPY INCREASES ( $dS > 0$ )
- ENTROPY of the system will continue to INCREASE as long as changes occur. When no more changes takes place, the system is said to attain equilibrium and the entropy has reached the maximum value.
- Thus, the condition of equilibrium in an ISOLATED SYSTEM is that the ENTROPY has the MAXIMUM VALUE.

## Application to Transformations in REAL systems

- From Clausius inequality

$$dS > \frac{\partial q_{irrev}}{T}$$

$$\oint \frac{dq}{T} \leq 0 \quad \text{contains} \quad \begin{cases} \oint \frac{dq_{rev}}{T} = 0 \\ \oint \frac{dq_{irrev}}{T} < 0 \end{cases}$$

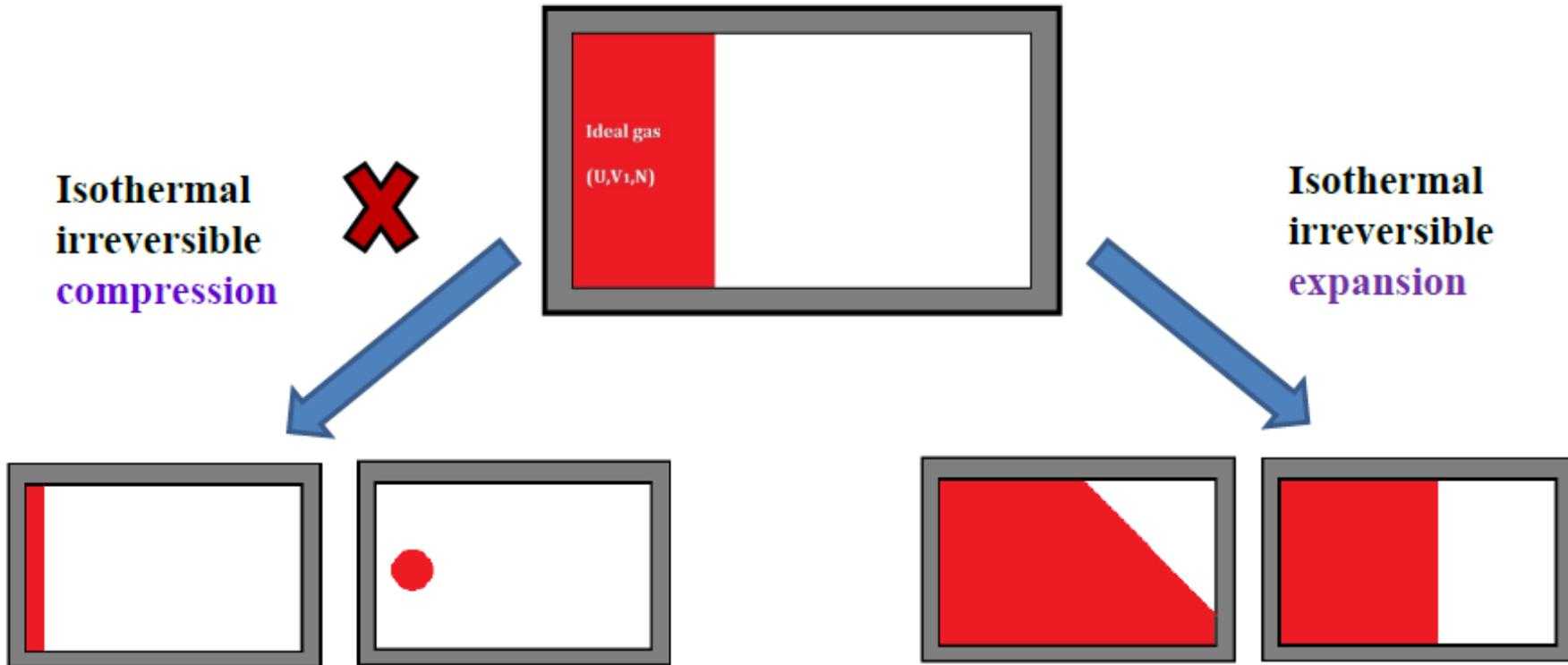
- In an isolated system, during an irreversible process,

$$\partial q_{irrev} = 0 \Rightarrow dS > 0$$

- For a real transformation in an isolated system, upon withdrawal of an internal constraint, the system spontaneously changes towards that direction that increases the entropy.

**Initial equilibrium state**  $(T, V_i, n)$

**Final equilibrium state**  $(T, V_f, n)$



What is  $\Delta S$  as the system goes from  $(T, V_i, n)$  to  $(T, V_f, n)$ ?

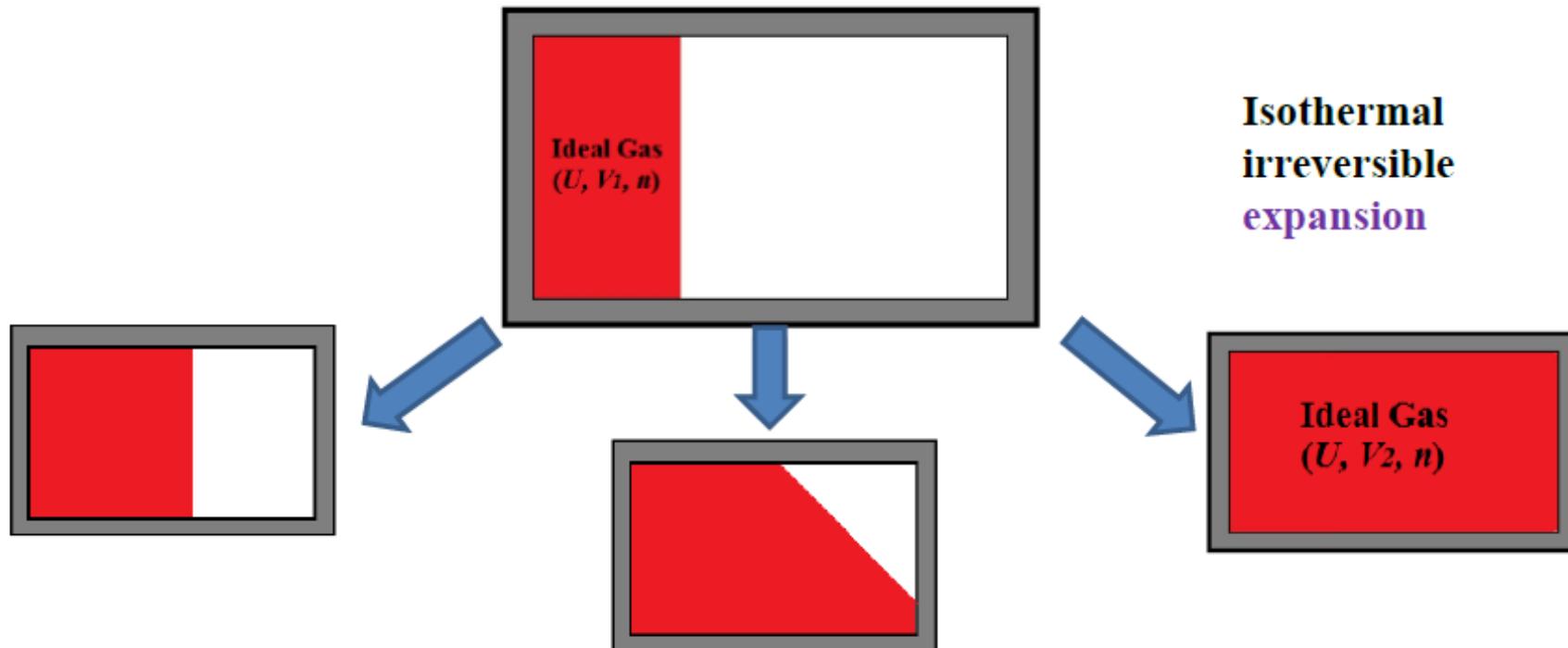
$$\Delta S = R \ln \left( \frac{V_f}{V_i} \right)$$

$$\Delta S > 0 \quad \text{if} \quad V_f > V_i$$

The ideal gas will spontaneously expand under the given experimental condition

**Initial equilibrium state**  $(T, V_i, n)$

**Final equilibrium state**  $(T, V_f, n)$



**Under what condition does the gas stop expanding any further so that a new equilibrium state is reached?**

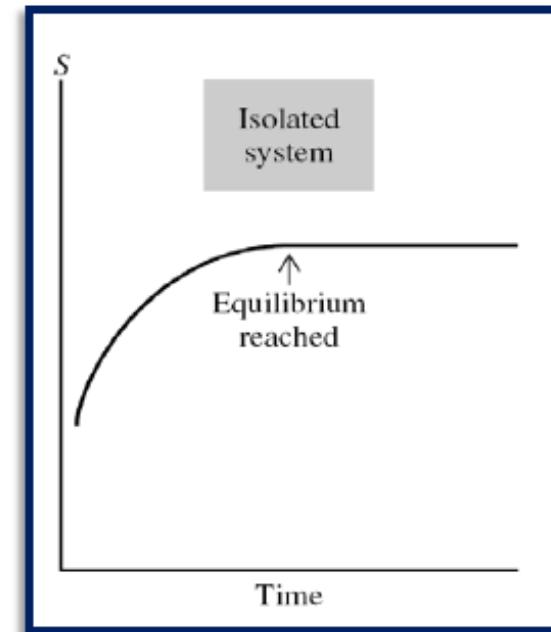
$$\Delta S = R \ln \left( \frac{V_f}{V_i} \right)$$

**$\Delta S$  reaches a maximum when  $V_f$  is maximum**  
 **$\Rightarrow S_{final}$  is maximum when  $V_f = V_2$**

**The ideal gas will spontaneously expand till it fills up the entire available volume**

# Entropy Change in an Isolated System

- Any natural change within an isolated system is accompanied by an increase in entropy
- The entropy continues to increase as long as the changes occur within the system
- When entropy attains its maximum value, the system reaches a new equilibrium state

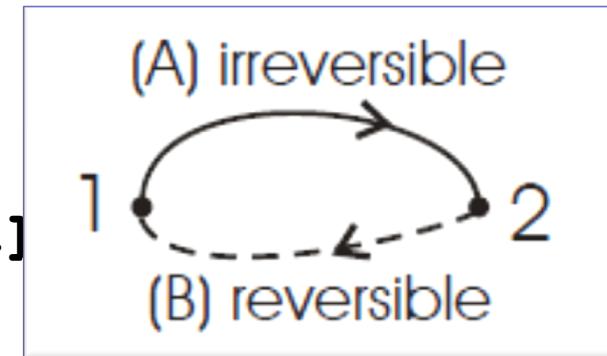


$dS > 0$	Irreversible and spontaneous change in state
$dS = 0$	No further change, a new equilibrium is reached
$dS < 0$	Process associated with the change in state is NOT permitted

# Irreversible Processes: Clausius Inequality

(A): The system is isolated and irreversibly (spontaneously) changes from [1] to [2]

(B): The system is brought into contact with a heat reservoir and reversibly brought back from [2] to [1]



Path (A):  $q_{irrev} = 0$  (isolated)

For the cycle  $[1] \rightarrow [2] \rightarrow [1]$

Clausius  $\oint \frac{dq}{T} \leq 0 \Rightarrow \cancel{\int_1^2 \frac{dq_{irrev}}{T}^{=0!}} + \int_2^1 \frac{dq_{rev}}{T} \leq 0$

$$\Rightarrow \int_2^1 \frac{dq_{rev}}{T} = S_1 - S_2 = -\Delta S \leq 0$$

$$\therefore \boxed{\Delta S = S_2 - S_1 \geq 0}$$

## For isolated systems

$\Delta S > 0$	Spontaneous, irreversible process
$\Delta S = 0$	Reversible process
$\Delta S < 0$	Impossible

This gives the direction of spontaneous change!

## Summary: Calculation of Entropy Change of Ideal gas under various process

$$\begin{aligned}
 dS &= \frac{dq_{rev}}{T} = \frac{dU - w_{rev}}{T} = \frac{dU + pdV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V} \\
 \Leftrightarrow dS &= \frac{dq_{rev}}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V} \\
 \Leftrightarrow \Delta S &= S_2 - S_1 = \int_1^2 dS = \int_1^2 C_V \frac{dT}{T} + \int_1^2 nR \frac{dV}{V}
 \end{aligned}$$

### General Expression of Entropy change for ideal gases

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{p_1}{p_2} + C_p \ln \frac{T_2}{T_1}$$

**Heating at cons. pressure**

$$\Delta S_p = \int \frac{C_p}{T} dT = C_p \ln \frac{T_2}{T_1}$$

**Heating at const. volume**

$$\Delta S_V = \int \frac{C_V}{T} dT = C_V \ln \frac{T_2}{T_1}$$

**Exp. at const. Temp.**

$$\Delta S_T = R \ln \frac{p_1}{p_2}$$

## 2<sup>nd</sup> law: SUMMARY of Mathematical definition of Entropy: Clausius inequality

For any Spontaneous Process (i.e., Irreversible Process):

$$dS_{\text{Univ}} = dS_{\text{sys}} + dS_{\text{surr}} > 0 \text{ or,}$$

$$\Delta S_{\text{Univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

} For any discrete change

For any Reversible Process:

$$\oint \left( \frac{dq_{rev}}{T} \right)_{\text{Univ}} = \oint \left( \frac{dq_{rev}}{T} \right)_{\text{sys}} + \oint \left( \frac{dq_{rev}}{T} \right)_{\text{surr}} = 0$$

$$dS_{\text{Univ}} = dS_{\text{sys}} + dS_{\text{surr}} = 0 \text{ or,}$$

$$\Delta S_{\text{Univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

} For any discrete change

For Impossible process:

$$dS_{\text{Univ}} = dS_{\text{sys}} + dS_{\text{surr}} < 0$$

Leads to Clausius inequality

$$\oint \frac{dq}{T} \leq 0$$

$$\text{contains } \begin{cases} \oint \frac{dq_{rev}}{T} = 0 \\ \oint \frac{dq_{irrev}}{T} < 0 \end{cases}$$

# SUMMARY: Irreversible Processes: Clausius Inequality

$$dS - \frac{\partial q_{irrev}}{T} \geq 0$$

$$\Leftrightarrow dS \geq \frac{\partial q}{T}$$

**But remember that:**  
 $dS_{sys} + dS_{surr} \geq 0$

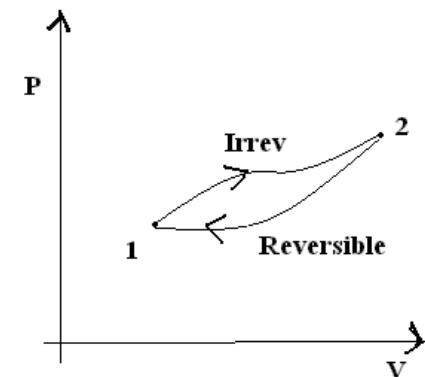
**Now, (a): In a cyclic Irreversible process**

$$\oint \frac{\partial q}{T} \leq 0 \quad (\text{where, } \partial q = \partial q_{rev} + \partial q_{irrev})$$

$$\therefore \text{we can rewrite as, } \oint \frac{\partial q_{rev}}{T} + \oint \frac{\partial q_{irrev}}{T} \leq 0$$

$$\Rightarrow \oint dS + \oint \frac{\partial q_{irrev}}{T} \leq 0 \quad \langle \because \oint \frac{\partial q_{rev}}{T} = \oint dS \rangle$$

$$\Rightarrow \oint \frac{\partial q_{irrev}}{T} < 0 \quad \langle \because \oint dS = 0 ; \text{ as entropy is a state function} \rangle$$



**Various forms of the Clausius Inequality**

$$dS - \frac{\partial q_{irrev}}{T} > 0$$

$$\Leftrightarrow dS \geq \int \frac{\partial q}{T}$$

$$\oint \frac{\partial q_{irrev}}{T} < 0$$

$$\oint \frac{\partial q}{T} \leq 0 \quad dS \geq (dq/T)$$

Leads to Clausius inequality

$$\oint \frac{dq}{T} \leq 0$$

contains

$$\begin{cases} \oint \frac{dq_{rev}}{T} = 0 \\ \oint \frac{dq_{irrev}}{T} < 0 \end{cases}$$

# SUMMARY: Mathematical definition of Entropy: Clausius inequality

**1. Entropy Change of the System:** For REVERSIBLE path:

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T}$$

**2. Entropy Change of the Surrounding:** For REVERSIBLE or, IRREVERSIBLE change

$$\Delta S_{surr} = \frac{-dq}{T_{surr}}$$

Thermal equilibrium between system and surroundings

**3. Definition of Entropy from Clausius Inequality:** -

$$dS - \frac{\partial q}{T} \geq 0 \Leftrightarrow$$

$$dS - \frac{\partial q_{irrev}}{T} \geq 0$$

$$\oint \frac{\partial q}{T} \leq 0$$

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

$dS > \frac{dq}{T}$ : Spontaneous/ Irreversible Process

$dS = \frac{dq}{T}$ : Reversible Process

$dS < \frac{dq}{T}$ : Impossible Process

Criterion for Spontaneity

$$dq_{rev} \geq dq$$

$$\left(\frac{dq_{rev}}{T}\right) - \left(\frac{dq}{T}\right) \geq 0$$

$$dS \geq (dq/T)$$

$$dS_{sys} + dS_{surr} \geq 0$$

# Thermodynamic Equations of State

$$U = f(V, T) \quad \Delta U = \int C_V dT + \int \left( \frac{\alpha T}{\kappa} - p \right) dV$$

where,  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$   
 $\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$

$$H = f(P, T) \quad \Delta H = \int C_p dT + \int (V - TV\alpha) dP$$

$$\left( \frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T} ; \left( \frac{\partial S}{\partial T} \right)_V = \frac{C_v}{T} ;$$

$$S = f(P, T) \quad \Delta S = \int \frac{C_p}{T} dT - \alpha V \int dP$$

$$\left( \frac{\partial S}{\partial P} \right)_T = -\alpha V \quad \left( \frac{\partial S}{\partial V} \right)_T = \frac{\alpha}{\kappa}$$

**Heating at constant pressure**

$$\Delta S_p = \int \frac{C_p}{T} dT = C_p \ln \frac{T_2}{T_1}$$

**Heating at constant volume**

$$\Delta S_v = \int \frac{C_v}{T} dT = C_v \ln \frac{T_2}{T_1}$$

## 2<sup>nd</sup> LAW: Clausius inequality

$$dS + dS_{\text{surr}} \geq 0$$

$dS + dS_{\text{surr}} > 0$  : Spontaneous (irreversible) process

$dS + dS_{\text{surr}} = 0$  : Reversible process

$$dS - dq/T \geq 0$$

$dS$  = difference in entropy between two equilibrium states.

Thermal equilibrium between system and surroundings

$$TdS - dq \geq 0$$

"=" for reversible process

">" for irreversible, spontaneous process

"<" for impossible process

$$dq = dU - dw$$

(closed system)

$$dU - TdS - dw \leq 0$$

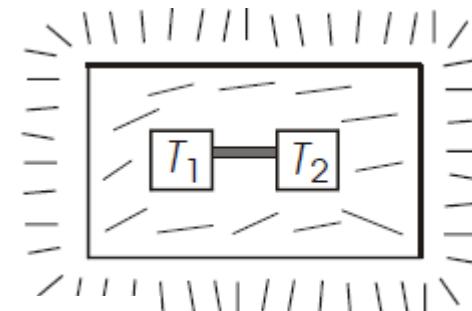
$$dU - TdS - dw_{p-V} - dw_{\text{non } p-V} \leq 0$$

## Examples of $\Delta S$ calculations

### Examples of $\Delta S$ calculation for a spontaneous process

Connect two metal blocks thermally in an isolated system ( $\Delta U = 0$ )

Initially  $T_1 \neq T_2$



$$dS = dS_1 + dS_2 = \frac{dq_1}{T_1} - \frac{dq_2}{T_2} = dq_1 \frac{(T_2 - T_1)}{T_1 T_2} \quad (dq_1 = -dq_2)$$

$dS > 0$  for spontaneous process

$$\Rightarrow \begin{cases} \text{if } T_2 > T_1 \Rightarrow dq_1 > 0 \\ T_2 < T_1 \Rightarrow dq_1 < 0 \end{cases} \left. \begin{array}{l} \text{in both cases heat flows} \\ \text{from hot to cold as expected} \end{array} \right\}$$

## Examples of $\Delta S$ calculations

### Examples of $\Delta S$ calculation for a spontaneous process

Joule expansion with an ideal gas: Gas expands into vacuum to double in volume with no rise in temperature while the system is placed inside a thermally insulated container

$$1 \text{ mol gas } (V, T) \xrightarrow{\text{adiabatic}} 1 \text{ mol gas } (2V, T)$$
$$\Delta U = 0 \quad q = 0 \quad w = 0$$

$$\Delta S = -\Delta S_{\text{backwards}}$$

Compress back isothermally and reversibly

$$q_{\text{rev}} \neq 0$$

$$1 \text{ mol gas } (2V, T) \rightleftharpoons 1 \text{ mol gas } (V, T)$$

$$\Delta S_{\text{backwards}} = \int \frac{dq_{\text{rev}}}{T} = - \int \frac{dw}{T} = \int_{2V}^V \frac{RdV}{V} = R \ln \frac{1}{2} \quad \Delta S = -\Delta S_{\text{backwards}}$$

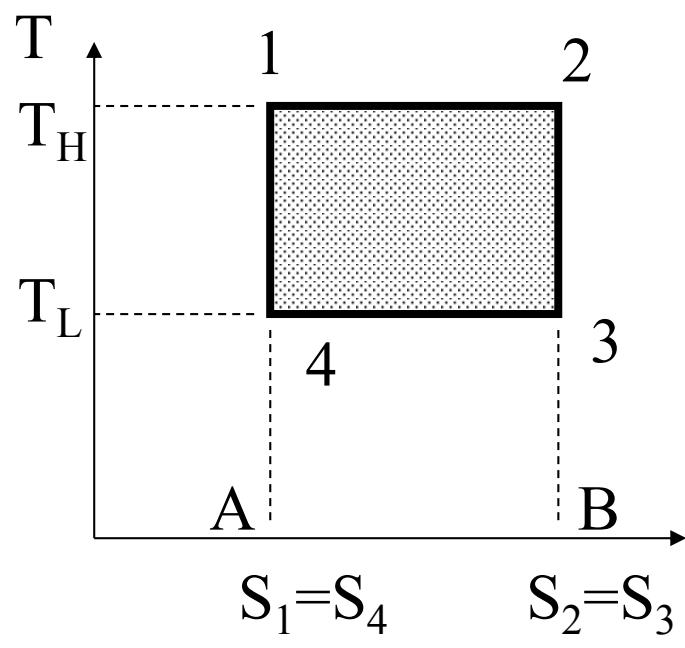
$$\therefore \boxed{\Delta S = R \ln 2 > 0}$$

spontaneous

Note that to calculate  $\Delta S$  for the *irreversible* process, we needed to find a reversible path so we could determine  $dq_{\text{rev}}$  and  $\int \frac{dq_{\text{rev}}}{T}$ .

## Carnot cycle: T-S diagram

- Show the **Carnot cycle** on a T-S diagram and identify the heat transfer at both the high and low temperatures, and the work output from the cycle.



- 1-2, reversible isothermal heat transfer

$$Q_H = \int T dS = T_H(S_2 - S_1) \text{ area 1-2-B-A}$$

- 2-3, reversible, adiabatic expansion  
**isentropic process**,  $S=\text{constant}$  ( $S_2 = S_3$ )

- 3-4, reversible isothermal heat transfer

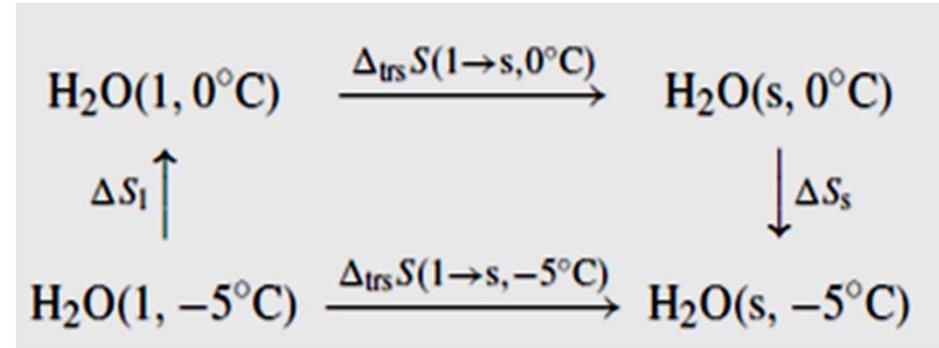
$$Q_L = \int T dS = T_L(S_4 - S_3), \text{ area 3-4-A-B}$$

- 4-1, reversible, adiabatic compression  
**isentropic process**,  $S_1 = S_4$

- Net work  $W_{\text{net}} = Q_H - Q_L$ , the area enclosed by 1-2-3-4, the shaded area

## Calculate Entropy Change in a Phase Change Process

Q. 1 mole of liquid water and ice at -5 °C and 1atm. Which one is more stable?



$$\Delta S = \Delta S_l + \Delta S_{trs} + \Delta S_s \quad \Delta S_{surr} = ?? \text{ (Homework)}$$

### Examples of $\Delta S$ calculations

In all cases, we must find a reversible path to calculate  $\Delta S$

(a) Mixing of ideal gases at constant  $T$  and  $p$

$$n_A A(g, V_A, T) + n_B B(g, V_B, T) = n(A + B)(g, V = V_A + V_B, T)$$

$$\Delta S_{mix} = -nR[X_A \ln X_A + X_B \ln X_B]$$

## Examples of $\Delta S$ calculations

In all cases, we must find a reversible path to find  $\Delta S$

(b) Heating (or cooling) at constant  $V$

$$A(T_1, V) = A(T_2, V)$$

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_V dT}{T} \stackrel{\substack{\text{if } C_V \text{ is} \\ T\text{-independent}}}{=} C_V \ln \frac{T_2}{T_1}$$

[Note  $\Delta S > 0$  if  $T_2 > T_1$ ]

(c) Reversible phase change at constant  $T$  and  $p$

e.g.  $H_2O(l, 100^\circ C, 1 \text{ bar}) = H_2O(g, 100^\circ C, 1 \text{ bar})$

$$q_p = \Delta H_{vap}$$

$$\Delta S_{vap}(100^\circ C) = \frac{q_p^{vap}}{T_b} = \frac{\Delta H^{vap}}{T_b} \quad (T_b = \text{boiling Temp at 1 bar})$$

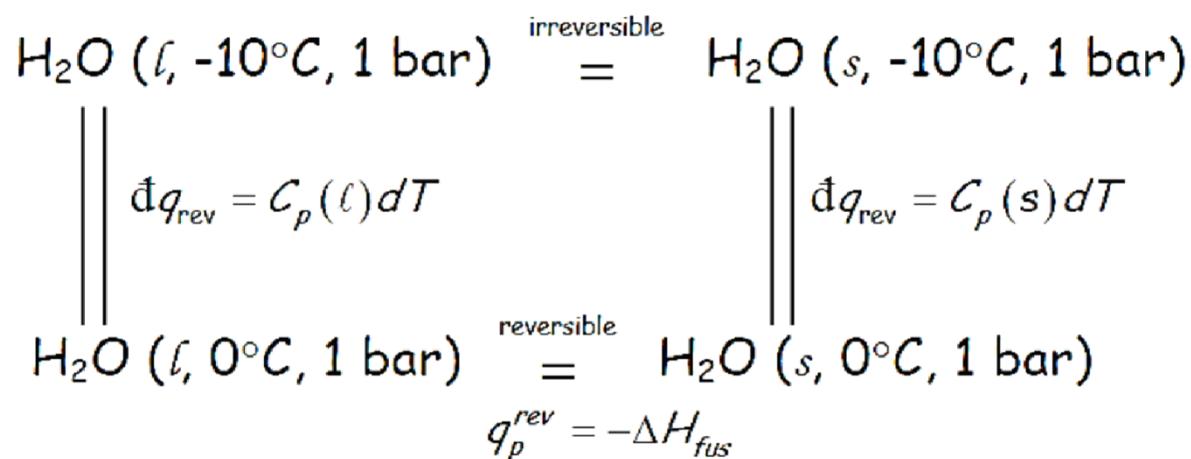
## Examples of $\Delta S$ calculations

(d) Irreversible phase change at constant  $T$  and  $p$

e.g.  $\text{H}_2\text{O} (\ell, -10^\circ\text{C}, 1 \text{ bar}) = \text{H}_2\text{O} (s, -10^\circ\text{C}, 1 \text{ bar})$

This is spontaneous and irreversible.

∴ We need to find a reversible path between the two states to calculate  $\Delta S$ .



## Examples of $\Delta S$ calculations

Consider the following sequence of processes for the substance A:

$$\begin{aligned}A(s, 0K, 1\text{bar}) &= A(s, T_m, 1\text{bar}) = A(l, T_m, 1\text{bar}) = A(l, T_b, 1\text{bar}) \\&= A(g, T_b, 1\text{bar}) = A(g, T, 1\text{bar})\end{aligned}$$

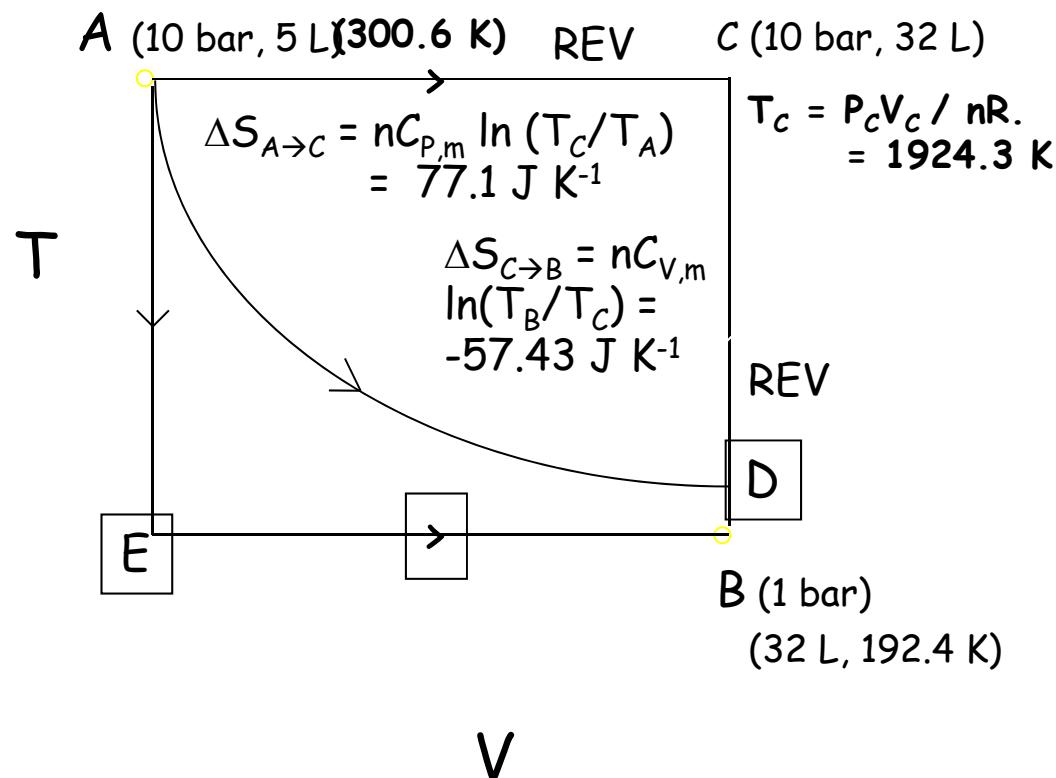
$$\begin{aligned}\Delta S &= \Delta S_{heating} + \Delta S_{fus} + \Delta S_{cooling} \\&= \int_{T_1}^{T_{fus}} \frac{C_p(\ell) dT}{T} + \frac{-\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_1} \frac{C_p(s) dT}{T}\end{aligned}$$

$$\therefore \boxed{\Delta S = \frac{-\Delta H_{fus}}{T} + \int_{T_1}^{T_{fus}} [C_p(\ell) - C_p(s)] \frac{dT}{T}}$$

$$\Delta S = \frac{-\Delta H_{fus}}{T} + [C_p(\ell) - C_p(s)] \ln \frac{T_{fus}}{T_1} \quad \text{if } C_p \text{ values are } T\text{-independent}$$

## Calculate Entropy Change in a Adiabatic Irreversible Process

**Q.** 2 mole of monoatomic ideal gas undergoing irreversible adiabatic expansion against constant final pressure of 1 bar, calculate  $\Delta S$



$$\Delta S_{A \rightarrow B} = \Delta S_{A \rightarrow C} + \Delta S_{C \rightarrow B} = 19.73 \text{ J K}^{-1}$$

A: (10 bar, 5 L, ? K, )

$$T_A = P_A V_A / n R$$
 $= (106 \times 5 \cdot 10^{-3}) / (2 \times 8.3145) = 300.68 \text{ K}$

$$dU_{A \rightarrow B} = q_{A \rightarrow B} + w_{A \rightarrow B}$$

$$dU_{A \rightarrow B} = C_V dT \quad w_{A \rightarrow B} = -p_{\text{ex}} dV$$

$$C_V(T_B - T_A) = 0 - p_B(V_B - V_A)$$

$$2 \times \frac{3}{2} R(T_B - T_A) = -p_B \left( \frac{2RT_B}{p_B} - V_A \right)$$

$$T_B = 192.44 \text{ K}$$

$$V_B = 32 \text{ L}$$

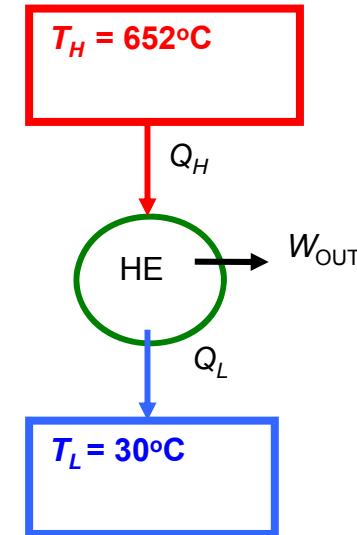
## Numerical Problems

A Carnot heat engine receives 500 kJ of heat per cycle from a high-temperature heat reservoir at 652°C and rejects heat to a low-temperature heat reservoir at 30°C. Determine

- The thermal efficiency of this Carnot engine.
- The amount of heat rejected to the low-temperature heat reservoir.

a.

$$\begin{aligned}\eta_{th, rev} &= 1 - \frac{T_L}{T_H} \\ &= 1 - \frac{(30 + 273)K}{(652 + 273)K} \\ &= 0.672 \quad or \quad 67.2\%\end{aligned}$$



b.

$$\begin{aligned}\frac{Q_L}{Q_H} &= \frac{T_L}{T_H} \\ &= \frac{(30 + 273)K}{(652 + 273)K} = 0.328\end{aligned}$$

$$Q_L = 500 \text{ kJ}(0.328)$$

$$= 164 \text{ kJ}$$

## Numerical Problems

Suppose a mole of a diatomic gas, such as  $O_2$ , is compressed adiabatically so the final volume is half the initial volume. The starting state is  $V = 1$  liter,  $T = 300$  K. What are the final temperature and pressure?

Equation relating  $p, V$  for adiabatic process in  $\alpha$ -ideal gas

$\gamma$  is the ratio of  $C_p/C_V$  for diatomic gas in this case

Solve for  $p_f$  from first equation

Substitute for  $p_i$

Use ideal gas law to calculate final temperature

OR use the equation relating  $T, V$  for an adiabatic process to get the final temperature ( $\alpha = 5/2$  for diatomic gas)

Solve for  $T_f$

$$p_i V_i^\gamma = p_f V_f^\gamma$$

$$\gamma = \frac{7/2}{5/2} = 1.4$$

$$p_f = p_i \left( \frac{V_i}{V_f} \right)^\gamma$$

$$= \frac{nRT_i}{V_i} \left( \frac{V_i}{V_f} \right)^\gamma$$

$$= 6.57 \times 10^6 \text{ Pa}$$

$$T_f = \frac{p_f V_f}{nR}$$

$$= 395 \text{ K}$$

$$T_i^\alpha V_i = T_f^\alpha V_f$$

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{\frac{1}{\alpha}}$$

$$= 395 \text{ K}$$

# Numerical: Entropy change in Heat engine

Consider a Carnot heat engine.

1. What is the sign of the entropy change of the hot reservoir during one cycle?

- a.  $\Delta S_h < 0$
- b.  $\Delta S_h = 0$
- c.  $\Delta S_h > 0$

Because energy is flowing out of the hot reservoir, its entropy (the number of microstates) is decreasing.

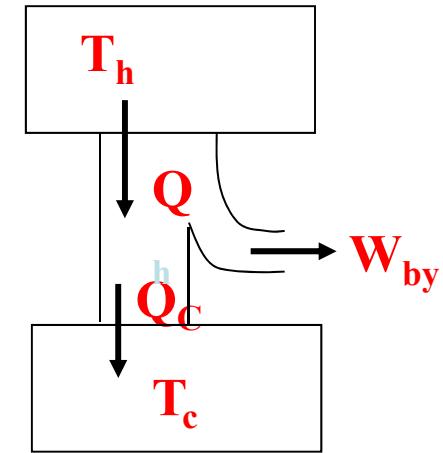
2. What is the sign of the entropy change of the cold reservoir?

- a.  $\Delta S_c < 0$
- b.  $\Delta S_c = 0$
- c.  $\Delta S_c > 0$

Because energy is flowing into the cold reservoir, it's entropy (number of microstates) is increasing.

3. Compare the magnitudes of the two changes.

- a.  $|\Delta S_c| < |\Delta S_h|$
- b.  $|\Delta S_c| = |\Delta S_h|$
- c.  $|\Delta S_c| > |\Delta S_h|$



## Numerical Problems

How much heat is absorbed by 3 moles of helium when it expands from  $V = 10$  liters to  $V = 20$  liters and the temperature is kept at a constant 350 K? What are the initial and final pressures?

$$Q = -W_{on}$$

$$\begin{aligned} W_{on} &= -nRT \ln(V_f/V_i) \\ &= -6048 \text{ J} \end{aligned}$$

$$\begin{aligned} p_i &= nRT/V_i = 8.72 \times 10^5 \text{ Pa} \\ p_f &= p_i/2 = 4.36 \times 10^5 \text{ Pa} \end{aligned}$$

### Solution:

From first law. For an ideal gas, isothermal means  $\Delta U = 0$ .

Positive Q means heat flows into the gas.

This was derived in lecture.  
 $R = 8.31 \text{ J/mole}\cdot\text{K}$

$$pV = nRT$$

Where is the heat coming from? In order to keep the gas at a constant temperature, it must be put in contact with a large object having that temperature. That object is called a "**heat reservoir**", and it supplies heat to the gas (or absorbs heat, if necessary) in order to keep the gas temperature constant.

# **Criteria for Spontaneous Change**

## Criteria for Spontaneous Change

The 2<sup>nd</sup> Law gave the Clausius inequality for spontaneous change

$$dS - \delta q/T_{\text{surr}} \geq 0$$

$$dS > \delta q/T_{\text{surr}}$$

$$T_{\text{surr}} dS - \delta q \geq 0$$

The 1<sup>st</sup> law gave us  $dU = \delta q + \delta w$

$$T_{\text{surr}} dS - (dU - \delta w) \geq 0$$

$$T_{\text{surr}} dS - (dU + p_{\text{ext}} dV) \geq 0$$

Putting the two together, assuming only pV work, gives us the following general criterion for spontaneous change:

$$\boxed{\star\star dU + p_{\text{ext}} dV - T_{\text{surr}} dS < 0 \star\star}$$

Equilibrium is when there is no possible change of state that would satisfy this inequality.

We can now use the general criterion above under specific conditions

# Criteria for Spontaneous Change

- Consider first an isolated system ( $q=w=0, \Delta V=0, \Delta U=0$ )

Since  $dU=0$  and  $dV=0$ , from the general criterion above, then

$$(dS)_{U,V} > 0$$

is the criterion for spontaneity for an isolated system

And equilibrium for an isolated system is then achieved when entropy is maximized. At maximum entropy, no spontaneous changes can

- Consider now S and V constant

$$** dU + p_{ext}dV - T_{surr}dS < 0 **$$

$$\Rightarrow (dU)_{S,V} < 0$$

is the criterion for spontaneity under constant V and S

At constant S and V, equilibrium is achieved when energy is minimized

# Criteria for Spontaneous Change

- Consider now  $S$  constant and  $p=p_{\text{ext}}$  constant

$$\Rightarrow dU + pdV < 0 \Rightarrow d(U + pV) < 0$$

$\downarrow$   
 $=H$

**\*\*  $dU + p_{\text{ext}}dV - T_{\text{surr}}dS < 0$  \*\***

So

$$\Rightarrow (dH)_{S,p_{\text{ext}}} < 0$$

is the criterion for spontaneity under constant  $S$  and constant  $p=p_{\text{ext}}$ .

- Consider now  $H$  constant and  $p=p_{\text{ext}}$  constant

$$dU + pdV - T_{\text{surr}}dS < 0$$

but  $dU + pdV = dH$ , which is 0 ( $H$  is constant)

So  $(dS)_{H,p=p_{\text{ext}}} > 0$

is the criterion for spontaneity under constant  $H$  and constant  $p=p_{\text{ext}}$ .

## Criteria for Spontaneous Change

- Consider now constant  $T = T_{\text{surr}}$  and constant  $V$

$$** dU + p_{\text{ext}} dV - T_{\text{surr}} dS < 0 **$$

$$\Rightarrow dU - TdS < 0 \Rightarrow d(U - TS) < 0$$

Define  $A = U - TS$ , the Helmholtz Free Energy

Then  $(dA)_{V,T=T_{\text{surr}}} < 0$

is the criterion for spontaneity under constant  $T = T_{\text{surr}}$  and constant  $V$ .

For constant  $V$  and constant  $T = T_{\text{surr}}$ , equilibrium is achieved when the Helmholtz free energy is minimized.

## Criteria for Spontaneous Change

We now come to the most important and applicable constraint:

- Consider now constant  $T=T_{\text{surr}}$  and constant  $p=p_{\text{ext}}$ .

$$(dU + pdV - TdS) < 0 \Rightarrow d(U + pV - TS) < 0$$

Define  $G = U + pV - TS$ , the Gibbs Free Energy

$$** dG = dU + p_{\text{ext}}dV - T_{\text{surr}}dS < 0 **$$

(can also be written as  $G = A + pV$  and  $G = H - TS$  )

Then  $(dG)_{p=p_{\text{ext}}, T=T_{\text{surr}}} < 0$

is the criterion for spontaneity under constant  $T=T_{\text{surr}}$  and constant  $p=p_{\text{ext}}$ .

At constant  $p=p_{\text{ext}}$  and constant  $T=T_{\text{surr}}$ , equilibrium is achieved when the Gibbs free energy is minimized.

# Criteria for Spontaneous Change

Consider the process:

$$A(p,T) \rightleftharpoons B(p,T) \quad (\text{keeping } p \text{ and } T \text{ constant})$$

Under constant  $p=p_{\text{ext}}$  and  $T=T_{\text{surr}}$ ,

$\Delta G < 0$      $A \rightarrow B$  is spontaneous

$\Delta G = 0$      $A$  and  $B$  are in equilibrium

$\Delta G > 0$     then  $B \rightarrow A$  is spontaneous

# Helmholtz and Gibbs energy

Clausius inequality:  $dS - \frac{dq}{T} \geq 0$

At constant volume:  $dS - \frac{dU}{T} \geq 0 \quad TdS - dU \geq 0$

At constant pressure:  $dS - \frac{dH}{T} \geq 0 \quad TdS - dH \geq 0$

Let's define:

- Helmholtz energy

$$A = U - TS$$

- Gibbs energy

$$G = H - TS$$

- Helmholtz energy:

- At equilibrium  $dA_{T,V} = 0$   
reaction would favorable if  $dA_{T,V} < 0$  meaning that total entropy of the system increases ( $dS$  entropy change of the system,  $-dU/T$  – of the surrounding)
- The change in Helmholtz energy is equal to the maximum work accompanying the process

- Gibbs energy (free energy):

- At constant T and P chemical reactions are spontaneous in the direction of decreasing Gibbs energy
- Maximum additional (non-expansion) work is given by the change in Gibbs energy.
- Standard Gibbs energy can be defined as:

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

Further, standard Gibbs energy of formation can be introduced:

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

# Criteria for Spontaneous Change

Criteria for spontaneity

$$dS_{\text{sys}} + dS_{\text{surr}} > 0$$

For **Closed system** (constant composition), **NO non p-V work**

$$dU_{S,V} < 0$$

$$dH_{S,p} < 0$$

$$dA_{V,T} < 0$$

$$dS_{U,V} > 0$$

$$dS_{H,p} > 0$$

$$dG_{p,T} < 0$$

At normal lab condition of const. T & p;  
**G** should **decrease** for spontaneous processes

Reversible processes will have an equality sign

## Spontaneous Change

For a system in thermal equilibrium with its surroundings,

$$dS \geq \frac{\delta q}{T} \quad \text{Clausius inequality}$$

At constant volume:

$$dq_V = dU \quad \text{no work}$$

$$TdS - dU \geq 0$$

$$(dS)_{U,V} \geq 0 \quad \text{isolated system}$$

$$(dU)_{S,V} \leq 0$$

At constant pressure:

$$dq_P = dH \quad \text{PV work only}$$

$$TdS - dH \geq 0$$

$$(dS)_{H,P} \geq 0 ; (dH)_{S,P} \leq 0$$

For convenience, define:

$$A = U - TS \quad dA = dU - TdS - SdT$$

$$G = H - TS \quad dG = dH - TdS - SdT$$

Then the conditions for spontaneous change become:

$$(dA)_{T,V} \leq 0 \quad (dG)_{T,P} \leq 0$$

## Gibbs Energy G

Gibbs free energy, Gibbs function

- Very important in chemistry since it tells whether a particular reaction can proceed at a given  $T$  and  $P$ .

For spontaneous change,

$$(dG)_{T,P} \leq 0 \quad \Delta G = G_{\text{products}} - G_{\text{reactants}} \leq 0$$

$\Delta G_{T,P}$  for reactions can be calculated from tabulated data

$$\Delta G^\circ(T) = \Delta H^\circ(T) - T\Delta S^\circ(T)$$

If $\Delta H$ is	and $\Delta S$ is	then $\Delta G$	the reaction proceeds
-ve	+ve	$< 0$	at all temperatures
+ve	-ve	$> 0$	at no temperatures
-ve	-ve	...	if $T < \Delta H / \Delta S$
+ve	+ve	...	if $T > \Delta H / \Delta S$

Maximum Work: Isothermal Reversible process

$$(dG)_T = dH - TdS$$

$$(dG)_{T,P} = dU + PdV - TdS$$

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

$$= \delta w_{\text{rev}} + PdV$$

$$= \delta w_{\text{max}} (\text{non-}PV)$$

$$\delta w_{\text{max}} (\text{non-}PV) = \Delta G \quad \text{constant } T, P$$

as,  $\delta w_{\text{rev}} = \delta w_{\text{max}} (\text{non-}PV) + (-PdV)$

# Helmholtz Energy A

## Maximum work function

For spontaneous change at constant  $T$  and  $V$

$$dA = dU - TdS \leq 0$$

Note that it is the *total* function  $A$  that tends to a minimum this is *not* the same as minimizing  $U$  and maximizing  $S$ .

## Maximum Work

Combine  $dU = \delta q + \delta w$  and  $TdS \geq \delta q$

$$\Rightarrow dU \leq TdS + \delta w \quad \text{equality for reversible change}$$

Work done by the system  $(-\delta w) \leq TdS - dU$

$$(-\delta w)_{\max} = TdS - \delta q_{\text{rev}} - \delta w_{\text{rev}} = -\delta w_{\text{rev}}$$

A system does maximum work when it is operating reversibly.

But  $(dA)_T = dU - TdS = dU - \delta q_{\text{rev}} = \delta w_{\text{rev}}$

Therefore, for macroscopic changes

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

( $-w$ ) can be more (or less) than  $U$  according to the sign of  $S$ .

If  $S > 0$ , heat flows into the system to fuel the extra work.

Therefore,  
Change in Gibbs Energy ( $G$ ) under is the measure of the Maximum Non-Expansive Work ( $w_{\max}$ ) a system can perform during the process.  
—  $G = -w_{\max}$  (non PV)

while,  
Change in Helmholtz Energy ( $A$ ) under Isothermal Reversible process is the measure of the Maximum Expansive Work ( $w_{\max}$ ) a system can perform.  
—  $A = -w_{\max}$  (PV work)

By definition:  $A = U - TS$   
—  $A = -\Delta(U - TS)$  at constant  $T$

# Summary of Spontaneity Conditions (General form) at Constant V and T

$$dU - TdS - dw_{p-V} - dw_{non\ p-V} \leq 0$$

Const. V       $dw_{p-V} = 0$

Const. T       $A = U - TS$

$$dU - TdS - dw_{non\ p-V} \leq 0$$

for  $dw_{non\ p-V} = 0$

$$dA - dw_{tot} \leq 0$$

Const. T       $A = U - TS$

$$dU - TdS \leq 0$$

$$dA \leq dw_{tot}$$

$$dA_{V,T} \leq dw_{non\ p-V}$$

$$dA \geq (-dw_{tot})$$

for  $dw_{non\ p-V} = 0$

$$dU_{S,V,\text{ no non p-V work}} \leq 0$$

$$dA = (-dw_{tot})_{max}$$

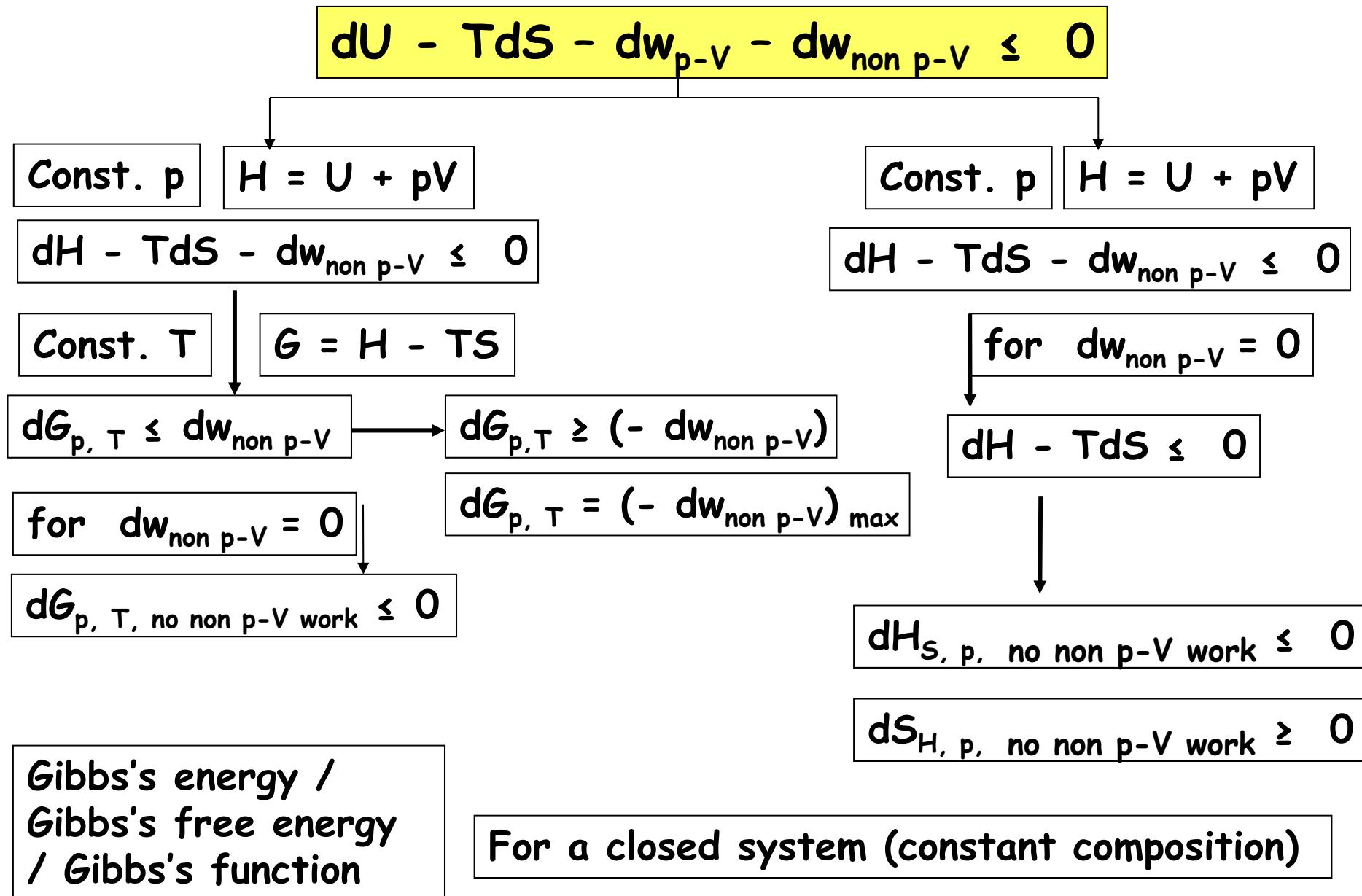
$$dA_{V,T,\text{ no non p-V work}} \leq 0$$

$$dS_{U,V,\text{ no non p-V work}} \geq 0$$

Helmoltz's energy /  
Helmoltz's free energy /  
Helmoltz's function

For a closed system (constant composition)

# Summary of Spontaneity Conditions (General form) at Constant P and T



# MAXWELL RELATIONS

# Fundamental Equations from H, A, G

Combination of 1st and 2nd Law  
(True for any path)

$$dU = dq + dw$$
$$dU = TdS - PdV$$

For a closed system (const. composition), no non p-V (additional) work

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$dA = TdS - PdV - TdS - SdT$$

$$dA = -PdV - SdT$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

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

$$dG = VdP - SdT$$

# Entropy Change Derived from the Fundamental Equations of U H

$$dU = -pdV + TdS$$

$$nC_VdT = -pdV + TdS$$

$$dS = \frac{p}{T}dV + nC_V \frac{dT}{T}$$

$$dS = nR \frac{dV}{V} + nC_V \frac{dT}{T}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1}$$

$$dH = Vdp + TdS$$

$$nC_pdT = -Vdp + TdS$$

$$dS = \frac{V}{T}dp + nC_p \frac{dT}{T}$$

$$dS = -nR \frac{dp}{p} + nC_p \frac{dT}{T}$$

$$\Delta S = nR \ln \frac{p_1}{p_2} + nC_p \ln \frac{T_2}{T_1}$$

# The Maxwell Relations

If  $Z=f(x, y)$ , and  $Z$  has continuous second partial derivatives, then

$$df = M(x, y)dx + N(x, y)dy$$

For exact differential

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$dU = -pdV + TdS$$

$$\left[ \frac{\partial}{\partial y} \left( \frac{\partial Z}{\partial x} \right)_y \right]_x = \left[ \frac{\partial}{\partial x} \left( \frac{\partial Z}{\partial y} \right)_x \right]_y$$

$$dH = Vdp + TdS$$

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$

That is:

$$\frac{\partial^2 Z}{\partial x \partial y} = \frac{\partial^2 Z}{\partial y \partial x}$$

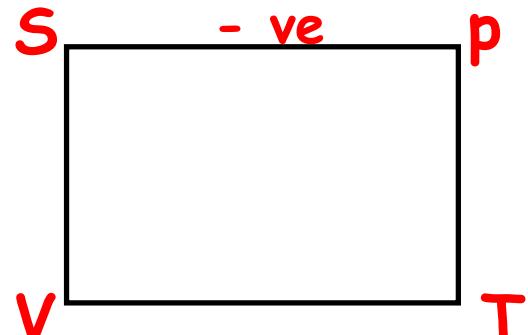
# The Maxwell Relations

$$dU = -pdV + TdS$$

$$dH = Vdp + TdS$$

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$



$$dU = -pdV + TdS$$

$$dU = f(V, S)$$

$$dU = \left( \frac{\partial U}{\partial V} \right)_S dV + \left( \frac{\partial U}{\partial S} \right)_V dS$$

$$dU = M(V, S) dV + N(V, S) dS$$

$$\left( \frac{\partial U}{\partial V} \right)_S = -p$$

$$\left( \frac{\partial U}{\partial S} \right)_V = T$$

As  $dU$  is an exact differential

Therefore,

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

# Basic Thermodynamic Relations 1

Laws

$$dU = \delta q - PdV \quad \dots(1)$$

$$dS = \delta q_{\text{rev}} / T \quad \dots(2)$$

Definitions

$$H = U + PV \quad \dots(3)$$

$$A = U - TS \quad \dots(4)$$

$$G = H - TS \quad \dots(5)$$

Fundamental Equations

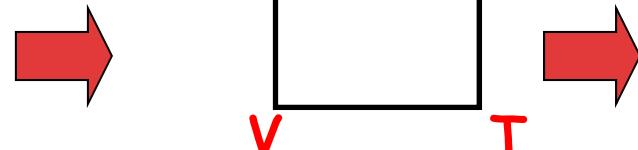
$$dU = TdS - PdV \quad \dots(6)$$

$$dH = TdS + VdP \quad \dots(7)$$

$$dA = -SdT - PdV \quad \dots(8)$$

$$dG = -SdT + VdP \quad \dots(9)$$

Maxwell Relations



Partial Differentials

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

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

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

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

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \dots(10)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \dots(11)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \dots(12)$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad \dots(13)$$

From (6)

From (7)

From (8)

From (9)

## These are the Maxwell Relations

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

The first two are little used.

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

The last two are extremely valuable.

The equations relate the isothermal pressure and Isobaric volume variations of entropy to measurable properties that can be obtained from an EQUATION OF STATE.

# Thermodynamic Equation of State

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

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

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

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

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

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

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

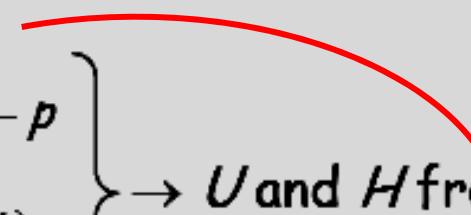
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

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

We can now also relate  $T$  and  $H$  to  $p$ - $V$ - $T$  data.

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

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

  **$U$  and  $H$  from equations of state!**

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) - P$$

# Thermodynamic Equation of State

We can now also relate  $T$  and  $H$  to  $p$ - $V$ - $T$  data.

$$\left. \begin{aligned} \left( \frac{\partial U}{\partial V} \right)_T &= T \left( \frac{\partial S}{\partial V} \right)_T - p = T \left( \frac{\partial p}{\partial T} \right)_V - p \\ \left( \frac{\partial H}{\partial p} \right)_T &= T \left( \frac{\partial S}{\partial p} \right)_T + V = V - T \left( \frac{\partial V}{\partial T} \right)_p \end{aligned} \right\} \rightarrow U \text{ and } H \text{ from equations of state!}$$

- For an ideal gas  $pV = nRT$

$$\left( \frac{\partial p}{\partial T} \right)_V = \frac{nR}{V} = \frac{p}{T} \Rightarrow \left( \frac{\partial U}{\partial V} \right)_T = 0$$

$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{p} = \frac{V}{T} \Rightarrow \left( \frac{\partial H}{\partial p} \right)_T = 0$$

This proves that for an ideal gas  $U(T)$  and  $H(T)$ , functions of  $T$  only. We had assumed this was true from Joule and Joule-Thomson expansion experiments. Now we know it is rigorously true.

- For a van der Waals gas

$$\begin{aligned} \left( p + \frac{a}{V^2} \right) (V - b) &= RT \\ p &= \frac{RT}{V - b} - \frac{a}{V^2} \end{aligned}$$

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{RT}{V - b} - p = \frac{a}{V^2} \neq 0 \Rightarrow U(T, V)$$

## Variation of ENTROPY with T at Constant p and V (From Maxwell's Relations)

$$dU = -pdV + TdS$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}}$$

$$dH = VdP + TdS$$

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

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

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}}$$

## Variation of ENTROPY with T and p

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad \begin{matrix} dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \\ \downarrow \qquad \qquad \qquad \downarrow \end{matrix} \quad \left(\frac{\delta}{\delta p}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_p = -\alpha V$$

$$\boxed{\Delta S = \int \frac{C_p}{T} dT - \int \alpha V dP}$$

# Dependence of state functions ( $U$ , $H$ , and $S$ ) on $T$ , $p$ , and $V$

1.  $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$  were  $\left(\frac{\partial U}{\partial T}\right)_V = C_V$  ;  $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\alpha T}{\kappa} - p\right)$   $\Rightarrow \Delta U = \int C_V dT + \int \left(\frac{\alpha T}{\kappa} - p\right) dV$

2.  $dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$  were  $C_p = \left(\frac{\partial H}{\partial T}\right)_p$  ;  $\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \alpha T)$   $\Rightarrow \Delta H = \int C_p dT + \int (V - TV\alpha) dp$

3.  $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$  were  $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$  ;  $\left(\frac{\partial S}{\partial p}\right)_T = -\alpha V$   $\Rightarrow \Delta S = \int \frac{C_p}{T} dT - \int \alpha V dP$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\alpha V \quad ; \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa} \quad ; \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad ; \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

Prove or Find the following :

1.  $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\alpha T}{\kappa} - p\right) = 0$  for ideal gas ;  $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\alpha T}{\kappa} - p\right) = an^2/V^2$  for vdW gas

2.  $\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \alpha T) = 0$  for ideal gas ;  $\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \alpha T) = ?$  for vdW gas

3.  $\mu_{JT} = \frac{V}{C_p} (\alpha T - 1) = 0$  for ideal gas ;  $C_p - C_V = \frac{TV\alpha^2}{\kappa} = nR$  for ideal gas

# How Free Energy Depends on $T$

$$G = H - TS \quad \dots(1)$$

definition

$$\Delta G = \Delta H - T\Delta S \quad \dots(2)$$

constant  $T$

$$dG = VdP - SdT \quad \dots(3)$$

fundamental eqn.

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \Rightarrow \int \partial G = - \int S \partial T$$

To proceed any further, we need  $S$  as a function of  $T$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G - H}{T} \quad \text{from (1)}$$

$$\therefore \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = -\frac{H}{T} \quad \dots(4)$$

Now suppose  $(G/T)$  is differentiated w.r.t.  $T$

we will get:  $\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2}$  ... (5) Now Substitute (4) in (5)

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

we get the Gibbs-Helmholtz Equation:

Alternate form the Gibbs-Helmholtz Equation:

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H$$

By applying the Gibbs-Helmholtz equation to both reactants and products of a chemical reaction, we get:

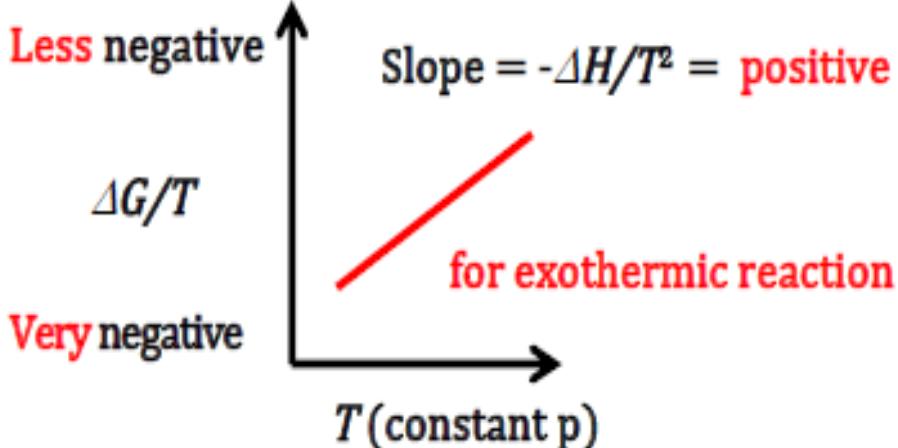
$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

# How Free Energy Depends on $T$

So, we have  $\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$  and  $\left(\frac{\partial(\Delta G / T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$  :Gibbs-Helmholtz Equation:

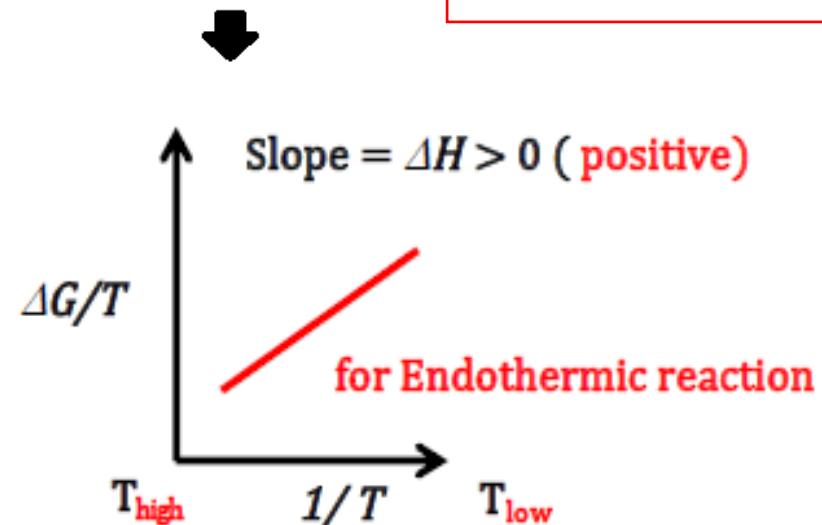
Therefore, changes in entropy or, more commonly, changes in enthalpy can be used to show how changes in the Gibbs energy vary with  $T$  in a reaction

For a spontaneous ( $\Delta G < 0$ ) exothermic reaction ( $\Delta H < 0$ ) the change in Gibbs energy increases with increasing temperature.



Another form of the  
Gibbs-Helmholtz Equ.:

$$\left(\frac{\partial(\Delta G / T)}{\partial(1/T)}\right)_p = \Delta H$$



# How Free Energy Depends on $P$

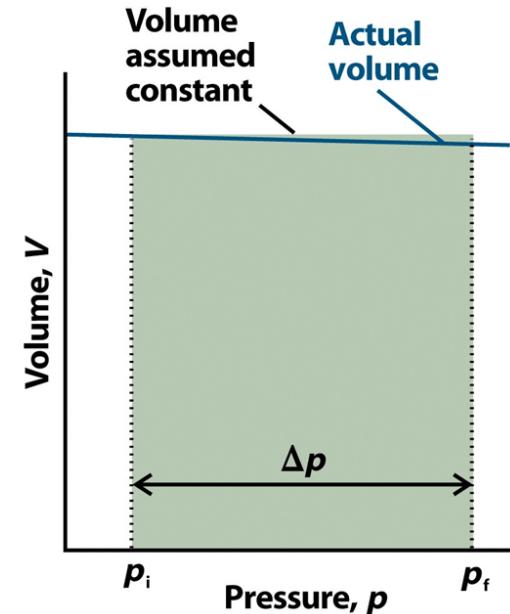
$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \therefore dG = Vdp$$

- For Isothermal Process ( $T$  consant)

$$\int dG = \int Vdp \implies G(p_f) = G(p_i) + \int_{p_i}^{p_f} Vdp$$

- For solids and Liquids,  $V$  does not change with  $p$  (they are incompressible)

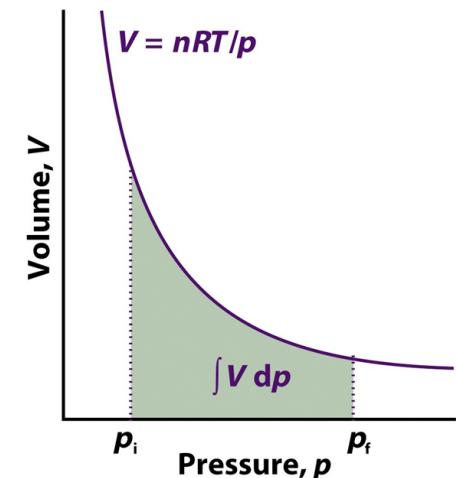
$$\therefore G(p_f) = G(p_i) + V\Delta p \text{ where, } G(p_f) \approx G(p_i) + V(p_f - p_i)$$



- For ideal gas:

$$V = \frac{nRT}{P} \quad \therefore G(p_f) = G(p_i) + \int_{p_i}^{p_f} \frac{nRT}{p} dp = G(p_i) + nRT \ln\left(\frac{p_f}{p_i}\right)$$

$$G(p) = G^\ddagger + nRT \ln\left(\frac{p}{p^\ddagger}\right)$$



# How Free Energy Depends on $P$

$$\Delta G_T = nRT \ln(P_2 / P_1)$$

$$G = G^\circ(T) + nRT \ln(P / P^\circ)$$

where  $G^\circ$  is the standard free energy defined at  $P^\circ=1$  bar

Standard Gibbs energy,  $G$ , varies with Temp.

□ For ideal gas:

$$\bar{G}(T, p_2) = \bar{G}(T, p_1) + \int_{p_1}^{p_2} \frac{RT}{p} dp = \bar{G}(T, p_1) + RT \ln \frac{p_2}{p_1}$$

where,  $p_1 = p^\circ = 1$  bar

And,  $\bar{G}(T, p) = \bar{G}^\circ(T) + RT \ln \frac{p}{p_0}$  or  $\bar{G}(T, p) = \bar{G}^\circ(T) + RT \ln p$

$\uparrow$   
( $p$  in bar)

From,  $S = -\left(\frac{\partial G}{\partial T}\right)_p \Rightarrow \bar{S}(T, p) = \bar{S}^\circ(T) - R \ln p$

Standard Gibbs energy,  $G$ , is defined as the free energy change accompanying the formation of a compound from the element, when all the reactant and product are in their standard state.

# Why Free Energy is Important in Chemistry??

The special role of  $G(T,p)$ :

$$dG = Vdp - SdT$$

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

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

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

$$U = H - pV \Rightarrow U = G - T\left(\frac{\partial G}{\partial T}\right)_p - p\left(\frac{\partial G}{\partial p}\right)_T$$

$$A = U - TS \Rightarrow A = G - p\left(\frac{\partial G}{\partial p}\right)_T$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \Rightarrow C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

If you know  $G(T,p)$ .  
you know everything!

# Properties of Gibbs energy

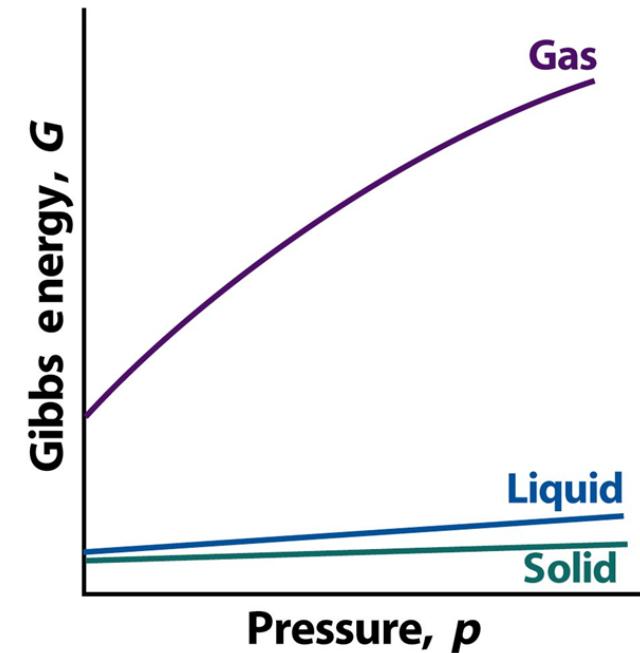
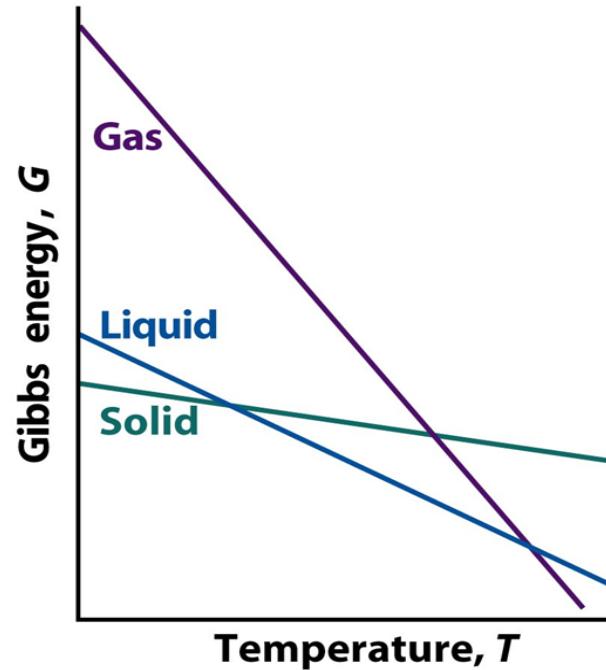
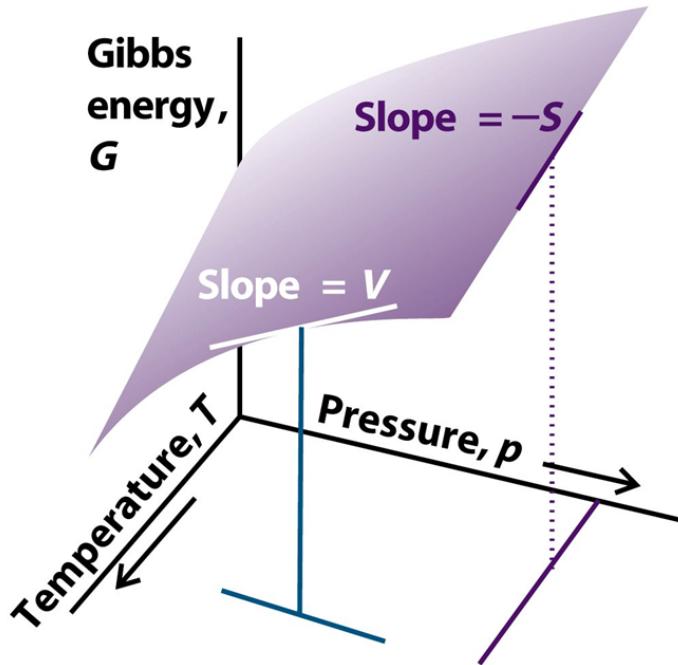
$$dG = -SdT + Vdp$$

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

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

G of a state **decreases** with in increase in T and is a **measure of the Entropy** of the state

G of a state **increases** with in increase in T and is a **measure of the Volume** of the state

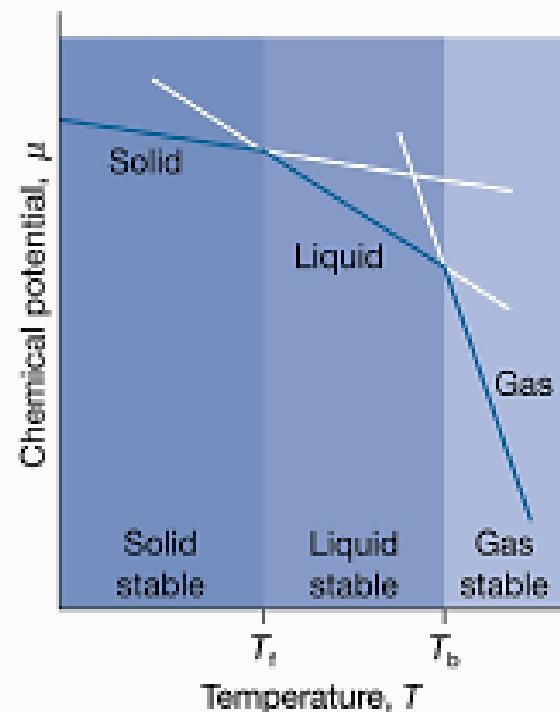


# Phase transitions

$$dG = -SdT + Vdp, \mu = G_m$$

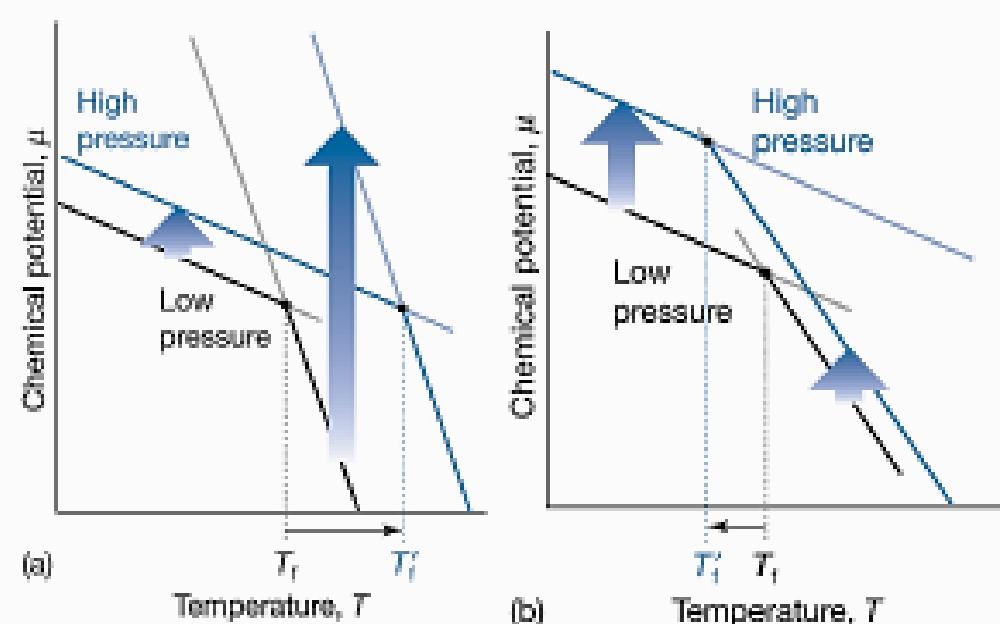
Temperature dependence

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -S_m$$



Melting point vs. applied pressure

$$\left(\frac{\partial\mu}{\partial p}\right)_T = V_m$$



This discussion is continued in the section on Phase Equilibrium

# THERMODYNAMICS OF OPEN SYSTEM

Limitations of the Fundamental Equation of Chemical Thermodynamics

$$dG = -SdT + Vdp$$

This equation is not applicable when:

- System **composition** is changing due to **exchange of matter with surroundings (open system)**
- An **irreversible chemical reaction** takes place
- An **irreversible inter-phase transport of matter** takes place

**CONCLUSION:** We need new sets of Fundamental Equations of Chemical Thermodynamics to deal with OPEN SYSTEMS

# Multicomponent Systems, Partial Molar Quantities, and the Chemical Potential

So far we've worked with **fundamental equations** for a closed (**no mass change**) system with no composition change. We had the following:

$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dA = -SdT - pdV$$

$$dG = -SdT + Vdp$$

- How does this change if we allow the composition of the system to change Like in a chemical reaction or a biochemical process
- Consider Gibbs free energy of a 2-component system  $G(T,P,n_1,n_2)$

$$dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2} dT}_{= -S} + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2} dp}_{= V} + \underbrace{\left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2} dn_1}_{= \mu_1} + \underbrace{\left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1} dn_2}_{= \mu_2}$$

$$dG = -SdT + Vdp + \sum_{i=1, i \neq j}^n \mu_i dn_i$$

$$\therefore \text{we can write, } dG_{T,P} = w_{e,max} = \sum_{i=1, i \neq j}^n \mu_i dn_i$$

We define the **chemical potential**,  $\mu_i$  of species **i**

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

$\mu_i(T,P,n)$  is an intensive variable

# OPEN SYSTEM

When exchange of matter is allowed between the System and the Surrounding, the composition can change. We then have to modify the Fundamental Equations

$$U = f(S, V, n_1, n_2, \dots)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_i} dV + \sum_{i=1}^n \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j} dn_i$$

$$dU = TdS - PdV + \sum_{i=1}^n \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j}$$

The modifications give rise to **NEW** sets of Fundamental Equations for **OPEN** systems

$$dU = TdS - PdV + \sum_{i=1}^n \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j}$$

$$dH = TdS + VdP + \sum_{i=1}^n \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j}$$

$$dA = -SdT - PdV + \sum_{i=1}^n \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T, V, n_j}$$

$$dG = -SdT + VdP + \sum_{i=1}^n \mu_i dn_i \quad \text{where, } \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j}$$

Special case for  $n$  moles of a pure substance at given  $T, P$ :

$$G = n G_m,$$

$G_m$  = Molar Gibbs Free Energy

$$\therefore \mu = G_m = \bar{G}$$

The chemical potential

These are applicable to single phase, multi-component open system in thermal and mechanical equilibrium and with ONLY  $pV$  (i.e., expansive) work done.

# The Chemical Potential

- So far, our thermodynamic relations applied to **closed** systems. However, **G, U, H etc.** are **extensive properties** (i.e., mass dependent)
- At equilibrium**, the chemical potential of a species is the same everywhere in the system, Therefore, we can write:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_{j\neq i}} = \left( \frac{\partial H}{\partial n_i} \right)_{S,p,n_{j\neq i}} = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_{j\neq i}} = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_{j\neq i}}$$

- The **chemical potential** of a **pure substance** is the molar Gibbs energy, **G<sub>m</sub>**:  $\mu = \bar{G} = \frac{G}{n}$

For an ideal gas:  $G = G^\circ + nRT \ln(P/P^\circ)$ ;  $\therefore$  we can write:  $\mu = \mu^\circ + RT \ln(P/P^\circ)$

And for a **multi-component system**:

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

- At equilibrium**, the chemical potential ( $\mu$ ) of a species is the same everywhere in the system and therefore there cannot be any spontaneous process taking place.
- G** is **extensive** but  $\mu_i$  (or,  $G_m$  or,  $\bar{G}$ ) is **Intensive** property, therefore we can write:

$$G = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + \dots n_i\mu_i = \sum_{i=1}^n n_i\mu_i \equiv \sum_{i=1}^n n_i\bar{G}_i$$

# Properties of Chemical Potential

## 1. For n moles of an ideal gas:

$$G = G^\circ + nRT \ln \frac{P}{P^\circ}$$

$$\mu = \mu^\circ + RT \ln \frac{P}{P^\circ}$$

one-component, pure substance:

$$\mu = \left( \frac{G}{n} \right)_{p,T}$$

multi-component system:

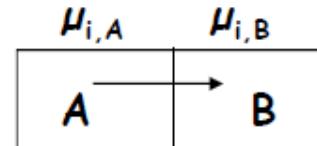
$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j}$$

## 2. Transfer of matter:

In a system that has one component  $i$  and two parts, (e.g., a solid and a liquid phase), consider moving an infinitesimal amount  $dn_i$  of component 1 from phase A to phase B at constant T and P.

The change in state can be represented as:

$$dn_i(T,p,\text{phase}) = -\delta n_i(T,p, \text{phase B})$$



Change in Gibbs free energy in A

$$\text{B: } dG^A = \mu_{i,A}(-dn_i) \quad \& \quad dG^B = \mu_{i,B}dn_i$$

Net change in Gibbs free energy:

$$dG = dG^A + dG^B = (\mu_{i,B} - \mu_{i,A})dn_i$$

**Case I:**  $\mu_{i,A} > \mu_{i,B}$        $dG < 0$

**Case II:**  $\mu_{i,A} < \mu_{i,B}$        $dG > 0$

**Case III:**  $\mu_{i,A} = \mu_{i,B}$        $dG = 0$

• Spontaneous transfer of matter from region of **high  $\mu$  to region of low  $\mu$**

• At equilibrium  **$\mu$  is the same everywhere**; and there cannot be any spontaneous process,

so,  $\mu_i^A = \mu_i^B$  e.g., coexistence of the species in both the phases : [e.g.  $\mu^{\text{ice}}(T, p) = \mu^{\text{water}}(T, p)$ ]

# Properties of Chemical Potential

Consider moving an infinitesimal amount  $d\eta_1$  of component #1 from phase a to phase b at constant  $T, p$ . Let's write the change in state.

$$d\eta_1(T, p, \text{phase a}) = -d\eta_1(T, p, \text{phase b})$$

$$dG = [\mu_1^{(b)} - \mu_1^{(a)}] d\eta_1$$

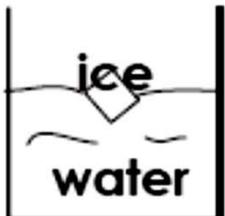
$\mu_1^{(b)} < \mu_1^{(a)}$   $\Rightarrow dG < 0 \Rightarrow$  spontaneous conversion from (a) to (b)

$\mu_1^{(a)} < \mu_1^{(b)}$   $\Rightarrow dG > 0 \Rightarrow$  spontaneous conversion from (b) to (a)

At equilibrium there cannot be any spontaneous processes, so

$$\mu_1^{(a)} = \mu_1^{(b)} \text{ at equilibrium}$$

e.g. liquid water and ice in equilibrium



$$\mu^{\text{ice}}(T, p) = \mu^{\text{water}}(T, p)$$

at coexistence equilibrium

## Properties of Chemical Potential

- At equilibrium, the chemical potential of a species is the same everywhere in the system

Let's show this in a system that has one component and two parts, (for example a solid and a liquid phase, or for the case of a cell placed in salt water, the water in the cell versus the water out of the cell in the salt water)

For the cell in a salt water solution,  $\mu^{\text{water}(cell)}(T, p) > \mu^{\text{water}(solution)}(T, p)$  and the cell dies as the water flows from the cell to the solution (this is what we call osmotic pressure)

The chemical potential and its downhill drive to equilibrium will be the guiding principle for our study of phase transitions, chemical reactions, and biochemical processes

# Partial molar quantities

- Partial molar quantities,  $\bar{J}$ , are used to describe quantities which depend on composition at constant  $T$  and  $P$

$$\bar{J}_i = \left( \frac{\partial J}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad J = U, H, S, A, G, V$$

$$J = \sum_i n_i \bar{J}_i$$

- $\bar{G}_i$  is the Gibbs free energy per mole of component  $i$ , i.e., the partial molar Gibbs free energy

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

- Partial molar quantities Intensive property, therefore we can write:
- We can define other partial molar quantities similarly

$$\left( \frac{\partial A}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \bar{A}_i \Rightarrow A = n_1 \bar{A}_1 + n_2 \bar{A}_2 + \dots + n_i \bar{A}_i = \sum_i n_i \bar{A}_i$$

partial molar Helmholtz free energy

note what is kept constant  $\Rightarrow$  not to be confused with  $\left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_{j \neq i}} = \mu_i$

# Partial molar quantities

- Similarly, partial molar enthalpy and partial molar energy can be given as:

$$\left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_j \neq i} = \bar{H}_i \Rightarrow H = n_1 \bar{H}_1 + n_2 \bar{H}_2 + \dots + n_i \bar{H}_i = \sum_i n_i \bar{H}_i$$

partial molar enthalpy

$$\left(\frac{\partial U}{\partial n_i}\right)_{T,p,n_j \neq i} = \bar{U}_i \Rightarrow U = n_1 \bar{U}_1 + n_2 \bar{U}_2 + \dots + n_i \bar{U}_i = \sum_i n_i \bar{U}_i$$

partial molar energy

- Chemical potential in a pure (1-component) ideal gas

From  $\bar{G}(T, p) = \bar{G}^\circ(T) + RT \ln \frac{P}{P_0} \Rightarrow \mu(T, p) = \mu^\circ(T) + RT \ln \frac{P}{P_0}$

- Chemical potential in a mixture of ideal gases

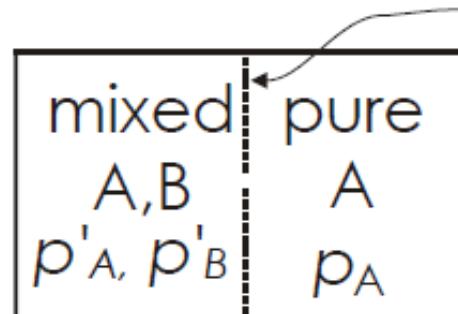
$$\mu_A(mix, T, p_{tot}) = \mu_A(pure, T, p_{tot}) + RT \ln X_A$$

$$\mu_A(mix, T, p_{tot}) < \mu_A(pure, T, p_{tot}) \quad \text{Since, } X_A \text{ (mole fraction of species A)} < 1$$

## Chemical Potential for a Mixture of Ideal Gases

Consider the equilibrium

$$p'_A + p'_B = p_{tot}$$

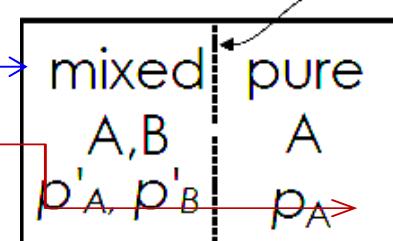


At equilibrium  $\mu_A(mix, T, p_{tot}) = \mu_A(pure, T, p_A)$

At equilibrium:  $p_A$  (partial pressure) +  $p_B$  (partial pressure) =  $p_{tot}$

Therefore, at equilibrium:

$$\mu_A(mix, T, p_{tot}) = \mu_A(pure, T, p_A)$$



Again, according to Dalton's Law of Partial Pressure, we have:

$$p_A(pure) = p_A(mix) = p_{tot} X_A \text{ where, } X_A \text{ is mole fraction of gas A}$$

$$\text{So, } \mu_A(mix, T, p_{tot}) = \mu_A(pure, T, p_{tot}, A) = \mu_A^\circ(T) + RT \ln\left(\frac{p_{tot} X_A}{p^\circ}\right)$$

$$\text{or, } \mu_A(mix, T, p_{tot}) = \mu_A^\circ(T) + RT \ln\left(\frac{p_{tot}}{p^\circ}\right) + RT \ln X_A \text{ where, } \mu_A \text{ is the Chemical potential of A in pure state}$$

$$\text{putting, } \mu_A(pure, T, p_{tot}) = \mu_A^\circ(pure, T, p_{tot}) + RT \ln\left(\frac{p_{tot}}{p^\circ}\right) \text{ species A in pure state}$$

We obtained:  $\mu_A(mix, T, p_{tot}) = \mu_A(pure, T, p_{tot}) + RT \ln X_A$  Since,  $X_A$  (mole fraction of species A) < 1

## Chemical Potential for a Mixture of Ideal Gases

We obtained:  $\mu_A(\text{mix}, T, p_{\text{tot}}) = \mu_A(\text{pure}, T, p_{\text{tot}}) + RT \ln X_A$

Note: Since  $X_A < 1$ ;

Therefore,  $\mu_A(\text{mix}, T, p^{\text{tot}}) < \mu_A(\text{pure}, T, p^{\text{tot}})$

The chemical potential of A in the mixture is always less than the chemical potential of A when pure, at the same total pressure. This is at heart a reflection about entropy, the chemical potential of "A" in the mixture is less than if it were pure, under the same (T,p) conditions, because of the underlying (but hidden in this case) entropy change!

# Gibbs-Duhem Equation for Partial Molar Quantities

- The Gibbs-Duhem equation

We know from the definition of **G** that it is an extensive property:

$$G = \sum_i n_i \mu_i$$

$$\sum_i n_i d\mu_i = 0$$

Therefore, from the definition, for a system containing two species A and B, **G** will be given as : 

$$G = n_A \mu_A + n_B \mu_B$$

## At const. p & T

Accordingly, the Change in Gibbs Energy,  $dG$ , with infinitesimally small change in composition of each species will be: 

But from the Fundamental Equation of G at constant T and p, we will have  $\Delta G$  as:

$$\Delta G_{T,p} = \sum_i \mu_i d n_i$$

Thus, at constant T and p, for a system having species A and B, the  $dG$  will be given as:

**Equating the two dG from  
and :  
:**

$$\mu_A dn_A + \mu_B dn_B = dG = n_A d\mu_A + n_B d\mu_B + \mu_A dn_A + \mu_B dn_B \Leftrightarrow dG = n_A d\mu_A + n_B d\mu_B$$

Thus, as  $G$  is state function, therefore we can write:  $dG = 0 \Rightarrow n_A d\mu_A + n_B d\mu_B = 0$  at const. p T

This gives the Gibbs-Duhem Equation: at const. p T

$$\sum_i n_i d\mu_i = 0$$

## For a binary mixture at const. p T:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \Rightarrow \quad \therefore d\mu_1 = -\left(\frac{n_2}{n_1}\right) d\mu_2$$

The chemical potential of one component in the mixture cannot change independently of the others. The same is true for all partial molar quantities ; System always tends to minimize the chemical potential.

## Ideal Gas Mixture

If the gases were not mixed:

$$G_{\text{before mixing}} = \sum_i n_i (\mu_i^0 + RT \ln p)$$

$$G_{\text{after mixture}} = \sum_i n_i \mu_i$$

$$G_{\text{after mixture}} = \sum_i n_i (\mu_i^0 + RT \ln p_i)$$

(where, p in bar;  $p_i$  partial pressure of  $i^{\text{th}}$  gas)

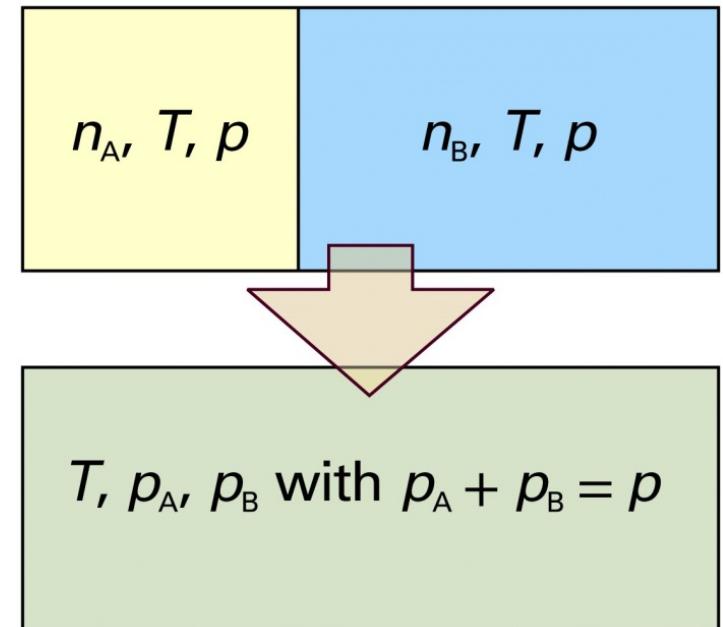
Dalton's Law:  $p_i = x_i p$        $p = \sum_i p_i$

$x_i$  = mole fraction of  $i^{\text{th}}$  gas

$$G_{\text{after mixture}} = \sum_i n_i (\mu_i^0 + RT \ln x_i p) \quad x_i = \frac{n_i}{n}$$

$$\Delta G_{\text{mix}} = G_{\text{for mixture}} - G_{\text{before mixing}}$$

$$\Delta G_{\text{mix}} = \sum_i n_i (\mu_i^0 + RT \ln p_i) - \sum_i n_i (\mu_i^0 + RT \ln p)$$



$$\therefore \Delta G_{\text{mix}} = nRT \sum_{i=1}^n x_i \ln x_i$$

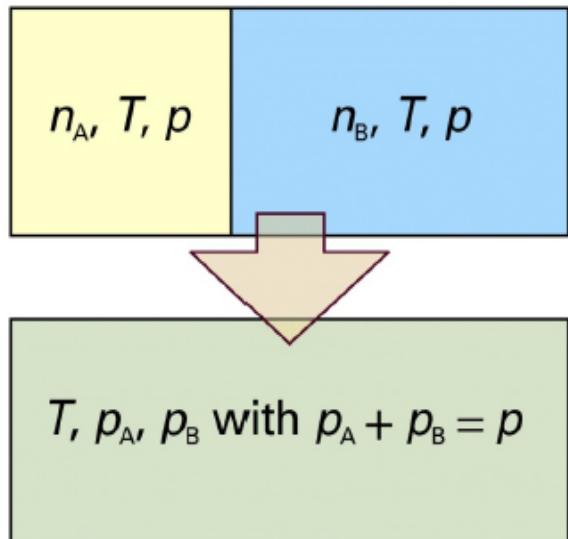
# Free Energy of Mixing

Consider the mixing of two *ideal* gases A and B at constant  $T$  and  $P$ .

Before:  $G_1 = n_A \mu_A(\text{pure}) + n_B \mu_B(\text{pure})$

where  $\mu_A(\text{pure}) = \mu_A^\circ + RT \ln(P/P_0)$

After mixing:  $G_A = n_A \left\{ \mu_A^\circ + RT \ln(p_A/P_0) \right\}$



$$\begin{aligned} &= n_A \left\{ \mu_A^\circ + RT \ln(P/P_0) + RT \ln \chi_A \right\} \\ &= n_A \mu_A(\text{pure}) + n_A RT \ln \chi_A \\ &= G_A + G_B < G_1 \end{aligned}$$

negative

Using Dalton's law:

where,  $p_A = \frac{n_A}{n} P$ ;  $p_B = \frac{n_B}{n} P$ ;  $\chi_A = \frac{n_A}{n}$ ;  $\chi_A < 1$

# Free Energy of Mixing

Change:

$$\begin{aligned}\Delta G_{\text{mix}} &= G_2 - G_1 \\ &= n_A RT \ln \chi_A + n_B RT \ln \chi_B \\ &= nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)\end{aligned}$$

$$\Delta G_{\text{mix}} = nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$

$\Delta G_{\text{mix}} < 0$  Mixing is spontaneous.

Entropy of Mixing  $\Delta S_{\text{mix}} = -(\partial \Delta G_{\text{mix}} / \partial T)_{P,n_i} = -nR \sum \chi_i \ln \chi_i$

Enthalpy of Mixing  $\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} = 0$

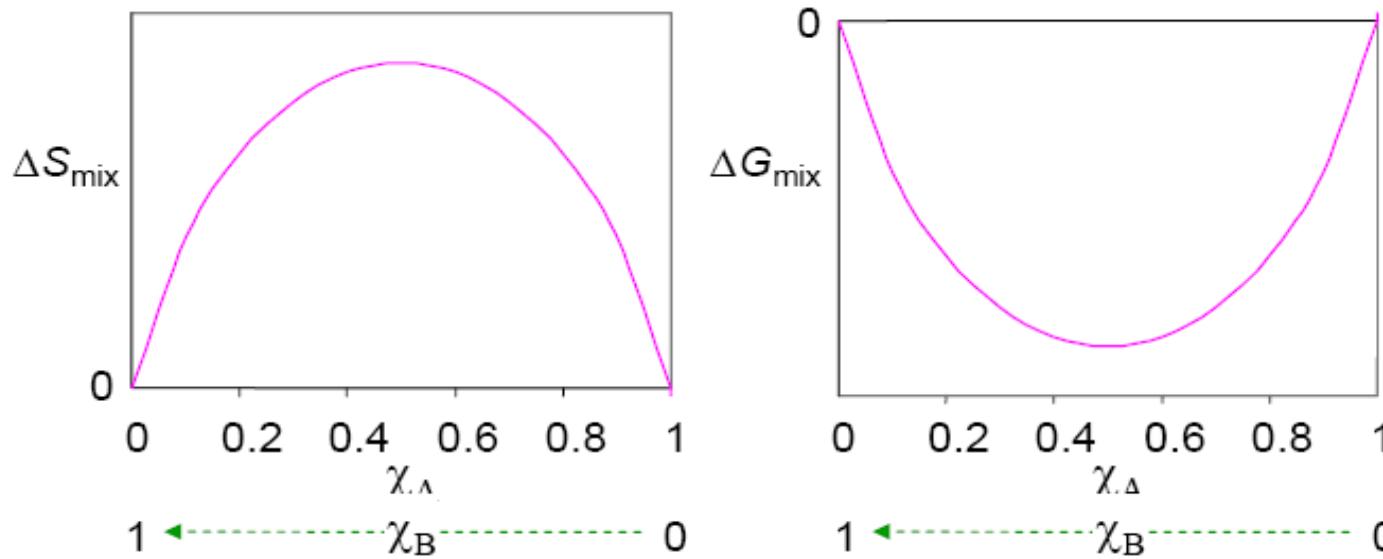
Similarly,  $\Delta U_{\text{mix}} = \Delta V_{\text{mix}} = 0$  for ideal gases and solutions

For what value of  $x$  is  $\Delta S_{\text{mix}}$  maximum?

For a binary system,  $\Delta G_{\text{mix}}$  is at its minimum and  $\Delta S_{\text{mix}}$  at its maximum when  $\chi_A = \chi_B = 0.5$

Perfect gases mix spontaneously in all proportions

# Free Energy of Mixing

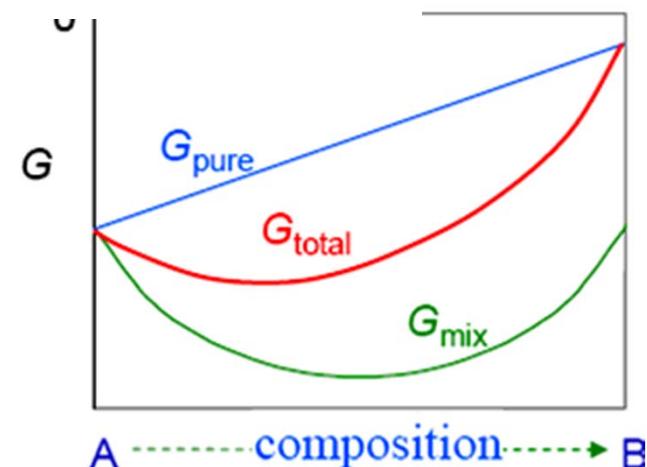


## Equilibrium and Mixing:

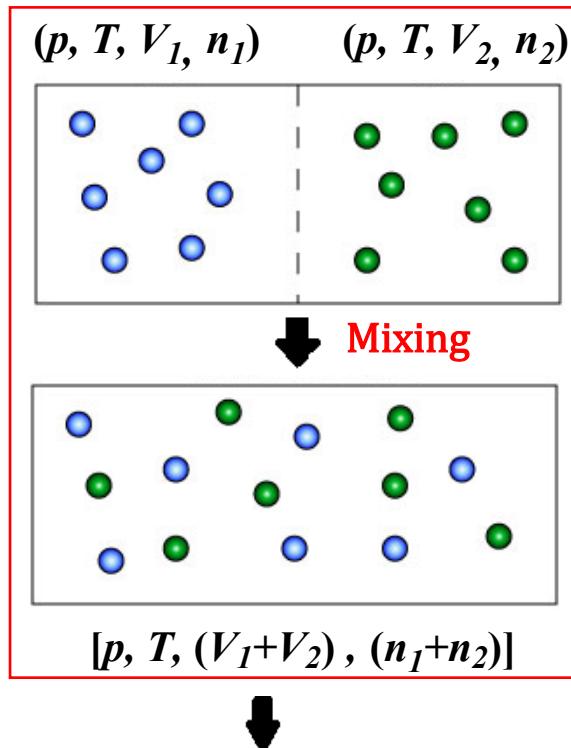
Consider an equilibrium between two ideal gases  $A \rightleftharpoons B$

$$\begin{aligned} G &= G_A(\text{pure}) + G_B(\text{pure}) + \Delta G_{\text{mix}} \\ &= n(\chi_A \mu_A + \chi_B \mu_B) + nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B) \end{aligned}$$

The equilibrium composition is determined by the minimum in  $G_{\text{total}}$ .



# Entropy of Mixing (Ideal Gases)



Total Entropy Change of the process  $\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2$

$$\text{where, } \Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1} \text{ and } \Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

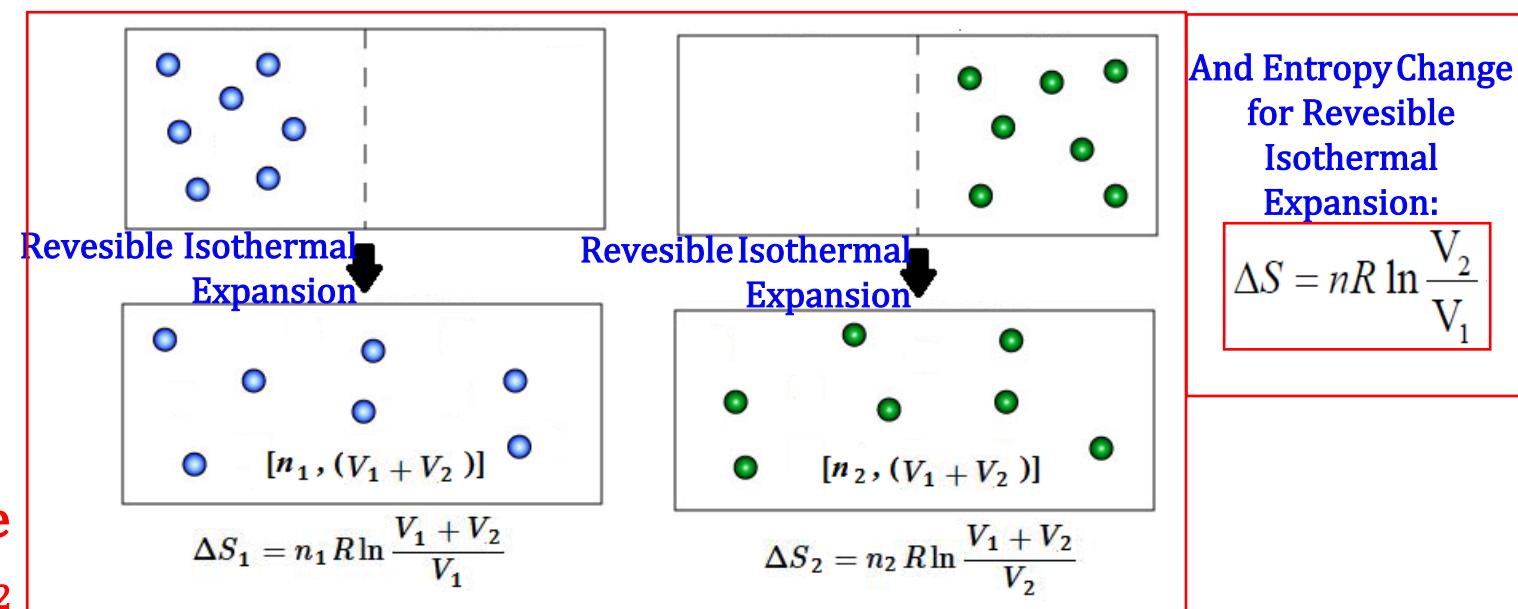
$$\therefore \Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2 = n_1 R \ln \frac{V_1 + V_2}{V_1} + n_2 R \ln \frac{V_1 + V_2}{V_2} \quad \text{where, } \frac{V_1}{V_1 + V_2} = \frac{p}{\frac{n_1 RT}{p} + \frac{n_2 RT}{p}} = \frac{n_1}{n_1 + n_2} = x_1$$

$$\Delta S_{\text{mix}} = -n_1 R \ln x_1 - n_2 R \ln x_2$$

$$\Delta S_{\text{mix}} = -nR(x_1 \ln x_1 + x_2 \ln x_2) \Leftrightarrow \Delta S_{\text{mix}} = -nR \sum_{i=1}^n x_i \ln x_i \quad (\text{where, } x_i \text{ mole fraction of } i \text{ species})$$

Mixing is an **Irreversible Process**. What will be the  $\Delta S$

Carry out **Reversible Isothermal Expansion** in two steps. Then add the Entropy change in each step to obtain the Total  $\Delta S$



## Perfect gases mix spontaneously in all proportions

$$\Delta S_{mix} = - \left( \frac{\partial(\Delta G_{mix})}{\partial T} \right)_{p,n}$$

$$\Delta V_{mix} = \left( \frac{\partial(\Delta G_{mix})}{\partial p} \right)_{T,n}$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix}$$

- **entropy of mixing**

$$\Delta S_{mix} = - \left( \frac{d(\Delta G_{mix})}{dT} \right)_{p,n} = - \left( nR \sum_{i=1}^n x_i \ln x_i \right) \equiv - nR(x_A \ln x_A + x_B \ln x_B + \dots)$$

- **enthalpy of mixing**

X (mole fraction of species) < 1

$$\Delta_{mix}H = \Delta_{mix}G + TdS = 0$$

Therefore, the driving force of mixing is purely ENTROPY driven

# Alternate Method of deducing Entropy of Mixing of Gases

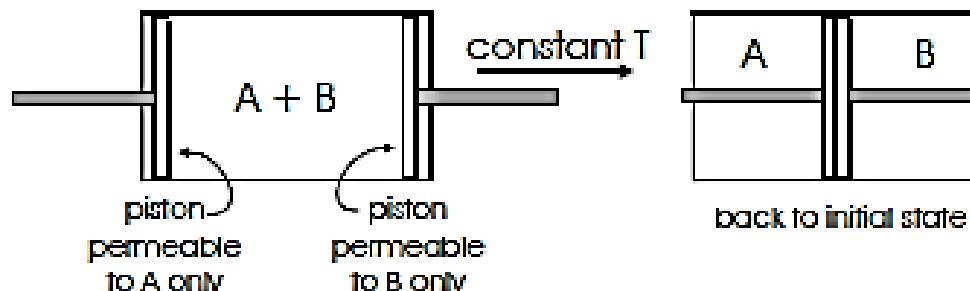
## Entropy and Disorder

- Mixing of ideal gases at constant  $T$  and  $p$

$$n_A A(g, V_A, T) + n_B A(g, V_B, T) = n(A + B)(g, V, T)$$



To calculate  $\Delta S_{mix}$ , we need to find a reversible path between the two states.



$$\Delta S_{demix} = -\Delta S_{mix} \quad \text{function of state}$$

## Alternate Method of deducing Entropy of Mixing of Gases

$$\Delta S_{\text{demix}} = -\Delta S_{\text{mix}} \quad \text{function of state}$$

For demixing process

$$\Rightarrow \Delta U = 0 \Rightarrow q_{\text{rev}} = -w_{\text{rev}} = p_A dV_A + p_s dV_s$$

work of compression of each gas

$$\therefore \Delta S_{\text{demix}} = \int \frac{dq_{\text{rev}}}{T} = \int_V^{V_A} \frac{p_A dV_A}{T} + \int_V^{V_s} \frac{p_s dV_s}{T} = n_A R \ln \frac{V_A}{V} + n_s R \ln \frac{V_s}{V}$$

Put in terms of mole fractions  $X_A = \frac{n_A}{n}$   $X_s = \frac{n_s}{n}$

$$\therefore \Delta S_{\text{demix}} = \int \frac{dq_{\text{rev}}}{T} = \int_V^{V_A} \frac{p_A dV_A}{T} + \int_V^{V_s} \frac{p_s dV_s}{T} = n_A R \ln \frac{V_A}{V} + n_s R \ln \frac{V_s}{V}$$

Put in terms of mole fractions  $X_A = \frac{n_A}{n}$   $X_s = \frac{n_s}{n}$

Ideal gas  $\Rightarrow X_A = \frac{V_A}{V}$   $X_s = \frac{V_s}{V}$

## Alternate Method of deducing Entropy of Mixing of Gases

$$\therefore \Delta S_{\text{demix}} = nR[X_A \ln X_A + X_B \ln X_B]$$

$$\Rightarrow \boxed{\Delta S_{\text{mix}} = -nR[X_A \ln X_A + X_B \ln X_B]}$$

Since  $X_A, X_B < 1 \Rightarrow \Delta S_{\text{mix}} > 0$  mixing is always spontaneous

The mixed state is more "disordered" or "random" than the demixed state.

$$S_{\text{mixed}} > S_{\text{demixed}}$$

This is a general result  $\Rightarrow$   
Entropy is a measure of the disorder of a system

$\therefore$  For an isolated system (or the universe)

$\Delta S > 0$  Spontaneous, increased randomness

$\Delta S = 0$  Reversible, no change in disorder

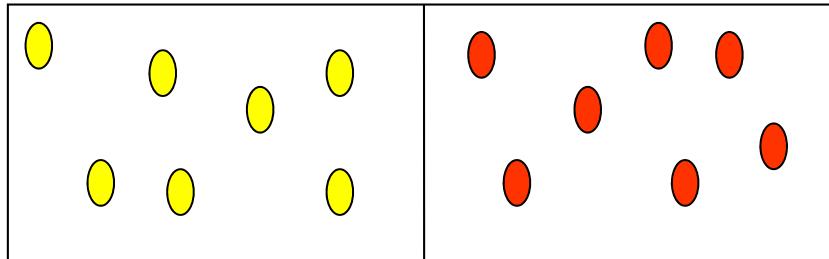
$\Delta S < 0$  Impossible, order cannot "happen" in isolation

There is an inexorable drive for the universe to go to a maximally disordered state.

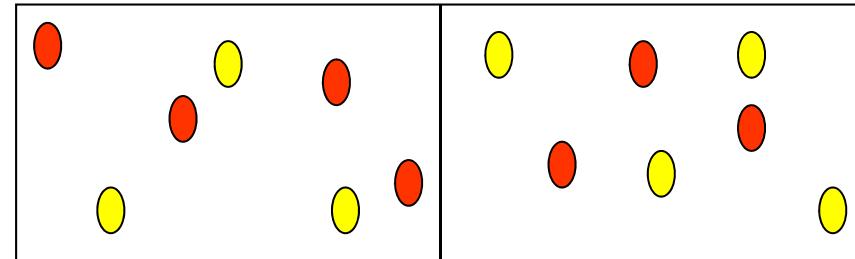
## Entropy of Mixing of Gases

Gibbs Paradox: The mixing of **NON-IDENTICAL** gases

Before Mixing



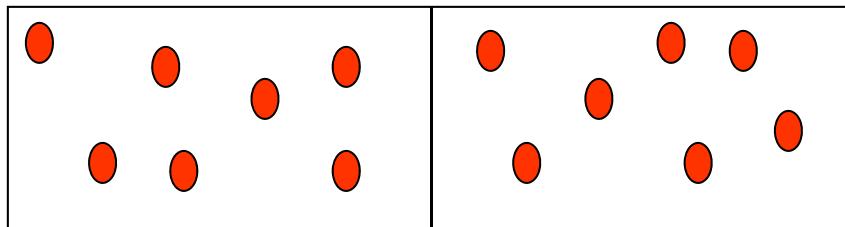
After Mixing



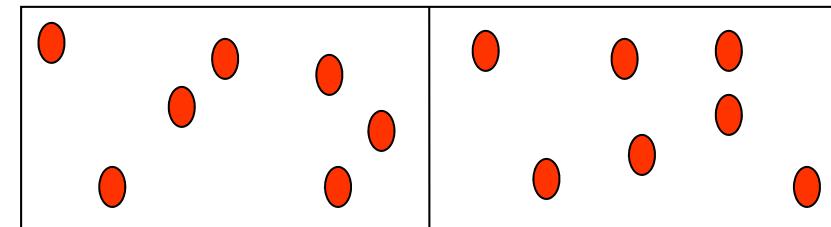
Shows obvious increase in entropy (disorder)

Now consider the mixing of **IDENTICAL** gases

Before Mixing



After Mixing



Shows zero increase in entropy as action is reversible

### Gibbs Paradox: Entropy of mixing

- When 2 non-identical gases mix and entropy increase, we imply that the gases can be separated and returned to their original state
- When 2 identical gases mix, it is impossible to separate the two gases into their original state as there is no recognizable difference between the gases
- Thus, these two cases stand on different footing and should not be compared with each other
- The mixing of gases of different kinds that resulted in the entropy change was independent of the nature of the gases
- Hence independent of the degree of similarity between them

## Assignment

### Examples of $\Delta S$ calculations

In all cases, we must find a reversible path to calculate  $\int \frac{dq_{rev}}{T}$

(a) Mixing of ideal gases at constant  $T$  and  $p$

$$n_A A(g, V_A, T) + n_B A(g, V_B, T) = n(A+B)(g, V = V_A + V_B, T)$$

$$\Delta S_{mix} = -nR[X_A \ln X_A + X_B \ln X_B]$$

(b) Heating (or cooling) at constant  $V$

$$A(T_1, V) = A(T_2, V)$$

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_V dT}{T} \stackrel{\substack{\text{if } C_V \text{ is} \\ T\text{-independent}}}{=} C_V \ln \frac{T_2}{T_1}$$

[Note  $\Delta S > 0$  if  $T_2 > T_1$ ]

## Assignment

(c) Reversible phase change at constant  $T$  and  $p$

e.g.  $\text{H}_2\text{O}(\ell, 100^\circ\text{C}, 1 \text{ bar}) = \text{H}_2\text{O}(g, 100^\circ\text{C}, 1 \text{ bar})$

$$q_p = \Delta H_{\text{vap}}$$

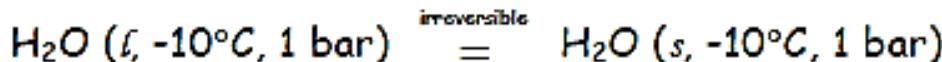
$$\Delta S_{\text{vap}}(100^\circ\text{C}) = \frac{q_p^{\text{vap}}}{T_b} = \frac{\Delta H^{\text{vap}}}{T_b} \quad (T_b = \text{boiling Temp at 1 bar})$$

(d) Irreversible phase change at constant  $T$  and  $p$

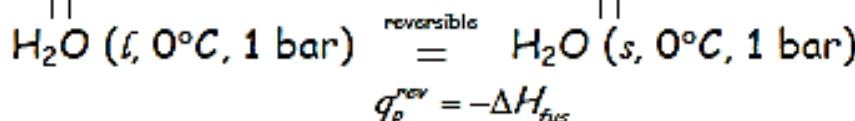
e.g.  $\text{H}_2\text{O}(\ell, -10^\circ\text{C}, 1 \text{ bar}) = \text{H}_2\text{O}(s, -10^\circ\text{C}, 1 \text{ bar})$

This is spontaneous and irreversible.

∴ We need to find a reversible path between the two states to calculate  $\Delta S$ .



$$\left| \begin{array}{l} dq_{\text{rev}} = C_p(\ell)dT \\ \end{array} \right| \quad \left| \begin{array}{l} dq_{\text{rev}} = C_p(s)dT \\ \end{array} \right|$$



## Assignment

$$\begin{aligned}\Delta S &= \Delta S_{\text{heating}} + \Delta S_{\text{fus}} + \Delta S_{\text{cooling}} \\ &= \int_{T_1}^{T_{\text{fus}}} \frac{C_p(\ell) dT}{T} + \frac{-\Delta H_{\text{fus}}}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^{T_1} \frac{C_p(s) dT}{T}\end{aligned}$$

∴ 
$$\boxed{\Delta S = \frac{-\Delta H_{\text{fus}}}{T} + \int_{T_1}^{T_{\text{fus}}} [C_p(\ell) - C_p(s)] \frac{dT}{T}}$$

$$\Delta S = \frac{-\Delta H_{\text{fus}}}{T} + [C_p(\ell) - C_p(s)] \ln \frac{T_{\text{fus}}}{T_1} \quad \text{if } C_p \text{ values are } T\text{-independent}$$

# Mixtures of Ideal Gases

and

Non-ideality

## Properties of Gibbs energy

## Non-ideality:

Gibbs energy for ideal gas at constant Temp was given as:

$$G = G^\circ + nRT \ln \frac{P}{P^\circ}; \text{ and } \mu = \mu^\circ + RT \ln P; \text{ where } P^\circ = 1 \text{ bar}$$

**For Real gases:** Lewis recognized that it would be convenient to keep same formal relation by defining a new function - **the fugacity function**, such that:

$$G = G^\circ + nRT \ln \left( \frac{f}{P^\circ} \right); \text{ and } \mu = \mu^\circ + RT \ln \left( \frac{f}{P^\circ} \right);$$

where,  $\left( \frac{f}{P} \right) = \phi$  (fugacity coefficient)

$$\lim_{P \rightarrow 0} \left( \frac{f}{P} \right) = 1 \quad \text{or,} \quad \lim_{P \rightarrow 0} (\phi) = 1$$

In solution : we use Activity  $\mu_i = \mu_i^\circ + RT \ln (a_i); \quad a_i = \frac{P_i}{P^\circ} = \frac{f_i}{P^\circ}$

Generally,

$$a_i = \gamma_i c \quad (\text{where, } \gamma_i = \text{activity coefficient})$$

## Properties of Gibbs energy

### Non-ideality:

$$\lim_{P \rightarrow 0} \left( \frac{f}{P} \right) = 1 \quad \text{or,} \quad \lim_{P \rightarrow 0} (\phi) = 1$$

Fugacity:

- Has units of pressure and is function of T and P
- As  $p \rightarrow 0$ , the gas approaches ideality and  $f$  (fugacity)  $\rightarrow P$
- It is the measure of the molar Gibbs free energy of a Real Gas
- Real gas behaves like ideal gas in the limits of **LOW Pressure** and **HIGH Temp** and they deviate at High P and Low Temp.
- **Compressibility factor** ,  $Z$ , is a measure of the deviation from ideality and it is defines as,

$$Z = \frac{\bar{V}}{\bar{V}_{id}} = \frac{PV}{RT} \quad (\text{where, } \bar{V} = \text{molar Vol})$$

Fugacity of a Real gas can be calculated at constant T and a particular P from the equation of state

## To Calculate Fugacity or, fugacity coeff. at constant T for a given P

$$G = G^\circ + nRT \ln f \quad \text{or, } \mu = \mu^\circ + RT \ln f$$

$$dG = -SdT + VdP \quad \text{or, } d\mu = -\bar{S}dT + \bar{V}dP$$

$dG = VdP$  (at constant T)

$\therefore d\mu = \bar{V}dP$  (when  $dT = 0$ )

$$\text{and, } d\mu^{id} = \bar{V}^{id} dP$$

$$d(\mu - \mu^{id}) = (\bar{V} - \bar{V}^{id})dP \quad \text{putting, } \lim_{P \rightarrow 0} \left( \frac{f}{P} \right) = 1$$

$$\int_0^P (\bar{V} - \bar{V}^{id}) dP = RT \ln \left( \frac{f}{P} \right)$$

$$\text{where, } \bar{V} = \frac{RTz}{P}; \quad \bar{V}^{id} = \frac{RT}{P}$$

$$z = \frac{\bar{V}}{\bar{V}_{id}} = \frac{PV}{RT} \quad (\text{where, } \bar{V} = \text{molar Vol})$$

$$\therefore \left( \frac{f}{P} \right) = \exp \left[ \int_0^P \frac{z-1}{P} dP \right]$$

# Properties of Gibbs energy

**Fugacity**

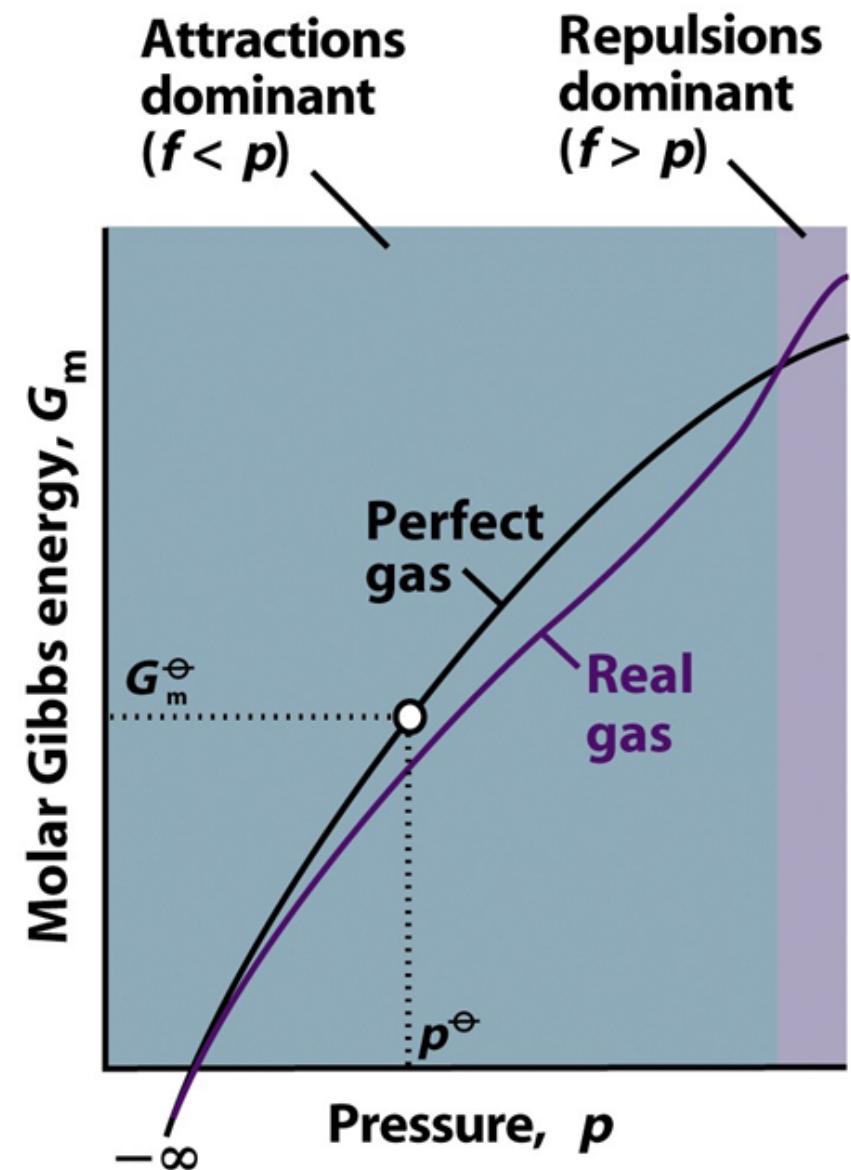
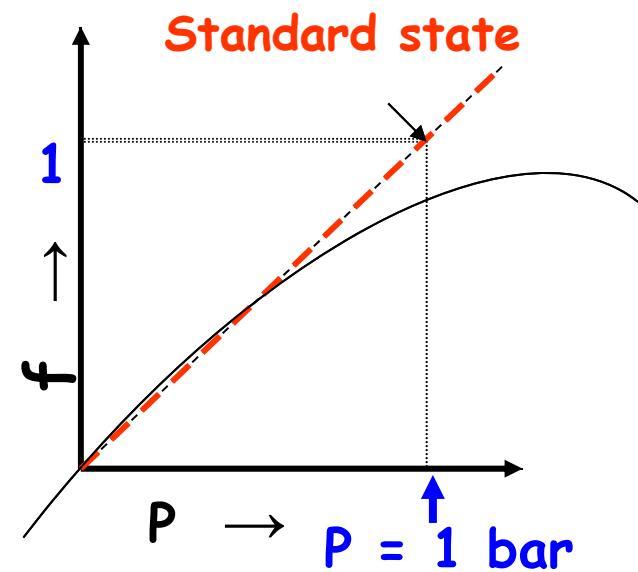
$$G(p) = G^\ominus + nRT \ln\left(\frac{f}{p^\ominus}\right)$$

$$f = \phi p$$

**Fugacity coefficient**

$$\ln \phi = \int_0^p \frac{Z-1}{p} dp$$

**Compressibility factor**



# Interactions and nonideal behavior

---

From our definition of the Gibbs free energy:

$$dG = -SdT + VdP$$

For constant T:

$$dG = VdP$$

For ideal behavior:

$$= \frac{RT}{P} dP$$

$$= RT d \ln P$$

Integrating from  $P_1$  to  $P_2$ :

$$\Delta G = RT \ln\left(\frac{P_2}{P_1}\right)$$

$$G(P_2) - G(P_1) = RT \ln\left(\frac{P_2}{P_1}\right)$$

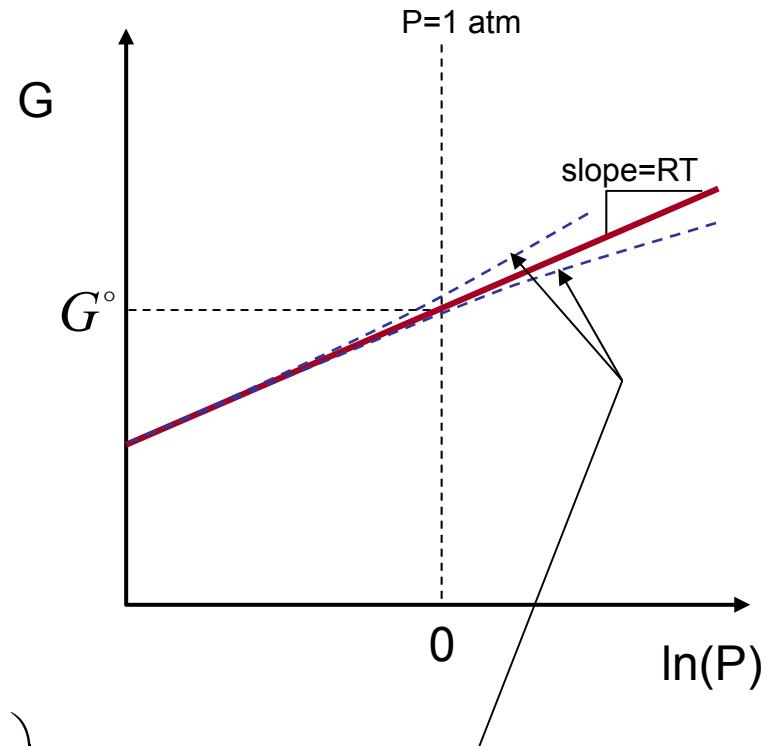
$$G(P_2) = G(P_1) + RT \ln\left(\frac{P_2}{P_1}\right)$$

Let  $P_1 = 1 \text{ atm}$ :  
(a reference state)

$$G(P_2) = G(1) + RT \ln\left(\frac{P_2}{1}\right)$$

Ideal behavior:

$$G(P) = G^\circ + RT \ln P$$



Nonideal behavior:

$$G(P) = G^\circ + RT \ln f$$

“Fugacity”

## Summary: Pure Real/Non-Ideal Gas

$$\mu_2 = \mu_1 + \int_{P_1}^{P_2} V_m dP$$

Recall that for an ideal gas

$$\mu = \mu^o + \int_{P^o}^P V_m(p) dP$$

$$\mu = \mu^o + RT \ln \frac{p}{p^o}$$

$$\mu = \mu^o + RT \ln \frac{f}{p^o} \quad f = \text{fugacity, effective pressure} \quad \lim_{p \rightarrow o} f(p) = p$$

$$\mu = \mu^o + RT \ln \frac{\phi p}{p^o} \quad \phi = \text{fugacity coefficient}$$

$$\mu = \mu^{id} + RT \ln \phi$$

$$\ln \phi = \int_0^p \frac{Z-1}{p} dp$$

Z = Compressibility factor

# **Phase Equilibrium and Phase Transitions**

## **Conditions for a Single Component System**

## Phase Equilibrium and Phase Transitions Conditions for a Single Component System

- Chemical Potential  $\mu$  controls phase transitions and phase equilibrium.
- Equilibrium condition - at equilibrium  $\mu$  must be identical throughout the system
- If several phases are in equilibrium, then the chemical potential of each species must have the same value in every phase in which it appears.

For example, consider two phases (liquid and solid) of water at a fixed  $(T, p)$ .

If  $\mu_s(T, p) = \mu_l(T, p)$  then... liquid water and ice coexist **at melting point**

If  $\mu_s(T, p) > \mu_l(T, p)$  then... the water is in the liquid phase

If  $\mu_s(T, p) < \mu_l(T, p)$  then... the water is in the solid phase

Start with Fundamental Equation for Gibbs (hence for  $\mu$ )

$$dG = -SdT + Vdp \quad d\mu = -\bar{S}dT + \bar{V}dp \quad \left( \mu = \frac{G}{n} \right)$$

$\bar{S}$  and  $\bar{V}$  are molar quantities

$$\left( \frac{\partial \mu}{\partial T} \right)_p = -\bar{S} \quad \left( \frac{\partial \mu}{\partial p} \right)_T = \bar{V}$$

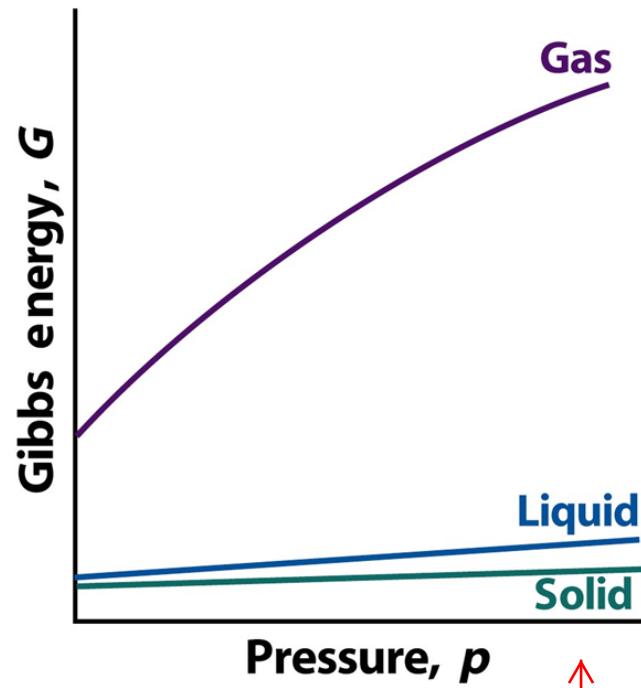
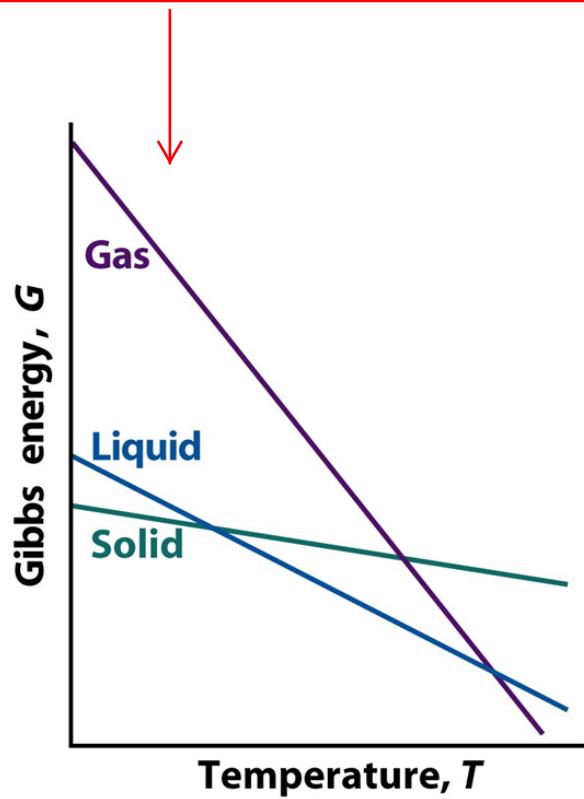
# Properties of Gibbs energy

$$dG = -SdT + Vdp$$

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

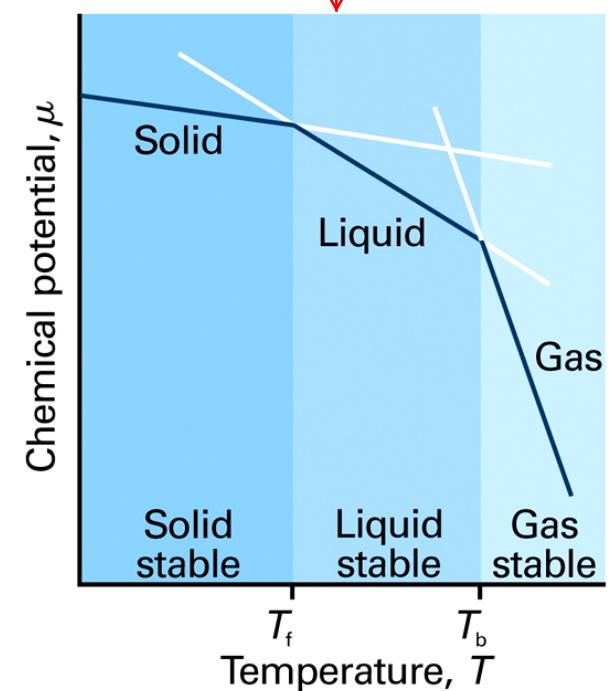
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

**G** decreases with Temperature; proportional to entropy, **S**



**G** increases with pressure; proportional to volume, **V**

Dependence of Chemical potential,  **$\mu$** , on Temp



# Phase Equilibria

Consider a closed system of a single component.

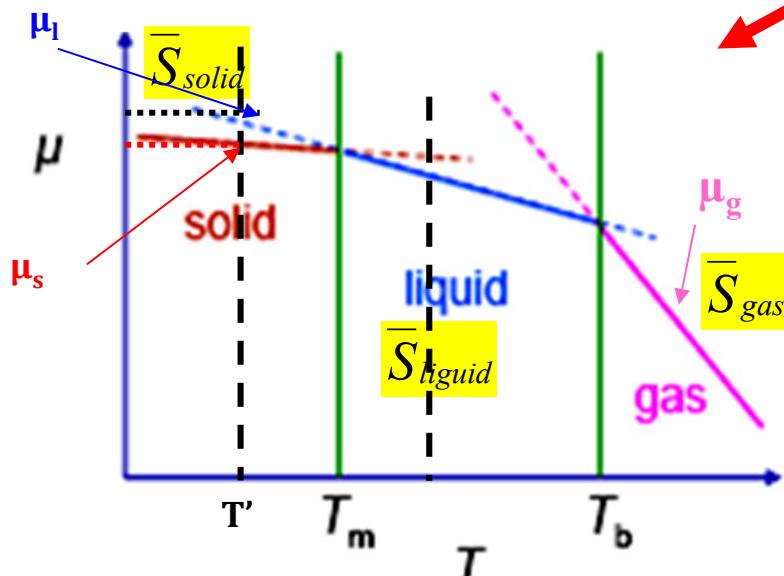
$$\mu = \frac{G}{n}$$

The chemical potential determines which phase is stable at a particular  $T$  and  $P$ .  $\mu$  tends to a minimum.

At the melting point  $T_m$ ,  $\mu(s) = \mu(l)$

At the boiling point  $T_b$ ,  $\mu(l) = \mu(g)$

These points depend on temperature and pressure.



$$dG = VdP - SdT$$

$$\left( \frac{\partial \mu}{\partial T} \right)_P = -\bar{S}$$

$$\left( \frac{\partial \mu}{\partial P} \right)_T = \bar{V}$$

$\left( \frac{\partial \mu}{\partial T} \right)_P$  -ive as from 2<sup>nd</sup> Law, the entropy of a substance is always +ive.

Consequently, the plot of  $\mu$  versus  $T$  at constant pressure is a curve (should be slightly concave downwards) with a negative slope

At any temperature,  $\bar{S}_{\text{gas}} \geq \bar{S}_{\text{liquid}} > \bar{S}_{\text{solid}}$

**Melting (freezing) temp.** - the temp at which the liquid and solid phases coexist in equilibrium (at given  $P$ ).

**Melting temp at 1 atm** - called normal m.p.,

**Melting temp at 1 bar** - called standard m.p

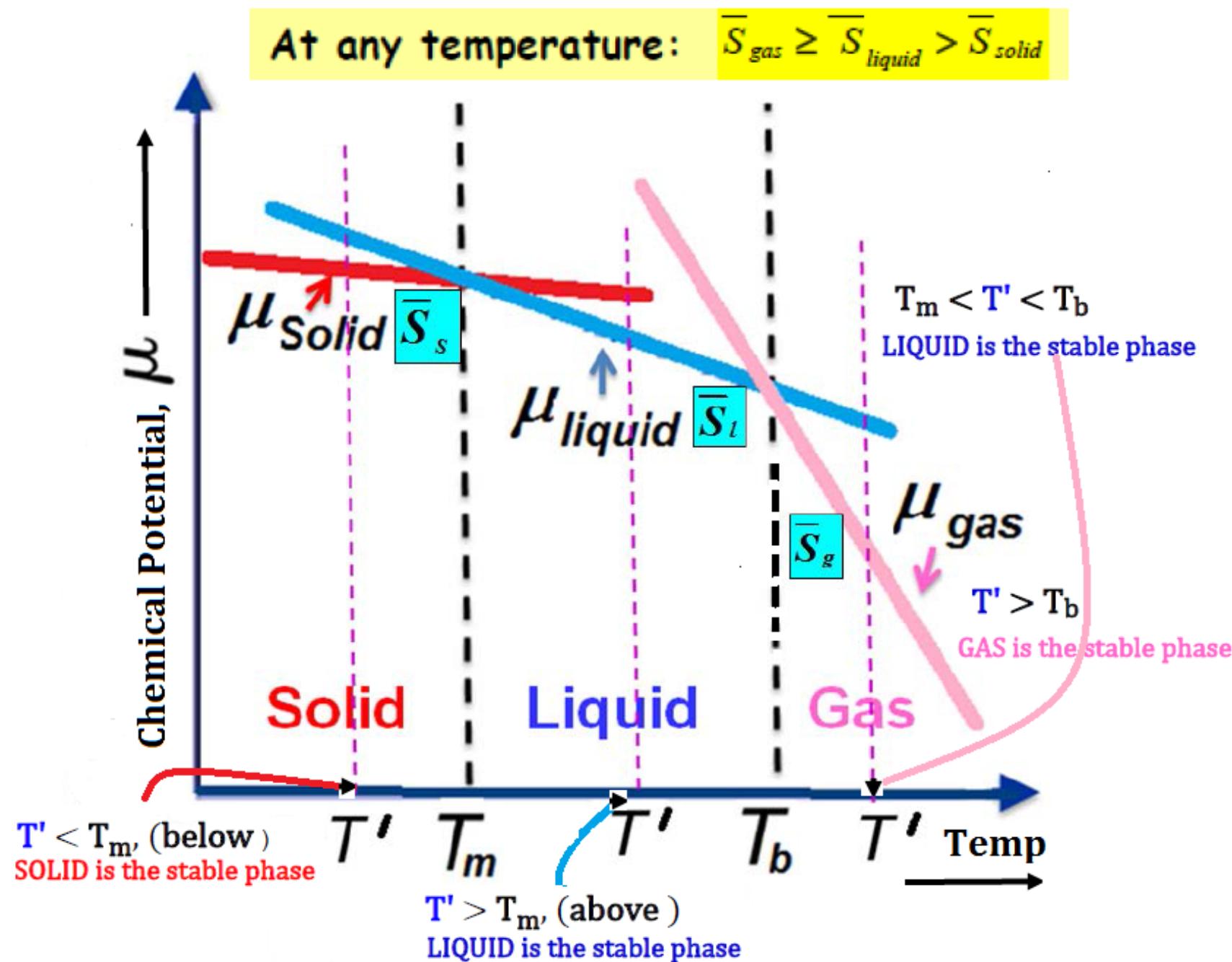
**Triple point ( $T_3$ )** - the point at which the three phases coexist.

At the critical point the gas-liquid line stops. Beyond the  $T_c$  the liquid and gas phase become indistinguishable, they merge into a single phase.

**Sequence of phase changes observed if a solid is heated under constant pressure**

- At  $T'$  (below  $T_m$ ), Liquid ( $\mu_l$ ) is greater than solid ( $\mu_s$ ), so liquid freezes spontaneously, since this will minimize the Gibbs energy (or,  $\mu$ ) of the system.
- At a temperature above  $T_m$  the situation is reversed : the  $\mu_s$  of solid is greater than that of the  $\mu_l$  of liquid and the solid melts spontaneously to decrease the Gibbs energy. **Consequence : heat is absorbed in the transformation from solid to liquid, and from liquid to gas.**

The following curves are obtained if a SOLID is HEATED under constant pressure to form LIQUID and finally to GAS



# Phase transitions

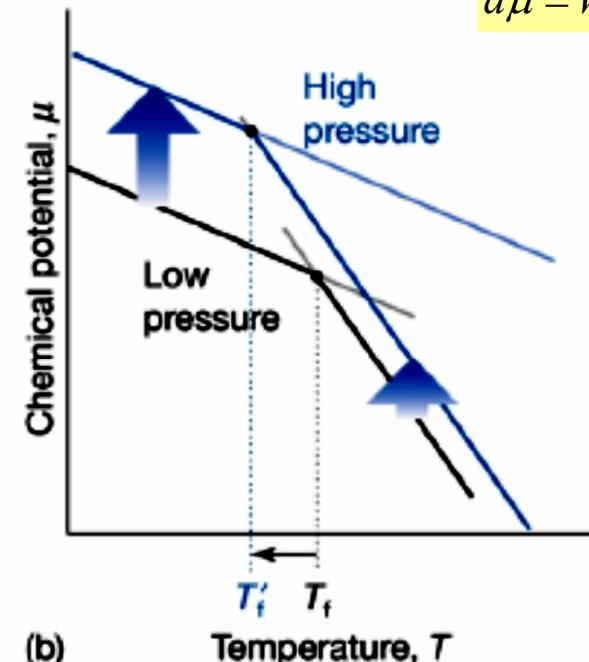
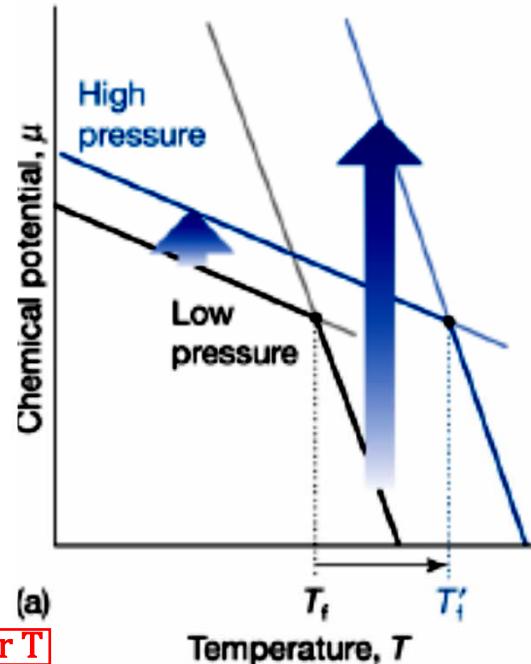
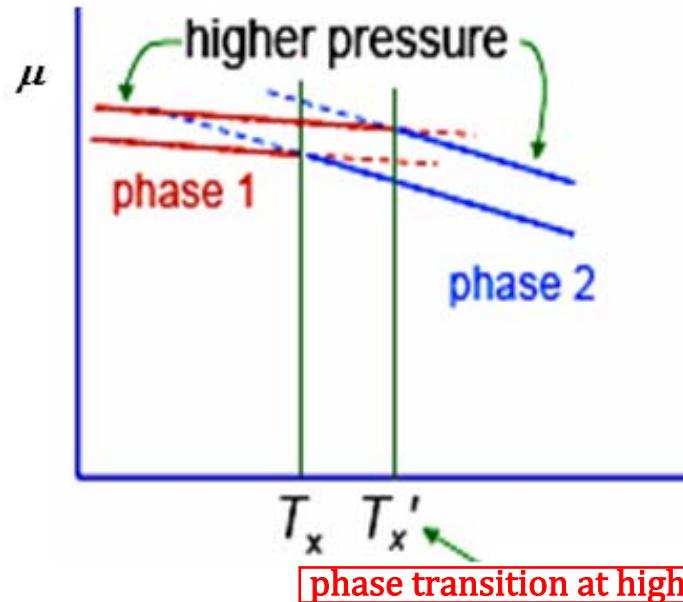
Melting point vs. applied pressure

$$\left( \frac{\partial \mu}{\partial p} \right)_T = V_m$$

$$\bar{V}_{\text{gas}} > \bar{V}_{\text{liq}} > \bar{V}_{\text{solid}}$$

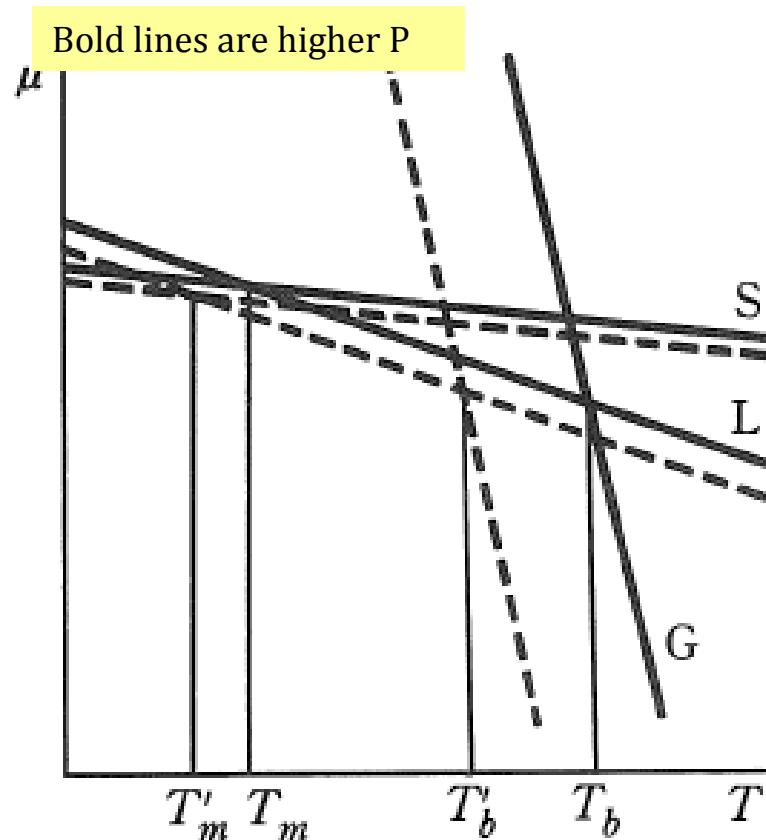
If the **pressure** is **decreased**,  $d\mu$  is negative, as  $V$  cannot be negative ; hence  **$d\mu$  is negative**, and the  $\mu$  decreases in proportion to the volume of the phase.

$$d\mu = \bar{V} dp$$

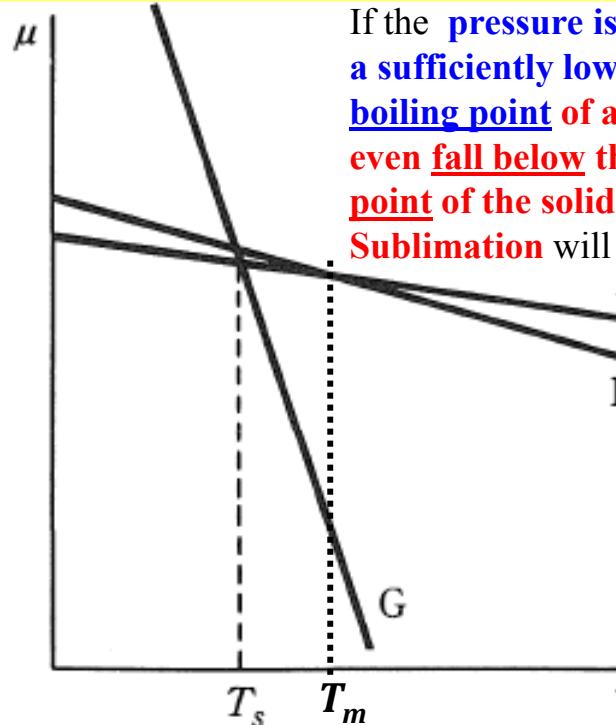


- Figure shows that the **equilibrium temperatures** ( intersection points) have shifted with change in Pressure.
- Since ,  $\bar{V}_{\text{liq}}$  and  $\bar{V}_{\text{solid}}$  are small difference, so the value of  $\mu$  is decreased only slightly. The volume of the gas is roughly 1000 times larger than that of the solid or liquid, so the  $\mu$  of the gas decreases greatly  $\therefore$  Shift in  $T_m$  is small while shift in  $T_b$  is rather large
- At the lower pressure, the range of stability of a phase is noticeably decreased.
- If the **pressure is reduced to a sufficiently low value**, the **boiling point of a liquid may even fall below the melting point of the solid**. Then there is no temperature at which the **liquid is stable** ; **the solid sublimes**.
- At the **sublimation temperature**,  $T_s$ , the solid and vapor coexist in equilibrium.  $T_s$  is very much P dependent.

# Phase transitions



$\mu$  vs T plot for substance that sublimes.



If the pressure is reduced to a sufficiently low value, the boiling point of a liquid may even fall below the melting point of the solid. Then Sublimation will take place.

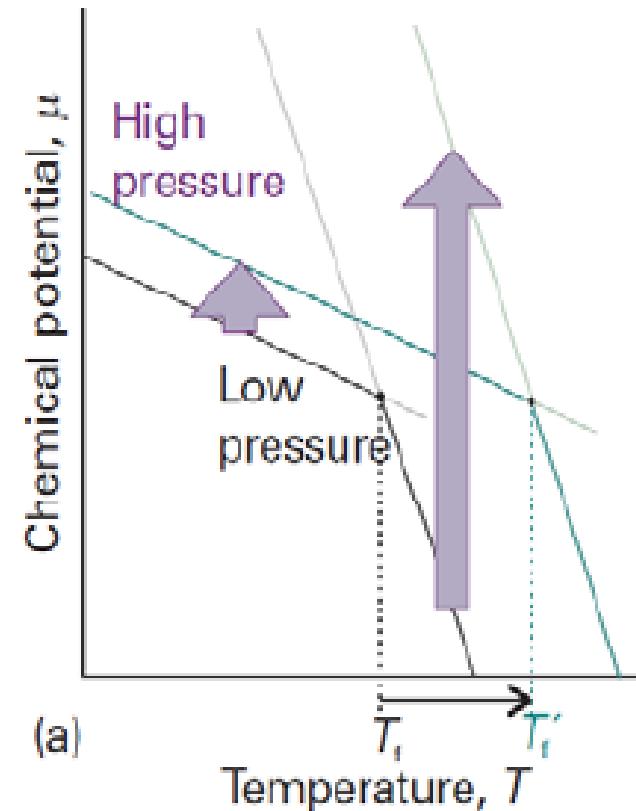
- Whether or not a particular material will sublime under reduced pressure rather than melt depends entirely on the **individual properties of the substance**.
- Water, for example, **sublimes at pressures below 611 Pa**.
- The **higher the melting point**, and the **smaller the difference** between the **melting point and boiling point** at 1 atm pressure, the **higher** will be the **pressure** below which **sublimation is observed**.
- The pressure (in atm) below which sublimation is observed can be estimated for substances obeying Trouton's rule by the formula

$$\ln p = -10.8 \left( \frac{T_b - T_m}{T_m} \right)$$

# Effect of pressures on Melting Point

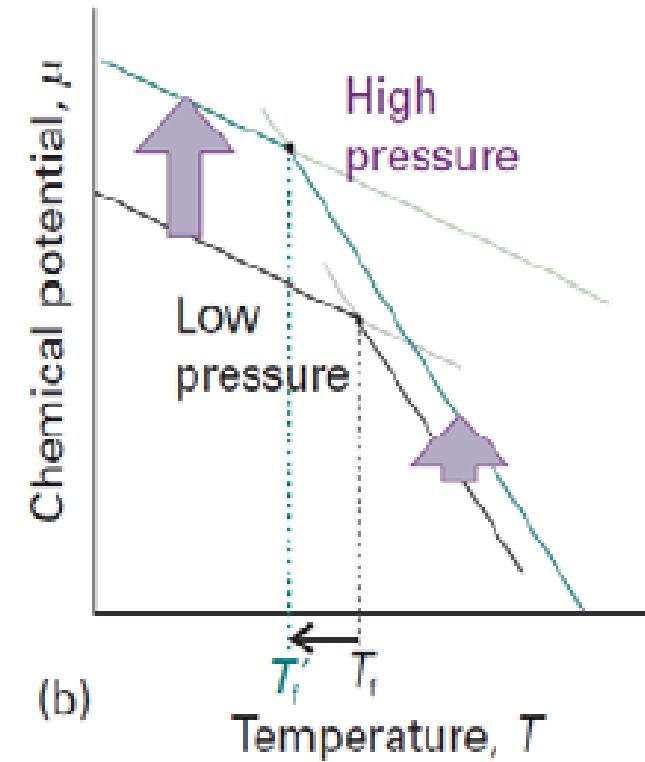
$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m$$

$$V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$



Melting point increases with pressure when  $V_m(\text{l}) > V_m(\text{s})$

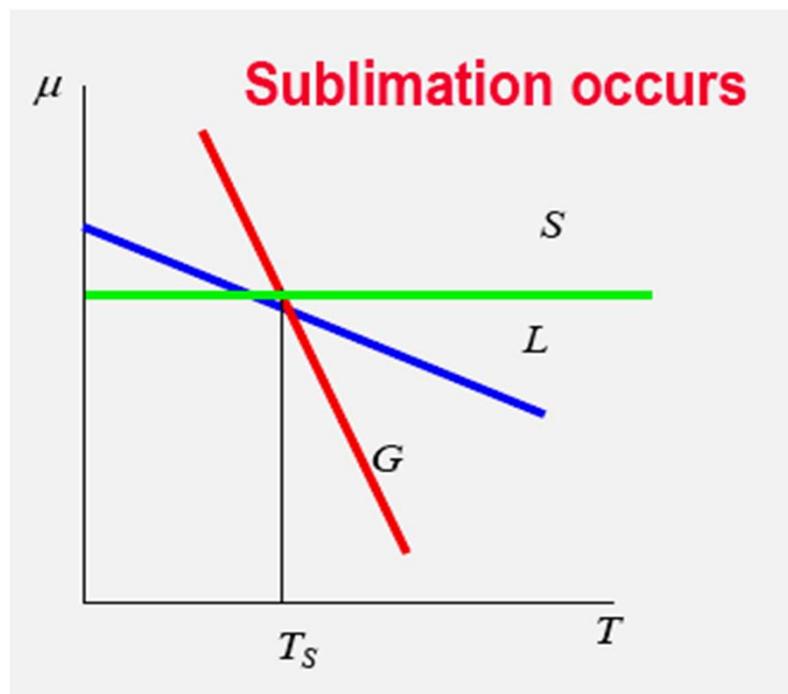
$$dG = Vdp - SdT$$
$$d\mu = V_m dP - S_m dT$$



Melting point decreases with pressure when  $V_m(\text{l}) < V_m(\text{s})$

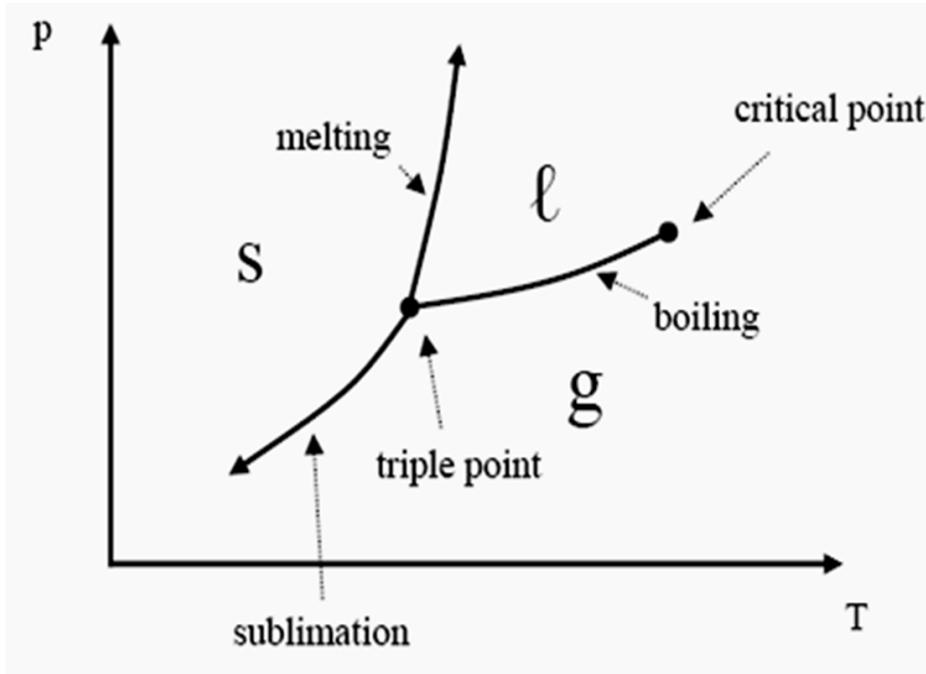
## BOILING POINT and MELTING POINT shifts with change in pressure

- A special condition could arise as result of this shift. The **boiling point of the liquid** may come lower than the **melting point of solid**. This corresponds to the system evaporating below the melting happens, this is SUBLIMATION.
- As can be seen, the system which sublimes can be made to melt and then boil depending on the pressure above it.



## Phase Diagram

Phase Diagram describe the phase properties as a function of state variables, for example in terms of  $(T, p)$ .



For the melting line, for example, solid and liquid coexist, and  $\mu_s(T, p) = \mu_l(T, p)$

Here we have, ONE Equation, and TWO Variables  $(T, p)$ . This means that coexistence of two phases is described by  $T(p)$  or  $p(T)$ . i.e., it is represented as a line in the  $(T, p)$  phase diagram

At the triple point, the chemical potentials of all three phases are the same solid, liquid and gas coexist.  $s(T, p) = (T, p) = g(T, p)$

Here we have, TWO Equations, and TWO Variables. It is thus represented by a unique point  $(T_t, p_t)$  in the  $(T, p)$  phase diagram.

In the single phase (planar) regions of the diagram,  $T$  and  $p$  can be changed independently without changing phases; one of the chemical potentials is lower than the other two.

# The Phase Rule

How many intensive variables are needed to describe fully a system of  $C$  components and  $P$  phases?

- Two for temperature and pressure.
- How many for the composition of each phase?

Take mole fractions of each component in each phase

$$\Rightarrow P \times (C - 1) \quad C-1 \text{ because for each phase } \sum \chi_i = 1$$

but since the phases are in equilibrium,

$$\mu(\text{phase 1}) = \mu(\text{phase 2}) = \dots$$

$(P - 1)C$  variables are redundant

∴ Number of independent concentration variables

$$= P(C - 1) - (P - 1)C = C - P$$

∴ Total number of variables  
**(degrees of freedom)**

$$F = C - P + 2$$

## Triple Point:

The solid, liquid and gas phases are all in equilibrium. This happens at the pressure where the sublimation temperature and the boiling temperature coincide.

## At the triple point:

1. vapour pressure of liquid      vapour pressure of solid
2.  $T_{\text{triple}}$  and  $P_{\text{triple}}$  are fixed.

## Phase:

A state of matter that is uniform throughout, in both chemical composition and physical state.

## Component:

The number of components is the minimum number of independent species necessary to define the composition of all phases in the system. Reactions and phase equilibria must be taken into account.

# Phase Diagrams of Pure Materials

All these cases can be summarized by the **Phase Rule**.

$$F = C - P + 2 \quad \text{with } C = 1 \Rightarrow F = 3 - P$$

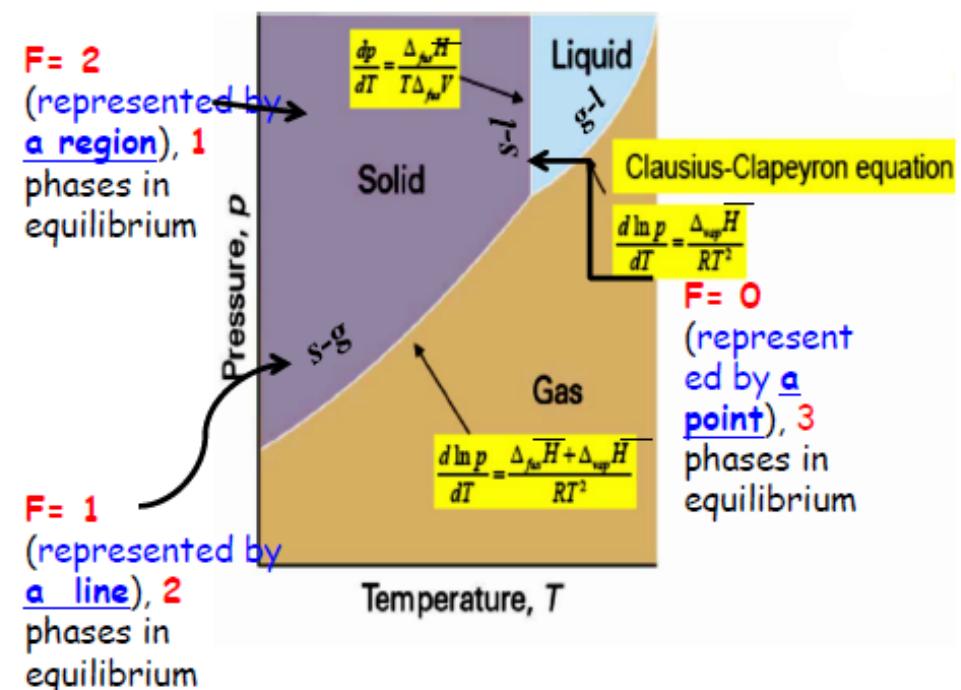
For single phase regions there are 2 degrees of freedom

For phase boundaries there is 1 degree of freedom.

At the **triple point** there is no freedom.

e.g. one-component systems

- $P = 1 \Rightarrow F=2 \Rightarrow p, T$  independently variable
- $P = 2 \Rightarrow F=1 \Rightarrow p$  or  $T$  variable, the other automatically set
- $P = 3 \Rightarrow F=0 \Rightarrow p$  and  $T$  fixed
- $P = 4 \Rightarrow$  impossible

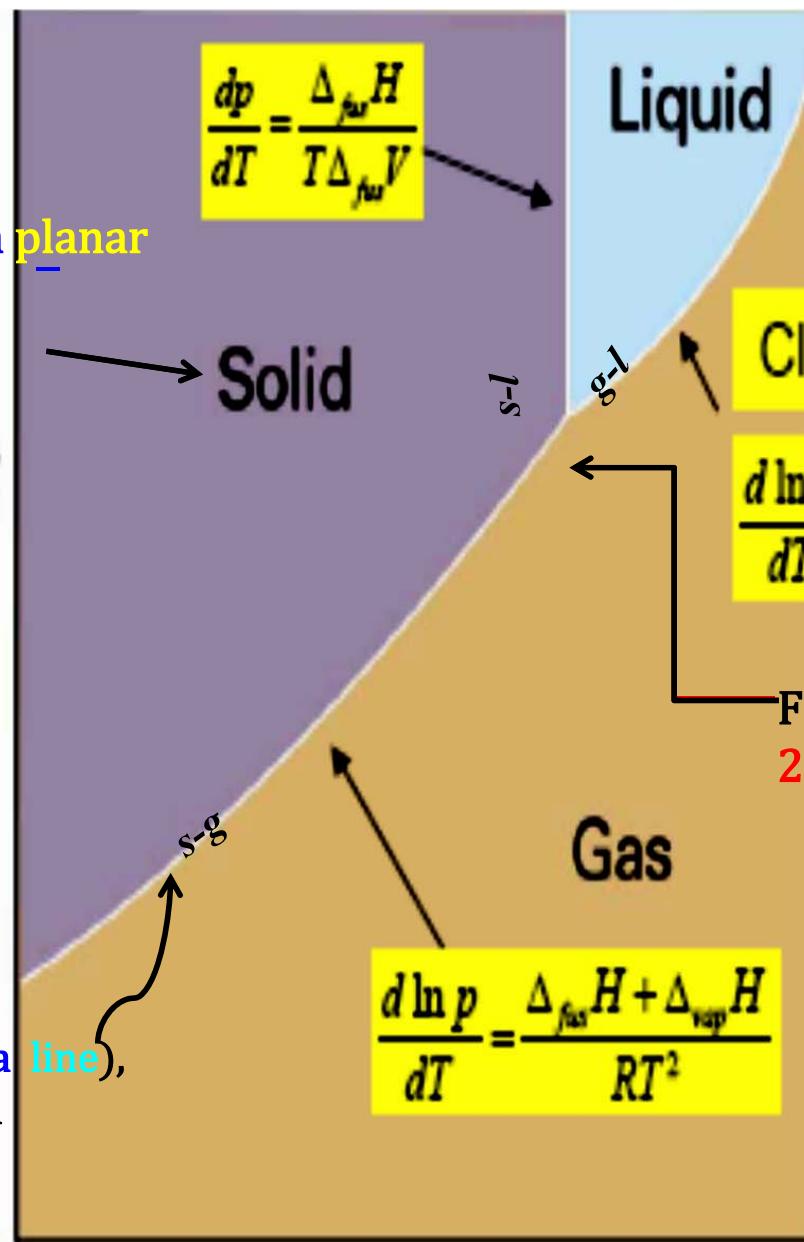


## Phase Diagrams of Pure Materials

F 2 (represented by a planar region), 1 phases in equilibrium

Pressure,  $P$

F 1 (represented by a line),  
2 phases in equilibrium



Temperature,  $T$

F 0 (represented by point),  
2 phases in equilibrium

## Phase Diagram

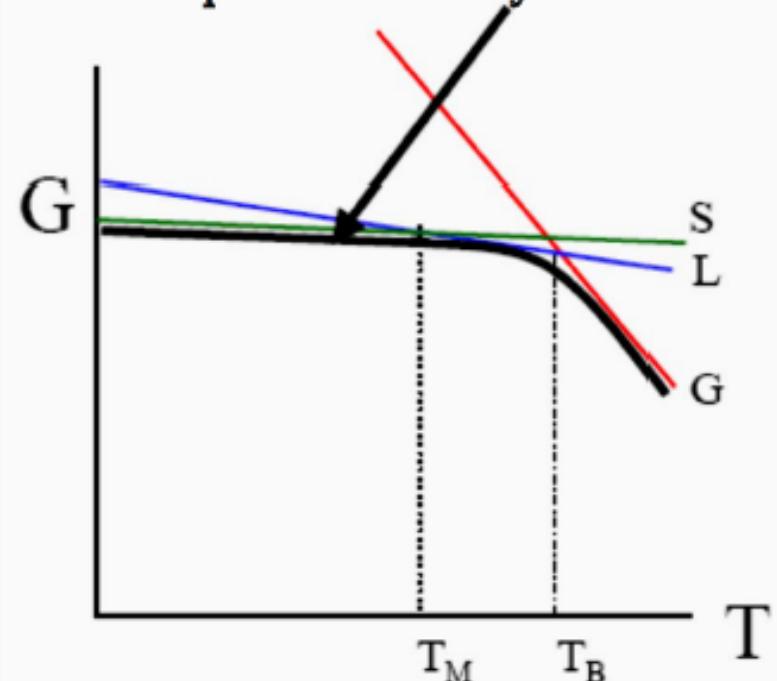
Stability of phases depends on the free energy condition.

For all temperatures below  $T_B$  the liquid is stable;

For all temperatures below  $T_M$  the solid is stable.

For all temperatures above  $T_B$  the gas is stable.

Which path will the system take?

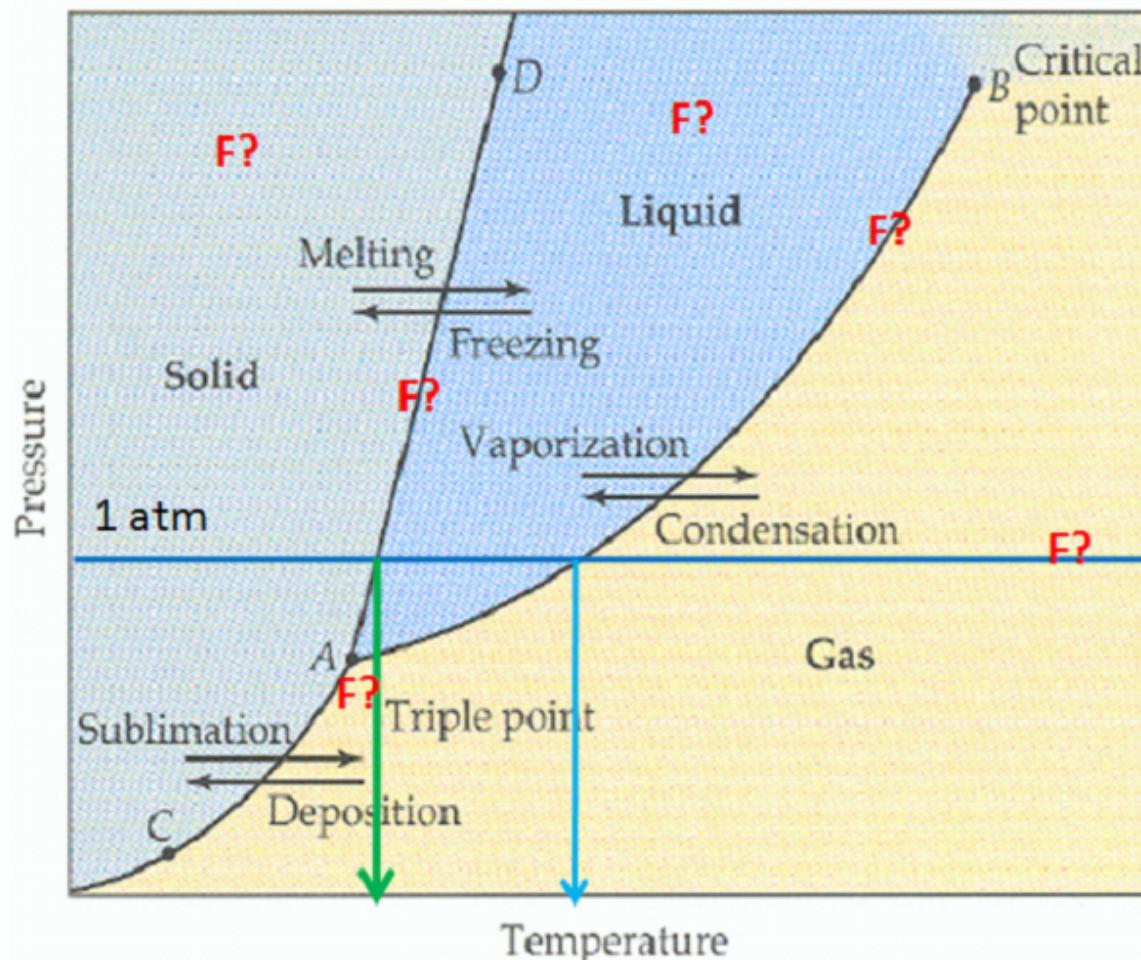


Phase diagram represents state of the system.

Any point in the phase diagram tells about the system completely.

The phase diagram is far more informative than the simple free energy vs. temperature diagram

# A typical phase diagram



**Phase Rule:**  $F = C - P + 2$

C: # of components

P: # of phases

F: # of parameters that can be varied independently

➤ Thermodynamic stability

➤ Metastable states

➤ Phase boundary/Coexistence curves

➤ Boiling/melting point

➤ Normal boiling/ normal melting point (1 atm)

➤ Standard boiling/ standard melting point (1 bar)

➤ Triple point

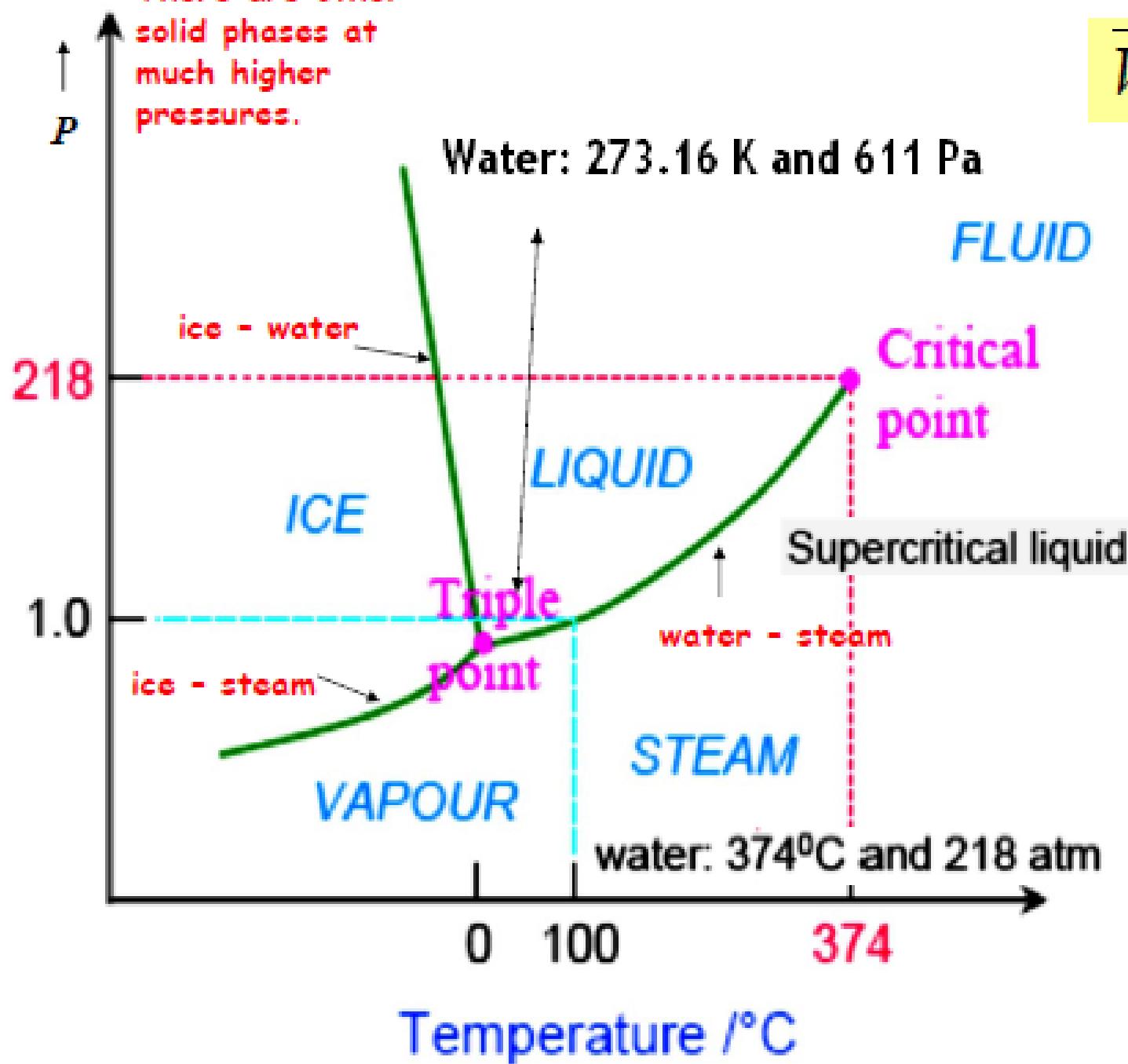
➤ Critical temperature

➤ Vapor pressure/ Sublimation vapor pressure

# Water

$$\left(\frac{dT}{dP}\right) = \left(\frac{\Delta V}{\Delta S}\right) \quad \text{or} \quad \left(\frac{dP}{dT}\right) = \left(\frac{\Delta S}{\Delta V}\right)$$

$$\overline{V}_{liq} < \overline{V}_{solid}$$

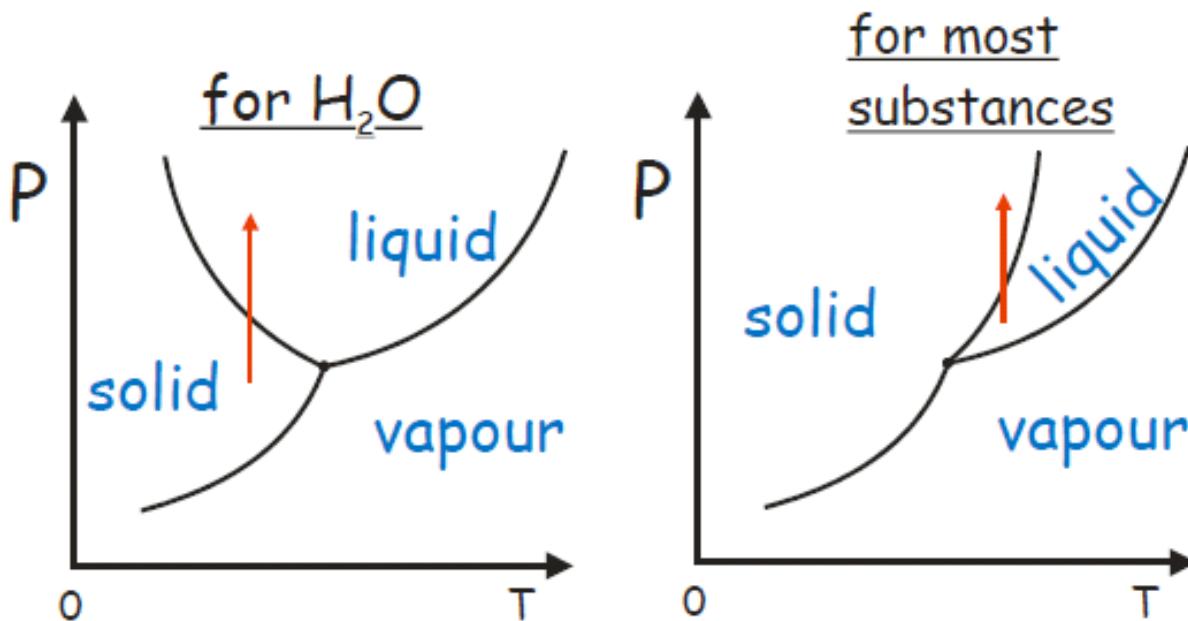


# Water

S-L line → change in m.pt. with pressure

S-G line → " in sub.pt. with pressure

L-G line → " in b.pt. with pressure



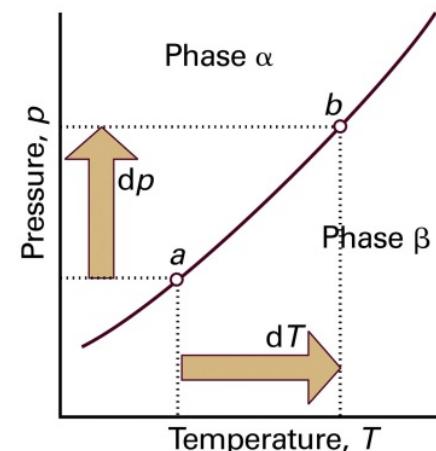
- The slope of the SOLID/LIQUID line is normally positive for most substance but for  $H_2O$  it is negative !
- Most liquids freeze at higher T when P↑
- $H_2O$  freezes (ice melts) at lower T when P↑.

# Phase Equilibria

## The Clapeyron Equation

Consider two phases  $\alpha$  and  $\beta$  in equilibrium at given  $T$  &  $p$ :

$$\text{So, } \mu(\alpha, T, p) = \mu(\beta, T, p)$$



Staying on the coexistence line, if  $T$  is changed by small value,  $dT$ , [i.e.,  $T \rightarrow T + dT$ ] and similarly, if  $p$  is changed by small value,  $dp$ , [i.e.,  $p \rightarrow p + dp$ ]

So, the chemical potentials,  $\mu$ , of species in phase  $\alpha$  will change by  $d\mu_\alpha$   
[i.e.,  $\mu_\alpha \rightarrow \mu_\alpha + d\mu_\alpha$ ]

So, the chemical potentials,  $\mu$ , of species in phase  $\beta$  will change by  $d\mu_\beta$   
[i.e.,  $\mu_\beta \rightarrow \mu_\beta + d\mu_\beta$ ]

If the small changes in  $T$  and  $p$  are made such that the phases  $\alpha$  and  $\beta$  are still in equilibrium, then we write:

$$\mu(\alpha, T, p) + d\mu(\alpha, T, p) = d\mu(\beta, T, p) + d\mu(\beta, T, p)$$

$$d\mu(\alpha, T, p) = d\mu(\beta, T, p) \quad \text{and from: } dG = Vdp - SdT \Leftrightarrow d\mu = \bar{V}dp - \bar{S}dT$$

**The Clapeyron Equation**

$$\begin{aligned} \text{we get, } & -\bar{S}(\alpha)dT + \bar{V}(\alpha)dp = -\bar{S}(\beta)dT + \bar{V}(\beta)dp \\ \Rightarrow & [\bar{V}(\alpha) - \bar{V}(\beta)]dp = [\bar{S}(\alpha) - \bar{S}(\beta)]dT \end{aligned}$$



$$\left( \frac{dp}{dT} \right)_{\text{coexist}} = \frac{[\bar{S}(\alpha) - \bar{S}(\beta)]}{[\bar{V}(\alpha) - \bar{V}(\beta)]} = \left( \frac{\Delta \bar{S}}{\Delta T} \right)_{\text{coexist}}$$

- Exact equation that applies to any phase transition of pure substance

Alternately, we can derive another expression of Clapeyron Equation

Another way to write this is using  $\mu = \bar{G} = \bar{H} - T\bar{S}$  so that  $\mu_\alpha = \mu_\beta$  on the coexistence line implies  $\bar{H}_\alpha - T\bar{S}_\alpha = \bar{H}_\beta - T\bar{S}_\beta$  or  $\Delta\bar{H}_{\alpha \rightarrow \beta} = T\Delta\bar{S}_{\alpha \rightarrow \beta}$ .

Therefore we can rewrite: 
$$\left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta\bar{S}}{\Delta\bar{V}}\right)_{\alpha \rightarrow \beta}$$
 as

$$\left(\frac{dp}{dT}\right)_{\text{coexists}} = \frac{\Delta\bar{S}_{\alpha \rightarrow \beta}}{\Delta\bar{V}_{\alpha \rightarrow \beta}} = \frac{(\Delta\bar{H})_{\alpha \rightarrow \beta}}{T\Delta\bar{V}}$$

$$\text{as, } \Delta\bar{H}_{\alpha \rightarrow \beta} = T\Delta S_{\alpha \rightarrow \beta}$$

Using this then we obtain the two forms of the Clapeyron Equation

$$\left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta S}{\Delta V}\right)_{\alpha \rightarrow \beta}$$

and

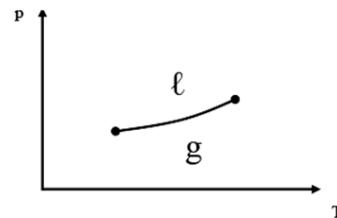
$$\left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta\bar{H}}{T\Delta\bar{V}}\right)_{\alpha \rightarrow \beta}$$

# Location of phase boundaries

Now use the Clapeyron equation to understand the phase diagram

$$\frac{dp}{dT} = \frac{S_{\alpha,m} - S_{\beta,m}}{V_{\alpha,m} - V_{\beta,m}}$$

## Vaporation:



[since,  $V_g \gg V_l$ ,  $\therefore$  large decrease in  $T_b$ ]

$$\Delta \bar{S} > 0, \quad \Delta \bar{V} \gg 0$$

$$\left( \frac{dp}{dT} \right)_{\text{coexist}} = \left( \frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{\ell \rightarrow g} > 0, \text{ but small}$$

(not steep)

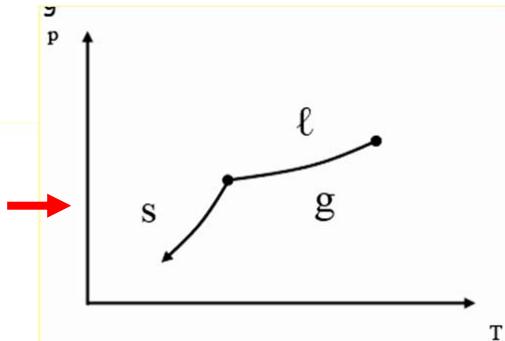
## Sublimation:



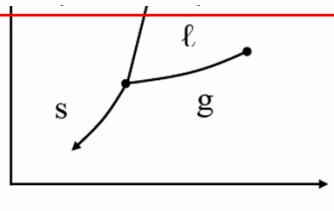
$$\Delta \bar{S} \gg 0, \quad \Delta \bar{V} \gg 0$$

$$\Rightarrow \left( \frac{dp}{dT} \right)_{\text{coexist}} = \left( \frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{s \rightarrow g} > 0, \text{ and } \rightarrow$$

steeper than for  $\ell \rightarrow g$



## Melting:



For most substances  $\bar{V}_l \geq \bar{V}_s$  (almost equal) and  $\bar{S}_l > \bar{S}_s$

$$\Rightarrow \left( \frac{dp}{dT} \right)_{\text{coexist}} = \left( \frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{s \rightarrow \ell} > 0, \text{ and very steep}$$

[when,  $V_l > V_s$ : decrease in  $T_m$   
when,  $V_l < V_s$ : increase in  $T_m$ ]

# Location of phase boundaries

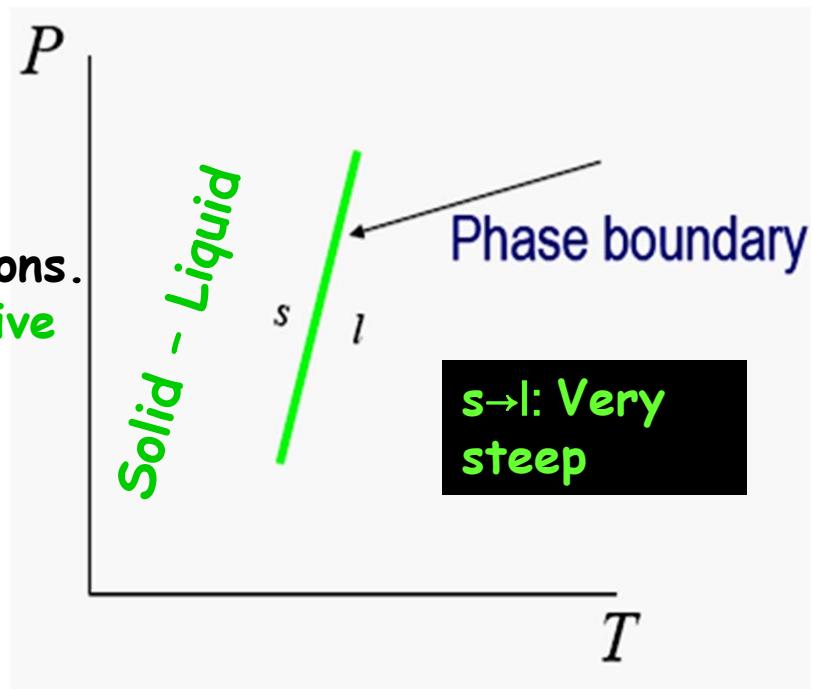
$$\left(\frac{dT}{dP}\right) = \left(\frac{\Delta V}{\Delta S}\right) \quad \text{or} \quad \left(\frac{dP}{dT}\right) = \left(\frac{\Delta S}{\Delta V}\right)$$

## Solid-liquid Equilibrium

Melting:  $\Delta S = S_{\text{liq}} - S_{\text{sol}} = \Delta H_{\text{fus}}/T$  : +ive for all transitions.

$\Delta V = \Delta V_{\text{fusion}} = V_{\text{liq}} - V_{\text{sol}}$  : +ive for most and -ive for some

$dP/dT = \Delta S/\Delta V$  : +ive for most

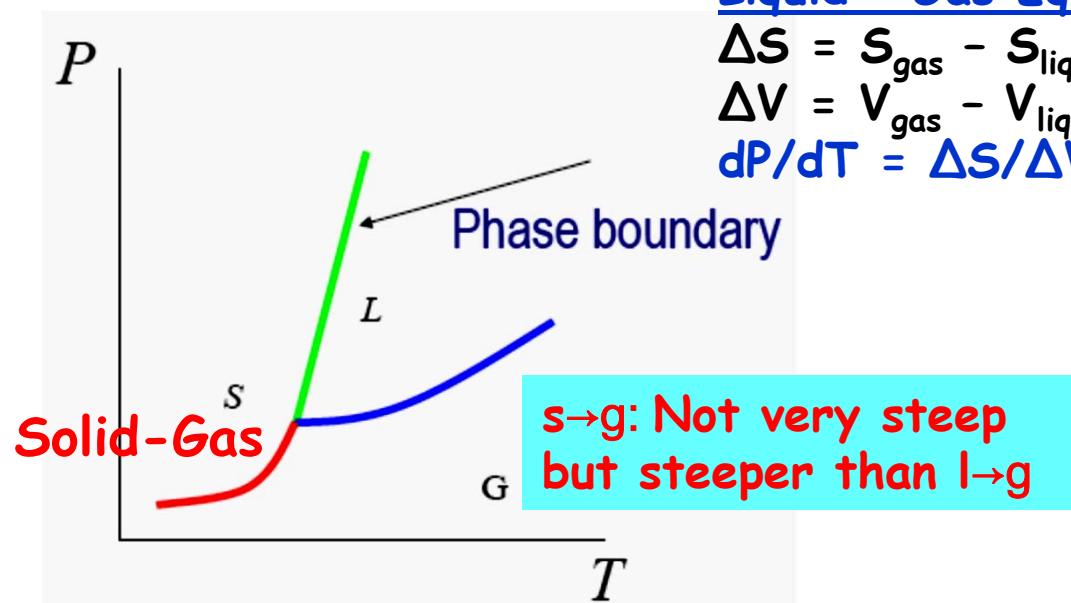


## Solid-Gas Equilibrium

Sublimation:  $\Delta S = S_{\text{gas}} - S_{\text{solid}} = \Delta H_{\text{sub}}/T$  : +ive

$\Delta V = V_{\text{gas}} - V_{\text{solid}}$  : +ive

$dP/dT = \Delta S/\Delta V$  : +ive

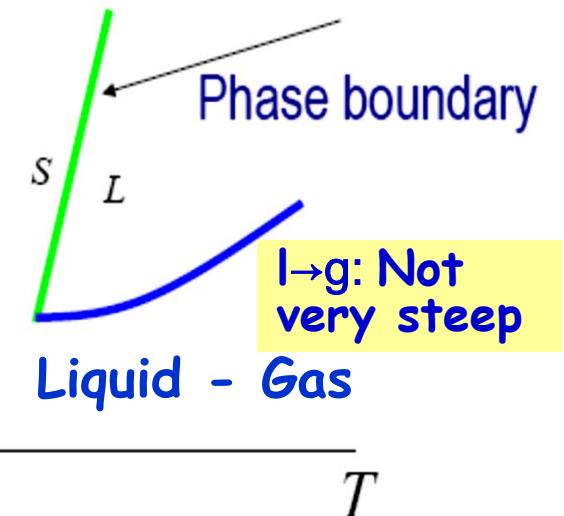


## Liquid - Gas Equilibrium

Vaporation:  $\Delta S = S_{\text{gas}} - S_{\text{liq}} = \Delta H_{\text{vap}}/T$  : +ive

$\Delta V = V_{\text{gas}} - V_{\text{liq}}$  : +ive

$dP/dT = \Delta S/\Delta V$  : +ive



# The Clausius-Clapeyron Equation

The Clausius-Clapeyron Equation relates the Temperature dependence of Vapour Pressure of a LIQUID or, a SOLID to  $\Delta H_{\text{vap}}$  or  $\Delta H_{\text{sub}}$  respectively

## 1. Liquid - Vapour (i.e., gas) Phase Transition:

Vaporization

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{T \Delta \bar{V}_{\text{vap}}} \approx \frac{\Delta \bar{H}_{\text{vap}}}{T \bar{V}(g)}$$

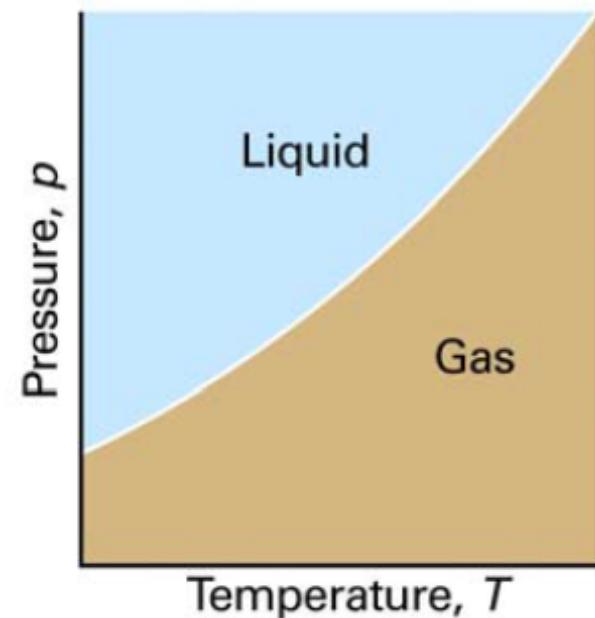
Assuming the vapour is an ideal gas,  $\bar{V}(g) = RT / P$

$$\frac{d \ln P}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2}$$

Integrating,

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\bar{V}_{\text{gas}} \gg \bar{V}_{\text{liquid}} ; \therefore \Delta \bar{V}_{\text{lig} \rightarrow \text{gas}} \approx \bar{V}_{\text{gas}}$$



# The Clausius-Clapeyron Equation

## 2. Solid - Vapour (i.e., Gas) phase Transition:

Taking the Clapeyron Equation (exact), for **Solid - Vapor** (or, gas) using the approximation:

$$\bar{V}_{\text{gas}} \gg \bar{V}_{\text{solid}}, \bar{V}_{\text{liquid}}$$

Under Solid-Vapour Equilibrium

$$\bar{V}_{\text{solid}} \ll \bar{V}_{\text{gas}} ; \therefore \Delta \bar{V}_{\text{solid} \rightarrow \text{gas}} \approx \bar{V}_{\text{gas}}$$

$$\frac{dp}{dT} = \frac{\Delta \bar{S}_{\text{subl}}}{\Delta \bar{V}_{\text{subl}}} = \frac{\Delta \bar{H}_{\text{subl}}}{T \Delta \bar{V}_{\text{subl}}} \approx \frac{\Delta \bar{H}_{\text{subl}}}{T \bar{V}_{\text{gas}}}$$

$$\frac{dp}{dT} = \frac{p \Delta \bar{H}_{\text{subl}}}{RT^2}$$

$$\frac{dp/p}{dT} = \frac{d \ln p}{dT} = \frac{\Delta \bar{H}_{\text{subl}}}{RT^2}$$

This is the Clausius-Clapeyron Equation

for liq-gas, replace  $\Delta \bar{H}_{\text{sub}}$  with  $\Delta \bar{H}_{\text{vap}}$

$$\text{i.e. } \frac{dp}{dT} = \frac{p \Delta \bar{H}_{\text{vap}}}{RT^2}$$

$$\frac{dp/p}{dT} = \frac{d \ln p}{dT} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2}$$

## 3. Solid - Liquid phase Transition:

$$\bar{V}_{\text{solid}} \leq \bar{V}_{\text{liq}} ;$$

$$\text{so, } \Delta \bar{V}_{s \rightarrow l} = \bar{V}_{\text{liquid}} - \bar{V}_{\text{solid}}$$

Under Solid-Liquid Equilibrium

$$\left( \frac{dP}{dT} \right)_{s \rightarrow l} = - \frac{\Delta H_{\text{fus}}}{T \Delta V}$$

# Location of phase boundaries

## solid-vapour boundary

$$\frac{dp}{dT} = \frac{\Delta_{sub}\bar{H}}{T\Delta_{sub}V} = \frac{\Delta_{fus}\bar{H} + \Delta_{vap}\bar{H}}{T\Delta_{sub}V}$$

$\approx \Delta V_{vap}$

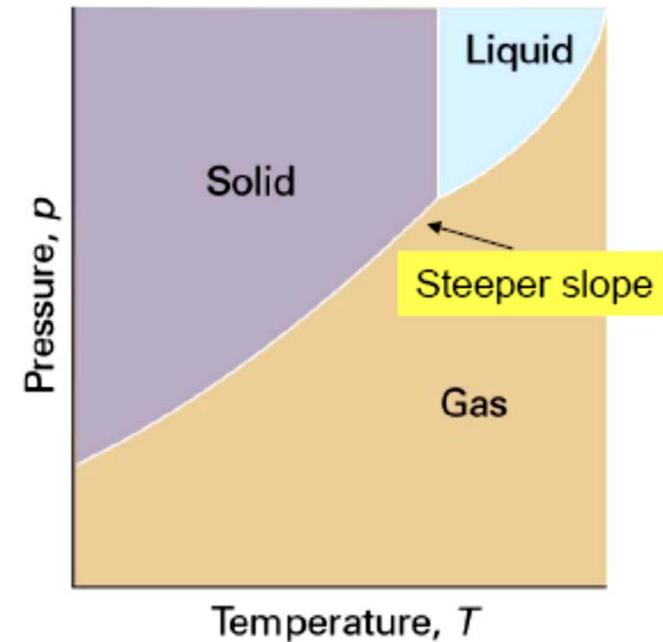
$$\sqrt{V_{gas}} \gg \sqrt{V_{solid}}, \sqrt{V_{liquid}}$$

Taking the Clapeyron equation (exact), e.g. for solid-gas eq. and using the approximation above:

$$\frac{dp}{dT} = \frac{\Delta \bar{S}_{subl}}{\Delta \bar{V}_{subl}} = \frac{\Delta \bar{H}_{subl}}{T \Delta \bar{V}_{subl}} \approx \frac{\Delta \bar{H}_{subl}}{T \sqrt{V_{gas}}} \quad \left( \frac{dp}{dT} \right)_{solid \rightarrow liq} = \left( \frac{\Delta \bar{S}_{trs}}{\Delta \bar{V}_{trs}} \right)_{solid \rightarrow liq} = \left( \frac{\Delta \bar{H}_{fus}}{T_{fus} \Delta \bar{V}_{fus}} \right)_{solid \rightarrow liq}$$

$$\frac{dp}{dT} = \frac{p \Delta \bar{H}_{subl}}{R T^2}$$

$$\frac{dp/p}{dT} = \boxed{\frac{d \ln p}{dT} = \frac{\Delta \bar{H}_{subl}}{R T^2}}$$



## Critical Point and Supercritical Fluids

Does the  $l \rightarrow g$  coexistence curve extend indefinitely high T and P?

NO - it stops at critical point ( $T_c, P_c$ )

Above ( $T_c, P_c$ ),  $l$  and  $g$  become indistinguishable: single fluid phase.

Supercritical fluids are finding remarkably practical applications.

Supercritical water ( $T_c = 375^\circ C, P_c = 221$  bar):

- organic molecules readily soluble

- inorganic salts nearly insoluble

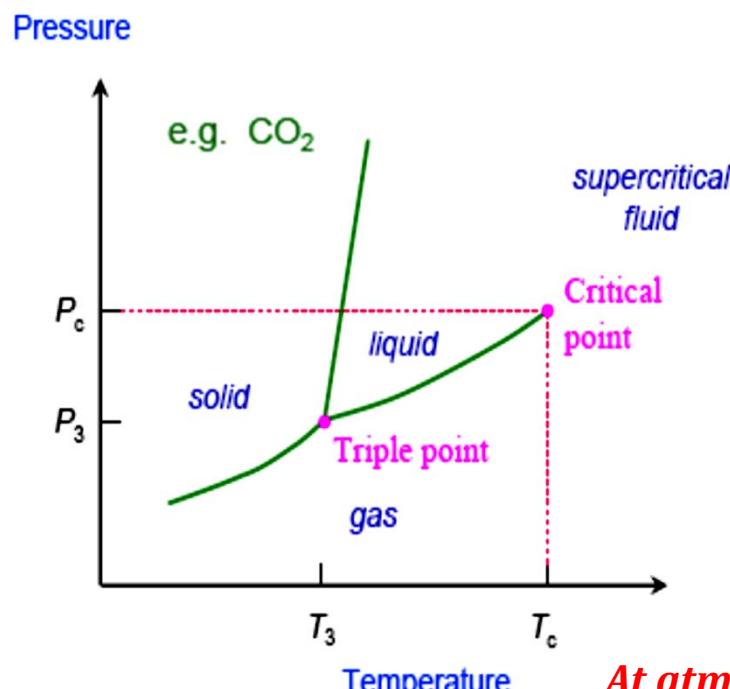
- organic compounds can be oxidized to  $CO_2, N_2$ , mineral salts

Supercritical carbon dioxide ( $T_c = 31^\circ C, P_c = 75$  bar):

- reaction solvent, replaces chlorinated and volatile organic compounds

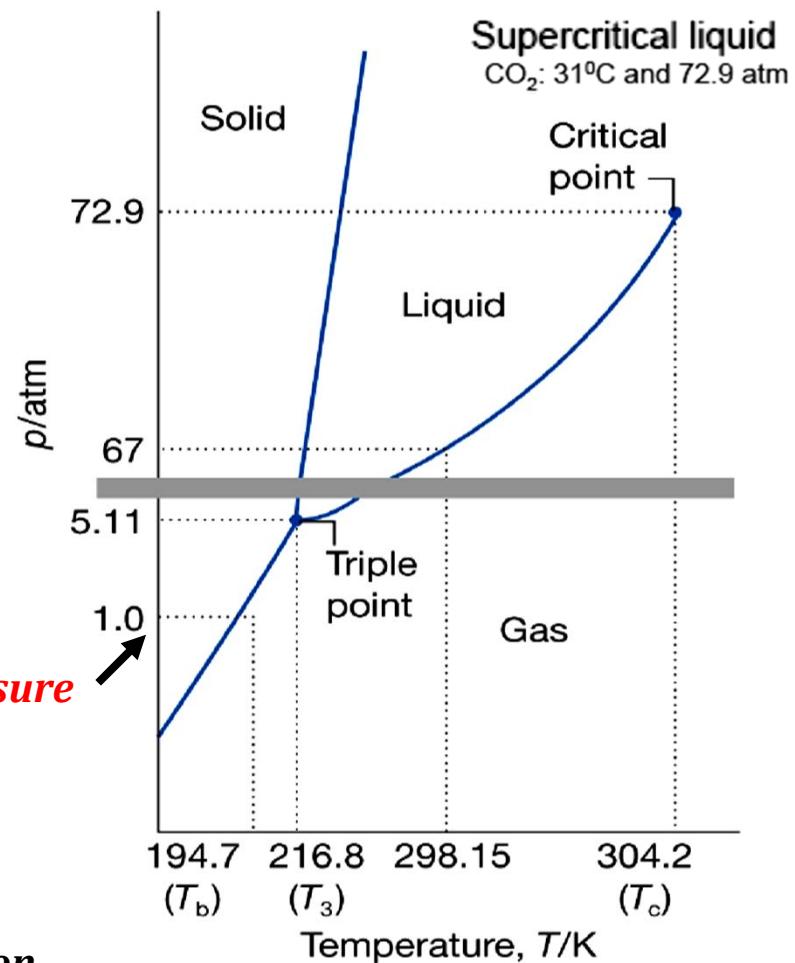
- dry cleaning solvent, replaces perchloroethylene

# Phase diagrams: CO<sub>2</sub>



*At atmospheric pressure  
"dry-ice", directly  
transforms to gas*

*Note that, as the triple point lies at pressures well above atmospheric pressure, therefore liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied).*



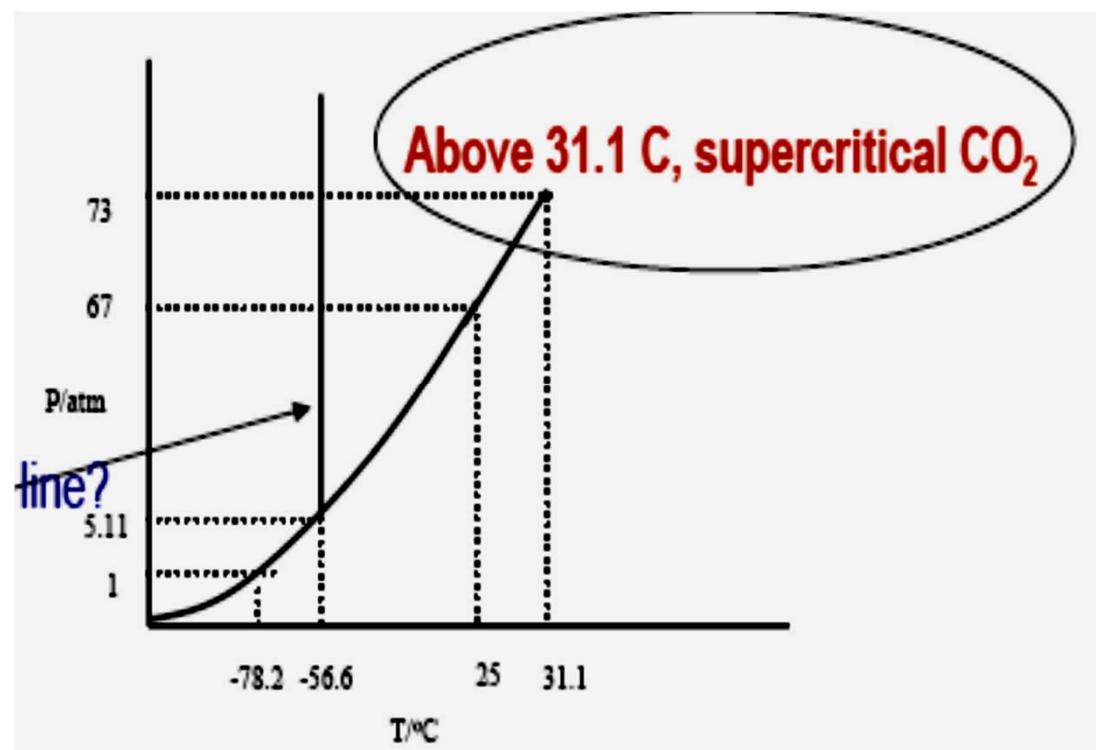
# CARBON DIOXIDE

$$\bar{V}_{liq} > \bar{V}_{solid}$$

Dry ice - No stable liquid phase at 1 atm, and therefore ice evaporates directly and thus dry.

In a  $\text{CO}_2$  cylinder, the critical point is above RT and

In  $\text{CO}_2$  cylinders at  $25^\circ\text{C}$ , gas will be in equilibrium with liquid and the pressure will be at 67 atm.



Sample Problem:

A new molecule (a drug), renol, has been synthesized and its phase diagram needs exploring. Near its triple point it is found that the vapor pressure over the liquid ( $p_l$ ) and over the solid ( $p_s$ ) are given by

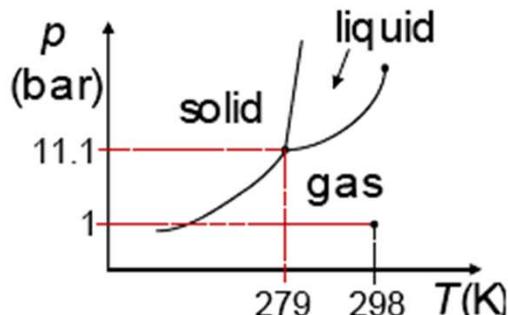
$$\ln p_l = -\frac{3,010 \text{ K}}{T} + 13.2 \quad \ln p_s = -\frac{3,820 \text{ K}}{T} + 16.1$$

- (a) Calculate the triple point temperature  $T_{tp}$  and pressure  $p_{tp}$ .

Set  $\ln p_s = \ln p_l \Rightarrow -\frac{3,010 \text{ K}}{T} + 13.2 = -\frac{3,820 \text{ K}}{T} + 16.1$

Solve for  $T \Rightarrow T_{tp} = 279 \text{ K}$   
 $\Rightarrow p_{tp} = 11.1 \text{ bar}$

- (b) Is renol a solid, a gas, or a liquid at (1 bar, 298 K)?



Phase diagram shows it's a gas.

Must be since slopes of (s,g) and (l,g) coexistence curves are always positive.

(c) What is  $\Delta\bar{H}_{\text{subl}}$ ? (approximate)

Use Clausius-Clapeyron equation:

$$\frac{d \ln p_s}{dT} = \frac{3,820 \text{ K}}{T^2} = \frac{\Delta\bar{H}_{\text{subl}}}{RT^2}$$

$$\Delta\bar{H}_{\text{subl}} = (8.314 \text{ J/K-mol})(3,820 \text{ K}) = 31,760 \text{ J} = 31.8 \text{ kJ}$$

# Reaction Equilibrium

## Equilibrium: Overview

### Describing Chemical Equilibrium

- Chemical Equilibrium – A Dynamic Equilibrium (the link to Chemical Kinetics)
- The Equilibrium Constant
- Heterogeneous Equilibria; solvents in homogeneous equilibria

### Using the Equilibrium Constant

- Qualitatively Interpreting the Equilibrium Constant
- Predicting the direction of a Reaction
- Calculating Equilibrium Concentrations

### Changing Reaction Conditions: Le Châtelier's Principle

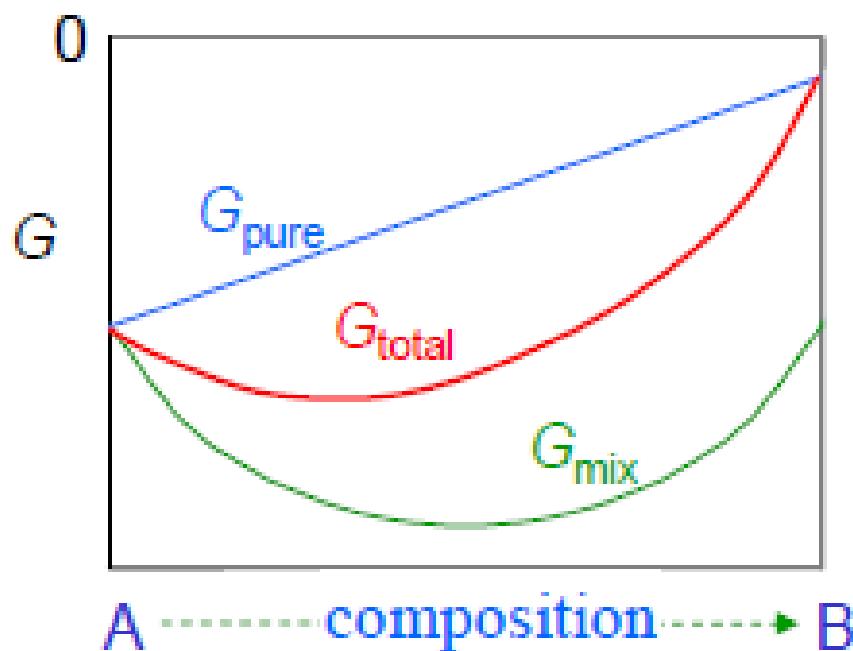
- Removing Products or Adding Reactants
- Changing the Pressure or Temperature
- Effect of a Catalyst

# Reaction Equilibrium and Mixing

## Equilibrium and Mixing:

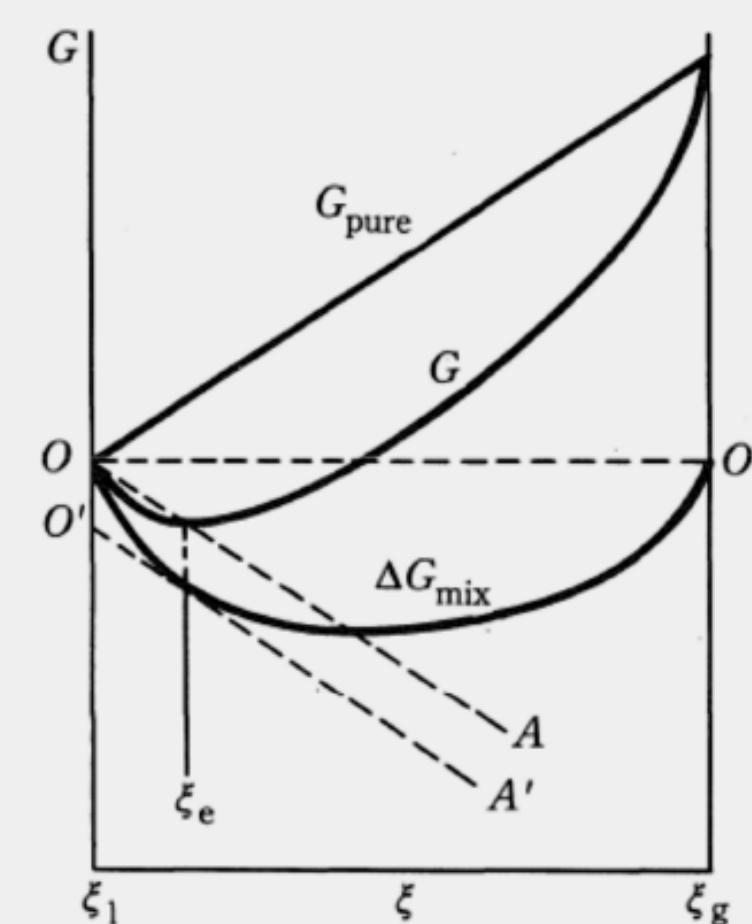
Consider an equilibrium between two ideal gases  $A \rightleftharpoons B$

$$\begin{aligned} G &= G_A(\text{pure}) + G_B(\text{pure}) + \Delta G_{\text{mix}} \\ &= n(\chi_A \mu_A + \chi_B \mu_B) + nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B) \end{aligned}$$



The equilibrium composition is determined by the minimum in  $G_{\text{total}}$ .

# Reaction Equilibrium and Mixing



The minimum in  $G$  occurs at the point where  $\Delta G_{\text{mix}}$  decreases as rapidly as  $G_{\text{pure}}$  increases

$$G = G_{\text{pure}} + \Delta G_{\text{mi}}$$

decreases as rapidly as  $G_{\text{pure}}$  increases; by differentiating,

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \left(\frac{\partial G_{\text{pure}}}{\partial \xi}\right)_{T,p} + \left(\frac{\partial \Delta G_{\text{mix}}}{\partial \xi}\right)_{T,p}.$$

At equilibrium

$$\left(\frac{\partial G_{\text{pure}}}{\partial \xi}\right)_{\text{eq}} = - \left(\frac{\partial \Delta G_{\text{mix}}}{\partial \xi}\right)_{\text{eq}}.$$

# Reaction Equilibrium

Consider  $A \rightleftharpoons B$

Suppose an amount  $dx$  of A turns into B at constant  $T$  and  $p$ .

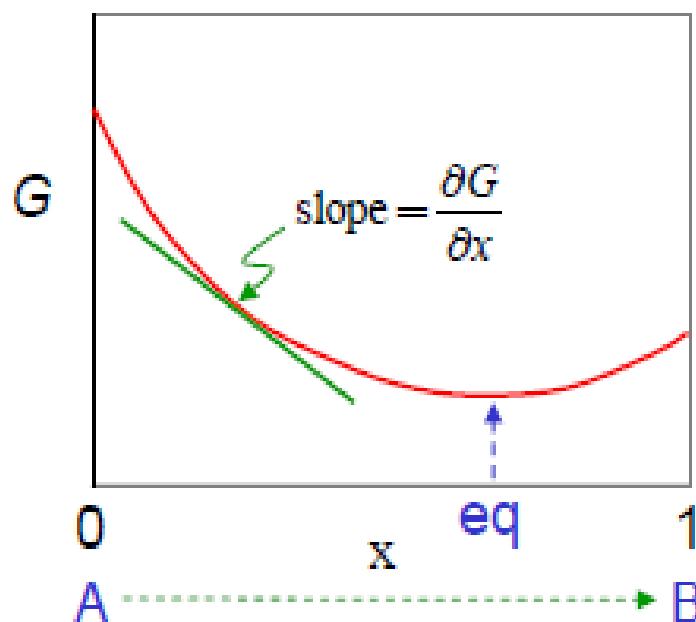
Then  $(dG)_{T,P} = \mu_A dn_A + \mu_B dn_B = -\mu_A dx + \mu_B dx$  where,

$$\Delta\bar{G}_{rxn}^\circ = \left( \frac{\partial G}{\partial x} \right)_{T,P} = \mu_B - \mu_A$$

$$n_A = n_A^\circ - \nu_A x \Rightarrow dn_A = -\nu_A dx$$

$$n_B = n_B^\circ + \nu_B x \Rightarrow dn_B = +\nu_B dx$$

$\mu_A$  and  $\mu_B$  depend on composition, and therefore change during the reaction.



If  $\mu_A > \mu_B$  the reaction proceeds from  $A \rightarrow B$ .  
If  $\mu_A < \mu_B$  the reaction proceeds from  $B \rightarrow A$ .

At equilibrium  $\mu_A = \mu_B$

$$\mu_A^\circ + RT \ln(p_A^{\text{eq}} / P^\circ) = \mu_B^\circ + RT \ln(p_B^{\text{eq}} / P^\circ)$$

$$RT \ln(p_A^{\text{eq}} / p_B^{\text{eq}}) = \mu_B^\circ - \mu_A^\circ = \Delta\bar{G}_{rxn}^\circ$$

$$\frac{p_B^{\text{eq}}}{p_A^{\text{eq}}} = \exp(-\Delta\bar{G}_{rxn}^\circ / RT)$$

Thus, the reaction Gibbs energy is the difference between the chemical potential of product and reactant at the composition of the reaction mixture

# Reaction Equilibrium

A reaction such as  $2A + 3B \rightarrow C + 2D$  can be written as

$$0 = -2A - 3B + C + 2D$$

or completely generally as  $0 = \sum_i v_i R_i = 0$

Then  $\Delta\bar{G}_{rxn}^\circ = \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_i v_i \mu_i$  where,  $\mu_i(T) = \mu_i^\circ(T) + RT \ln p_i$

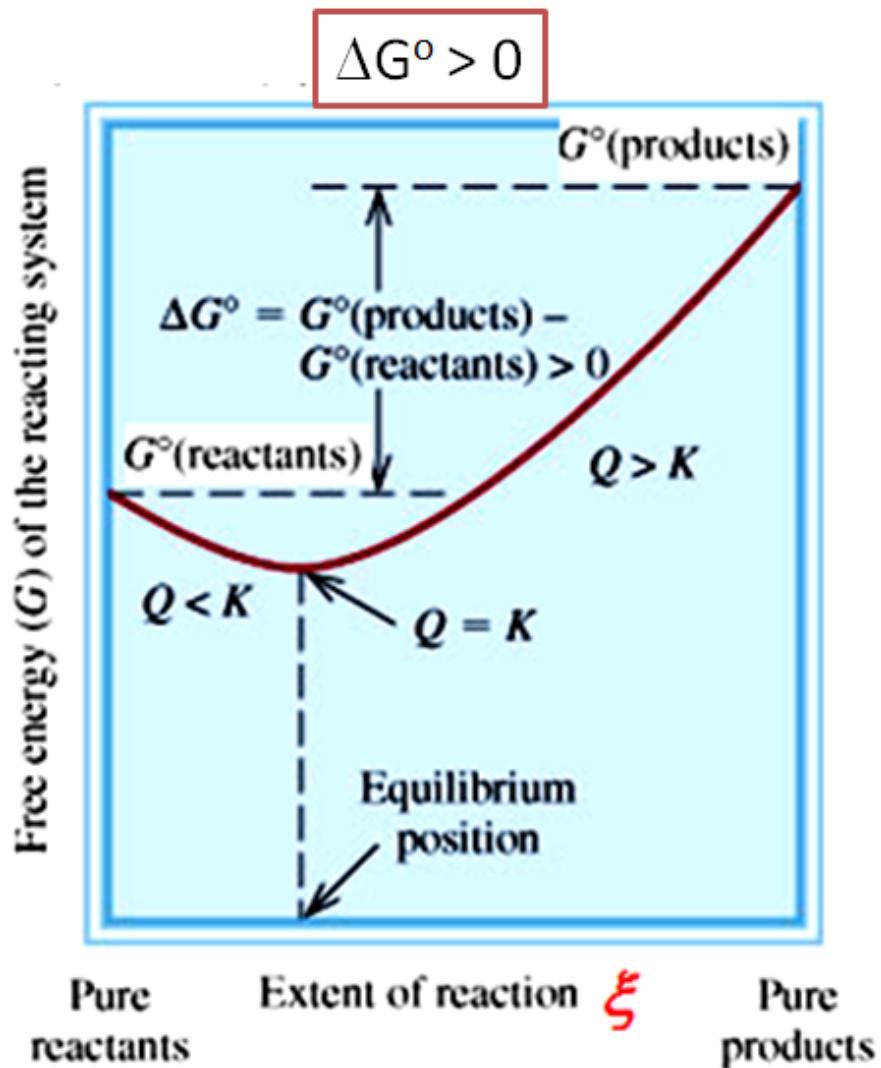
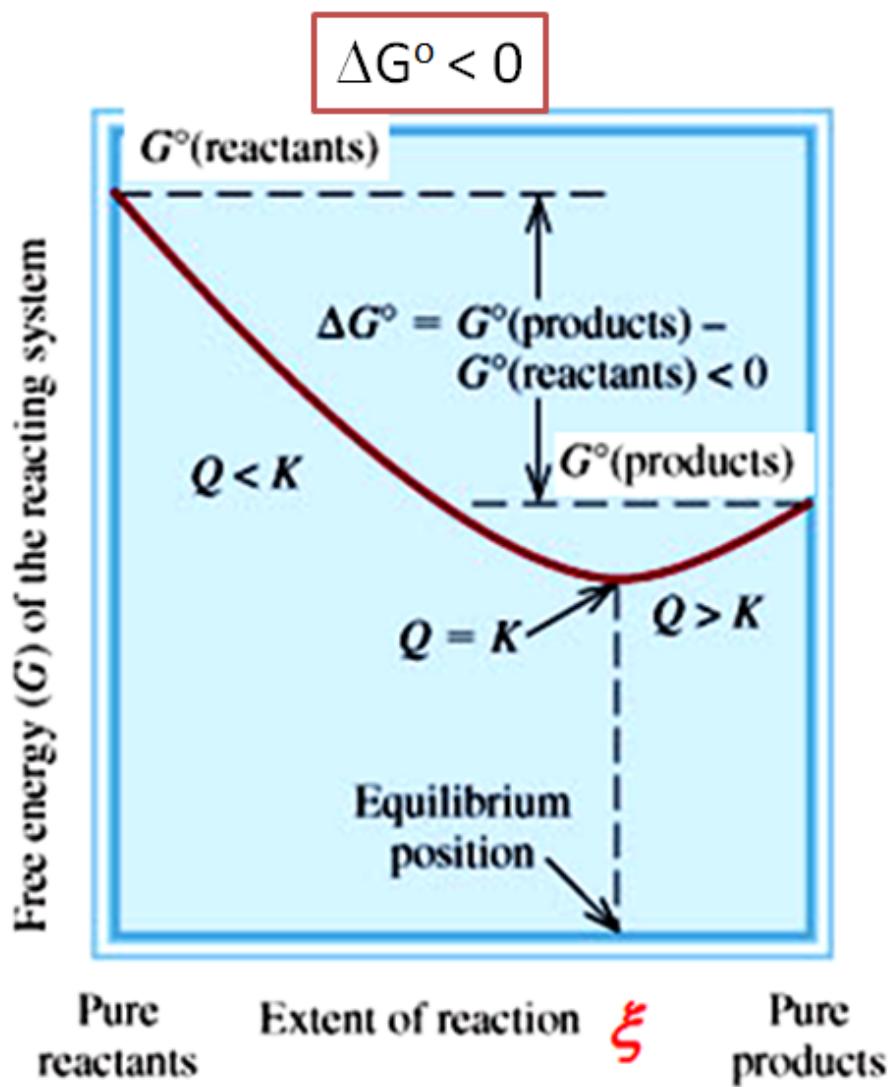
and at equilibrium,  $\sum_i v_i \mu_i = 0$

Therefore, we can write:  $\sum_i \left( v_i \mu_i^\circ + v_i RT \ln \frac{p_i^{\text{eq}}}{P^\circ} \right) = 0$

$$\rightarrow \Delta\bar{G}_{rxn}^\circ + RT \ln \left[ \prod_i \left( \frac{p_i}{P^\circ} \right)^{v_i}_{\text{eq}} \right] = 0 \rightarrow \Delta\bar{G}_{rxn}^\circ = -RT \ln K$$

where,  $K = \prod_i \left( \frac{p_i}{P^\circ} \right)^{v_i}_{\text{eq}}$

# Reaction Equilibrium



## Chemical Equilibrium



$$\Delta G_r^0 = \sum_{\text{pdts}} v \Delta G_f^0 - \sum_{\text{reactants}} v \Delta G_f^0$$

$$\Delta G_r^0 = c \Delta_f G_C^0 + d \Delta_f G_D^0 - a \Delta_f G_A^0 - b \Delta_f G_B^0$$

If  $\Delta_r G^\circ > 0$  then the reaction will not go as written (the reverse reaction will go); if  $\Delta_r G^\circ < 0$  then the reaction will go as written.

$\Delta G_r^0$  can also be written in terms of chemical potentials of the components.  
All components are in their standard states

$$\Delta G_r^0 = c \mu_C^0 + d \mu_D^0 - a \mu_A^0 - b \mu_B^0$$

$$\Delta G_r^0 \neq 0$$

Chemical reactions are not equilibrium processes

## Chemical Equilibrium

Criterion for equilibrium at constant p and T

$$dG_{p,T} \leq 0$$

$$dG_{p,T} = \sum_i \mu_i dn_i \leq 0$$

Let the reaction proceed by an amount  $dn$  ( $dn > 0$ )

$$dn_C = cdn$$

$$dn_D = ddn$$

$$dn_A = -adn$$

$$dn_B = -bdn$$

$$dG_{p,T} = c\mu_C dn + d\mu_D dn - a\mu_A dn - b\mu_B dn$$

$$= (c\mu_C + d\mu_D - a\mu_A - b\mu_B)dn$$

$$dG_{p,T} = \Delta G_r dn \leq 0$$

$$\boxed{\Delta G_r = c\mu_C + d\mu_D - a\mu_A - b\mu_B}$$

## Chemical Equilibrium

$$\Delta G_r^0 = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0$$

If the components are not in their standard states:

$$\Delta G_r = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

Write a general form of the chemical potential of component  $i$  in terms of the activity  $a_i$  – choose system e.g. ideal / real gas etc.

$$\mu_i = \mu_i^0 + RT \ln a_i$$

$$\Delta G_r = \Delta G_r^0 + RT(\ln a_C^c + \ln a_D^d - \ln a_A^a - \ln a_B^b)$$

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

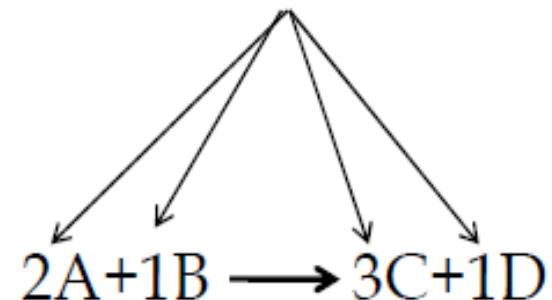
$$\Delta G_r = \Delta G_r^0 + RT \ln Q$$

# Chemical Equilibrium

$$\Delta G_r = \sum_i v_i \mu_i$$

$$\Delta G_r = 3\mu_C + \mu_D - 2\mu_A - \mu_B$$

Stoichiometric numbers  $v_i$



$$\Delta G_r = \sum_i v_i (\mu_i^0 + RT \ln a_i) = \sum_i v_i \mu_i^0 + RT \sum_i v_i \ln a_i$$

$$= \Delta G_r^0 + RT \ln \prod_i a_i^{v_i}$$

$$\boxed{\Delta G_r^0 = \sum_i v_i \mu_i^0 = \sum_{\text{pdts}} v \Delta G_f^0 - \sum_{\text{reactants}} v \Delta G_f^0}$$

$$\boxed{= \Delta G_r^0 + RT \ln Q}$$

$$Q = \prod_i a_i^{v_i}$$

## Chemical Equilibrium

$$\Delta G_r = \Delta G_r^0 + RT \ln \prod_i a_i^{v_i} = \Delta G_r^0 + RT \ln Q \quad Q = \prod_i a_i^{v_i}$$

At equilibrium:

$$K = \left[ \prod_i a_i^{v_i} \right]_{\text{equilibrium}}$$

Thermodynamic equilibrium constant

$$\Delta G_r = 0 = \Delta G_r^0 + RT \ln K$$

Practically  $a_i$  approximated by numerical values of molalities / by molar concentration / numerical values of partial pressures

$$\Delta G_r = 0 = \Delta G_r^0 + RT \ln K_a$$

$$\Delta G_r^0 = -RT \ln K_a$$

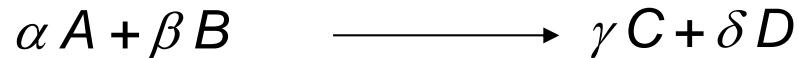
$$K_a = \exp^{-\frac{\Delta G^0}{RT}}$$

$$K_a = \exp^{-\frac{\Delta H^0 - T\Delta S^0}{RT}}$$

$$K_a = \exp^{-\frac{\Delta H^0}{RT}} \exp^{\frac{\Delta S^0}{R}}$$

# Equilibrium Constants

Chemical equilibrium in a mixture of Ideal gases at constant  $T = P$



The reaction Gibbs free energy can be written as:

$$\Delta G_{rxn} = \left( \frac{\partial G}{\partial \xi} \right)_{T,P} \quad \therefore \quad \Delta G_{rxn} = \sum_i \nu_i \mu_i, \quad \text{where } \mu_i = \mu_i^o + RT \ln p_i$$

and  $\nu_i < 0$  (reactants) and  $\nu_i > 0$  (products)

$$\Delta G_{rxn} = \Delta G_{rxn}^o + RT \ln \frac{p_C^\gamma p_D^\delta}{p_A^\alpha p_B^\beta},$$

$$\Delta G_{rxn}^o = \gamma \mu_C^o + \delta \mu_D^o - \alpha \mu_A^o - \beta \mu_B^o$$

At equilibrium,

$$\Delta G_{rxn} = 0, \Rightarrow \Delta G_{rxn}^o = -RT \ln \left( \frac{p_C^\gamma p_D^\delta}{p_A^\alpha p_B^\beta} \right)_{eq} = -RT \ln K_p$$

# Equilibrium Constants

Consider



Thermodynamic Equilibrium Constant

$$K^\circ = \prod_i \left( \frac{p_i}{P^\circ} \right)_{\text{eq}}^{v_i} = \frac{\left( p_Y / P^\circ \right)_{\text{eq}}^y \left( p_Z / P^\circ \right)_{\text{eq}}^z}{\left( p_A / P^\circ \right)_{\text{eq}}^a \left( p_B / P^\circ \right)_{\text{eq}}^b} \quad \text{where, } K_p = \frac{\left( p_Y \right)_{\text{eq}}^y \left( p_Z \right)_{\text{eq}}^z}{\left( p_A \right)_{\text{eq}}^a \left( p_B \right)_{\text{eq}}^b}$$

Some books still refer to the **pressure equilibrium constant** which in general has pressure units

The **equilibrium constant** can also be expressed in **mole fractions**:

$$K^\circ = \frac{\left( \chi_Y P_{\text{tot}} / P^\circ \right)_{\text{eq}}^y \left( \chi_Z P_{\text{tot}} / P^\circ \right)_{\text{eq}}^z}{\left( \chi_A P_{\text{tot}} / P^\circ \right)_{\text{eq}}^a \left( \chi_B P_{\text{tot}} / P^\circ \right)_{\text{eq}}^b} = K_x \left( \frac{P_{\text{tot}}}{P^\circ} \right)^{\Delta v}$$

And the **equilibrium constant** can also be expressed in **concentration units**, which is considered herein this example:  $p_i = n_i RT / V = c_i RT$

$$K^\circ = \prod_i \left( \frac{p_i}{P^\circ} \right)_{\text{eq}}^{v_i} = \prod_i \left( \frac{c_i RT}{P^\circ} \right)_{\text{eq}}^{v_i} = \left( \frac{c^\circ RT}{P^\circ} \right)^{\sum v} K_c \quad \text{where, } K_c = \frac{\left( [Y] / c^\circ \right)_{\text{eq}}^y \left( [Z] / c^\circ \right)_{\text{eq}}^z}{\left( [A] / c^\circ \right)_{\text{eq}}^a \left( [B] / c^\circ \right)_{\text{eq}}^b}$$

$$K_p = K_c \left( \frac{RT}{101.325 \text{ J/mol}} \right)^{\Delta v} = K_c (0.0820568 \text{ T/K})^{\Delta v}$$

$c$  is a quotient of equilibrium concentrations;  $c$  is a function of temperature only.

## Temperature Dependence of $K_P$ (van t Hoff Equation)

Gibbs-Helmholtz

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

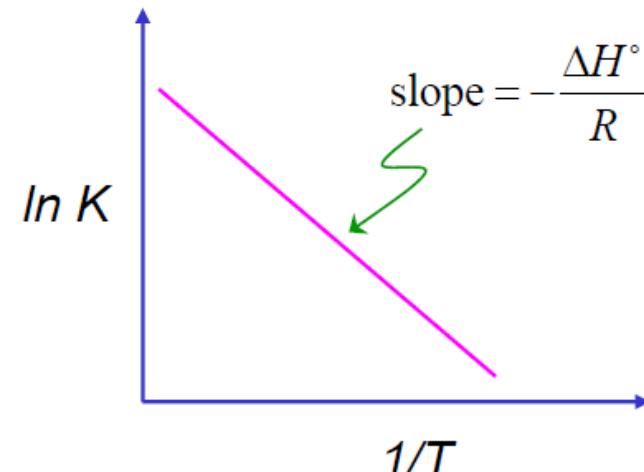
substitute

$$\Delta G_{rxn}^\circ = -RT \ln K$$

van't Hoff Equation

$$\left( \frac{\partial(\ln K)}{\partial T} \right)_P = \frac{\Delta_r H^\circ}{RT^2}$$

or  $\left( \frac{\partial(\ln K)}{\partial(1/T)} \right)_P = -\frac{\Delta_r H^\circ}{R}$



Exothermic reactions:  $\Delta H < 0$  so  $K$  falls with increasing  $T$ .

Endothermic reactions:  $\Delta H > 0$  so  $K$  rises with increasing  $T$ .

Integrating,

$$\ln \left\{ \frac{K(T_2)}{K(T_1)} \right\} = -\frac{\Delta H^\circ}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

or from  $\Delta G_{rxn}^\circ = -RT \ln K$

$$\ln K(T) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

## Pressure Dependence of Equilibrium

Since,  $K^\circ = \exp(-\Delta G^\circ / RT)$ ,  $\left( \frac{\partial K^\circ}{\partial P} \right)_T = 0$

But  $K_x = K^\circ (P/P^\circ)^{-\Delta v}$

$\therefore \ln K_x = \ln K^\circ - \Delta v \ln(P/P^\circ)$

$\ln K_x = \ln K^\circ - \Delta v \ln P + \Delta v \ln P^\circ$

$$\left( \frac{\partial \ln K_x}{\partial \ln P} \right)_T = -\Delta v \quad \rightarrow \quad \left( \frac{\partial \ln K_x}{\partial P} \right)_T = -\frac{\Delta v}{P} = -\frac{\Delta V}{RT} \quad \text{ideal gas}$$

Although the thermodynamic equilibrium constant does not depend on pressure, the mole fraction does depend on pressure, if  $\neq 0$ .

However, the equilibrium composition depends on pressure even if  $\neq 0$

### Le Chatelier's Principle

A system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize the effect.

## Equilibrium Calculations

	2 NO	+	Cl <sub>2</sub>	→	2NOCl
stoichiometry	-2		-1		+2
initial moles	2		1		0
during reaction	$2(1-a)$		$1-a$		$2a$
mole fraction	$\frac{2(1-a)}{3-a}$		$\frac{1-a}{3-a}$		$\frac{2a}{3-a}$
partial pressure	$\frac{2(1-a)}{3-a} \frac{P}{P^\circ}$		$\frac{1-a}{3-a} \frac{P}{P^\circ}$		$\frac{2a}{3-a} \frac{P}{P^\circ}$

$$K_x = \frac{\left\{ \frac{2a}{(3-a)} \right\}^2}{\left\{ \frac{2(1-a)}{(3-a)} \right\}^2 \left\{ \frac{(1-a)}{3-a} \right\}} = \frac{a^2 (3-a)}{(1-a)^3}$$

$\rightarrow K^\circ = K_x \left( \frac{P^\circ}{P} \right)$

The value of  $a$  at equilibrium (and thus the equilibrium composition of the reaction mixture) depends on pressure

**Homogenous equilibrium** applies to reactions in which all reacting species **are in the same phase**



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

In most cases

$$K_c \neq K_p$$



$$K_p = K_c(RT)^{\Delta n}$$

$$\begin{aligned}\Delta n &= \text{moles of gaseous products} - \text{moles of gaseous reactants} \\ &= (c + d) - (a + b)\end{aligned}$$

## Equilibria Involving Condensed Matter

For example, consider:  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$\left( \frac{\partial G}{\partial \xi} \right)_{T,P} = -\mu(\text{CaCO}_3) + \mu(\text{CaO}) + \mu(\text{CO}_2)$$

where,  $\mu(\text{CO}_2) = \mu^\circ(\text{CO}_2) + RT \ln(p_{\text{CO}_2}/P^\circ)$

but  $\mu(\text{CaCO}_3) \approx \mu^\circ(\text{CaCO}_3)$   
 $\mu(\text{CaO}) \approx \mu^\circ(\text{CaO})$

At equilibrium,  $\left( \frac{\partial G}{\partial \xi} \right)_{T,P} = 0$

$$\Rightarrow \Delta \bar{G}^\circ + RT \ln(p_{\text{CO}_2}^{\text{eq}}/P^\circ) = 0$$

$$K^\circ = \left( p_{\text{CO}_2}^{\text{eq}} / P^\circ \right)$$

$K^\circ$  depends only on the partial pressures  
of the gaseous reaction components.

A special case is the evaporation of a liquid:  $\text{L(l)} \rightleftharpoons \text{G(g)}$

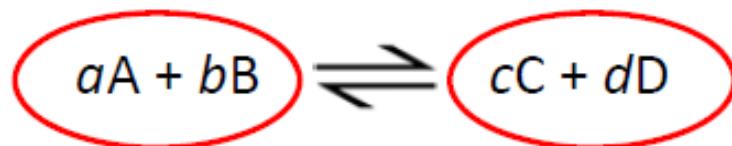
$$K^\circ = \left( p_{\text{G}}^{\text{eq}} / P^\circ \right) \quad \rightarrow$$

$$\frac{\partial \ln K^\circ}{\partial T} = \frac{\partial \ln P}{\partial T} = \frac{\Delta H_{\text{vap}}^\circ}{RT^2}$$

## Chemical Equilibrium – A Dynamic Equilibrium



$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3}$$



$$K = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

**Law of Mass Action**

### Equilibrium Will

$K \gg 1$	Lie to the right	Favour products
$K \ll 1$	Lie to the left	Favour reactants

# Applications of Equilibrium Constants

## Predicting the Direction of Reaction

- If  $Q > K$  then the reverse reaction must occur to reach equilibrium
- If  $Q < K$  then the forward reaction must occur to reach equilibrium

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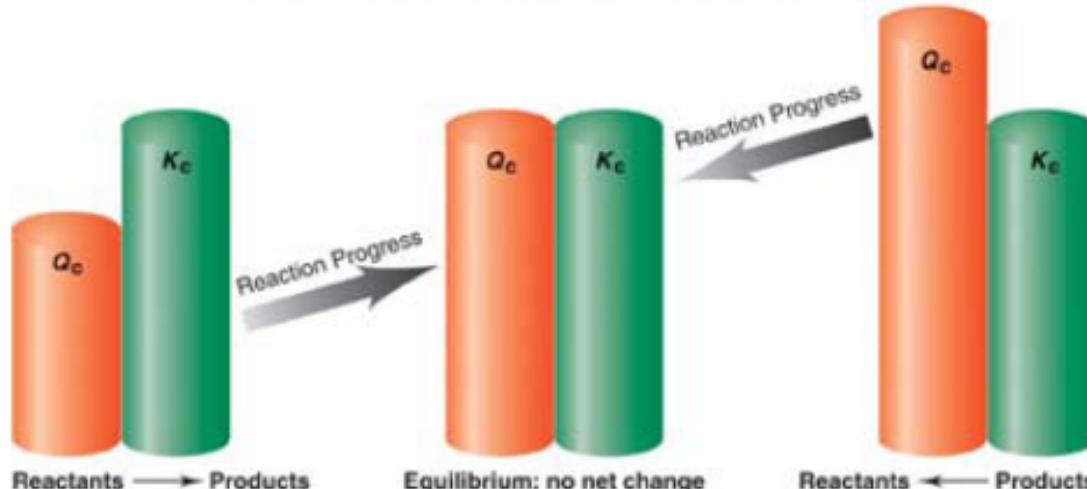


TABLE 18.4

Relation Between  $\Delta G^\circ$  and  $K$  as Predicted by the Equation  
 $\Delta G^\circ = -RT \ln K$

$K$	$\ln K$	$\Delta G^\circ$	Comments
$> 1$	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
$< 1$	Negative	Positive	Reactants are favored over products at equilibrium.

## Different types of equilibrium constants

$$K = \left[ \prod_i a_i^{\nu_i} \right]_{\text{equilibrium}}$$

Thermodynamic equilibrium constant in terms of activity coefficients ( $a_i$ )

$$K_p = \left[ \prod_i p_i^{\nu_i} \right]_{\text{equilibrium}}$$

Standard equilibrium constant for gaseous reaction  
 **$p_i$  (in bar)**

$$K_c = \left[ \prod_i c_i^{\nu_i} \right]_{\text{equilibrium}}$$

Standard concentration equilibrium constant  
 **$c_i$  in mol/L**

$$K_x = \left[ \prod_i x_i^{\nu_i} \right]_{\text{equilibrium}}$$

Mole-fraction equilibrium constant

## Different types of equilibrium constants

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Thermodynamic equilibrium constant in terms of activity coefficients ( $a_i$ )

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Standard equilibrium constant for gaseous reaction  
 $p_i$  (in bar)

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Standard concentration equilibrium constant  
 $c_i$  in mol/L

$$K_x = \left[ \prod_i x_i^{\nu_i} \right]_{\text{equilibrium}}$$

Mole-fraction equilibrium constant