

**LECTURE**

**1**

**CY11001  
Spring 2015-16**

# **Introduction**

- Course introduction
- Introduction: Basic Concepts, Definitions



Department of Chemistry  
Indian Institute of Technology  
Kharagpur

## Distribution of Marks:

**Mid Sem (Only Physical Chemistry): 30**

End Sem (Inorganic & Organic Chemistry): 50

**TA: 20**

**Physical Chemistry (6)**, Inorganic Chemistry (7), Organic Chemistry (7)

Physical Chemistry: TA marks to be based on

**class test + Assignment + Attendance in Class and Tutorials**

Class test: Nov 29, 2022

## **Books:**

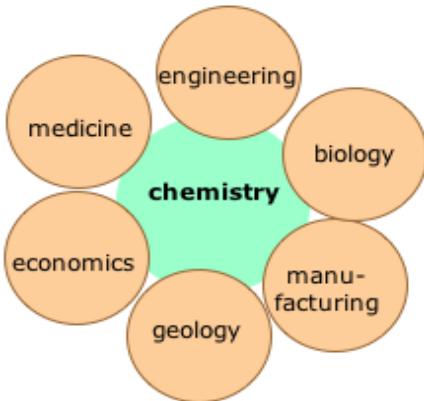
Atkin's Physical Chemistry by *Atkins & de Paula*

Physical Chemistry by *Levine*

Physical Chemistry by *Silbey, Alberty & Bawendy*

# Chemistry

- Chemistry is the *central science*



## Chemistry in daily life

### Food

antioxidants, sweeteners, food colouring, emulsifiers, flavour enhancers, flavours, preservatives, thickeners



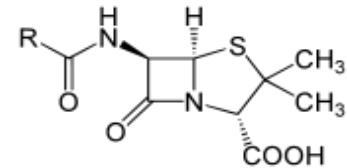
### Personal Care

Deodorant, Shampoo, Toothpaste, Shaving gel, Mouth wash, Talcum powder



### Industries and Transport

Cloth mills, leather factories, petro-chemical industries and refineries, metal industries, alternative energy sources



### Medicinal Chemistry

Drug discovery, drug metabolism



### Agriculture

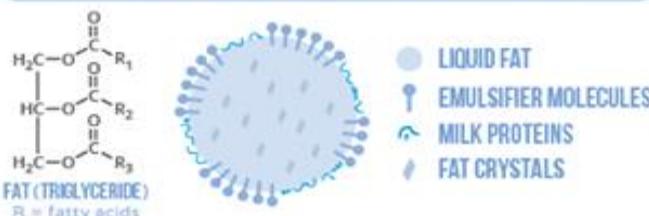
Pesticides, Genetically modified seeds



# THE CHEMISTRY OF ICE CREAM

Ice cream is a combination of air, ice crystals, fat globules, and a liquid syrup. These are combined to make a colloid, a solution with very small insoluble particles suspended in it. This graphic looks in detail at the components of this colloid, and some molecules that produce ice cream flavours.

## FATS, PROTEINS, & EMULSIFIERS



Fats are important for the creaminess of ice cream. Proteins from milk form a membrane around the fat droplets, making it harder for them to come in contact with each other. Emulsifiers replace some milk protein on the surface of the fat droplet. As ice cream is made, some of the fat in the droplet solidifies, and the fat 'needles' that form help droplets to partially cluster. These clusters, along with milk proteins, help stabilise air bubbles in the ice cream.

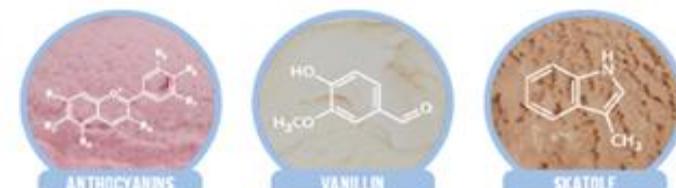
## THE STRUCTURE OF ICE CREAM



During freezing, most water is frozen into ice. Small ice crystals are needed for smooth ice cream. Beating and aeration occur at the same time as freezing to form small air bubbles, stabilised by de-emulsified fat. Air makes up 30-50% of ice cream's final volume. Sugar sweetens the ice cream, and lowers the freezing point of water, reducing the amount of ice. Soft ice cream contains less ice.

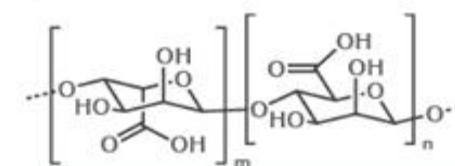


## FLAVOURS AND COLOURS



Natural ice cream flavours contain a number of flavour-contributing compounds. Flavouring can also be achieved artificially. Artificial vanilla flavouring is often simply vanillin; other artificial flavours are more complex. Other compounds can be used as flavour enhancers – an unusual example is skatole, also found in faeces, but which has a floral odour at lower concentrations. Colours can be added artificially; anthocyanins from plants are amongst the colouring agents used.

## STABILISERS



### ALGINIC ACID

Sodium alginate is the sodium salt of alginic acid. Another stabiliser that can be obtained from seaweed is carrageenan.

Stabilisers are added in small amounts (~0.2%) to ice cream. Often extracted from plants, a common example is sodium alginate, the sodium salt of alginic acid, extracted from brown seaweeds. Stabilisers reduce the rate at which ice cream melts, add smoothness, and increase the viscosity of the liquid phase of ice cream. Use of multiple stabilisers can produce synergistic effects.



# THE CHEMISTRY OF FIREWORKS

Colours in fireworks are generated by pyrotechnic stars, which produce coloured light when ignited. The stars contain five basic ingredients:

## COLOUR-PRODUCING COMPOUNDS

Specific compounds which produce an intense colour when burned. Some of the commonly used colour producing compounds are listed on the right; generally they tend to be metal salts.

## FUEL

Allows the star to burn; gunpowder, which contains a mix of potassium nitrate, sulfur and charcoal, is often used.

## OXIDISER

Usually nitrates, chlorates or perchlorates; required to provide oxygen for the combustion of the fuel.

## BINDER

Holds the mixture together; the most commonly used binder is a type of starch called dextin, dampened with water.

## CHLORINE DONOR

Chlorine donors can help strengthen some colours. Sometimes the oxidiser can also act as the chlorine donor.



# Chemistry and Prosperity

## Chemistry in the Nation Building:

- \$100 billion (2010) Indian chemical industry
- growing at a rate of 13%
- Contributes 3% to India GDP
- Constitutes 14% of its exports

Angew. Chem. Int. Ed. 2013, 52, 114 – 117

### THE BUSINESS OF CHEMISTRY BY THE NUMBERS

Chemistry is essential to our economy and plays a vital role in the creation of ground-breaking products that make our lives and our world healthier, safer, more sustainable and more productive.



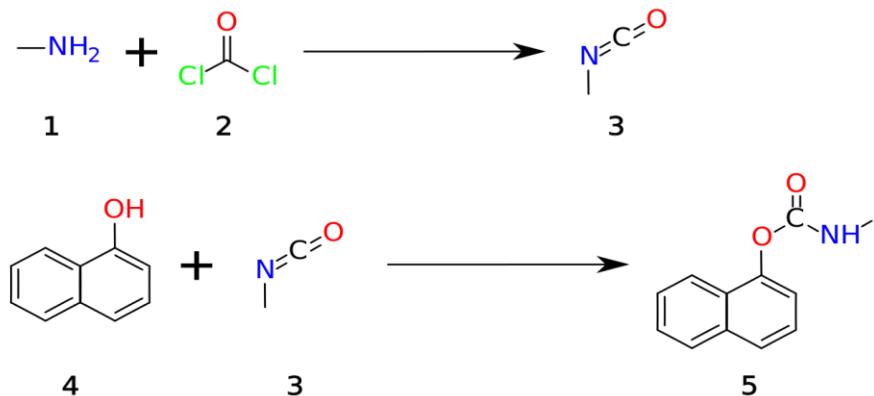
JUNE 2014



# Perils of Chemistry

## The Bhopal Tragedy:

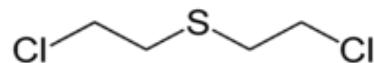
Water leaks into MIC tank and starts a thermal runaway reaction causing high temperature ( $200^{\circ}\text{C}$ ) and high pressure results in release of 30 metric ton of MIC in 1 hour.



Methylamine (1) reacts with phosgene (2) producing methyl isocyanate (3) which reacts with 1-naphthol (4) to yield carbaryl (5), the pesticide.

## Chemical Weapons:

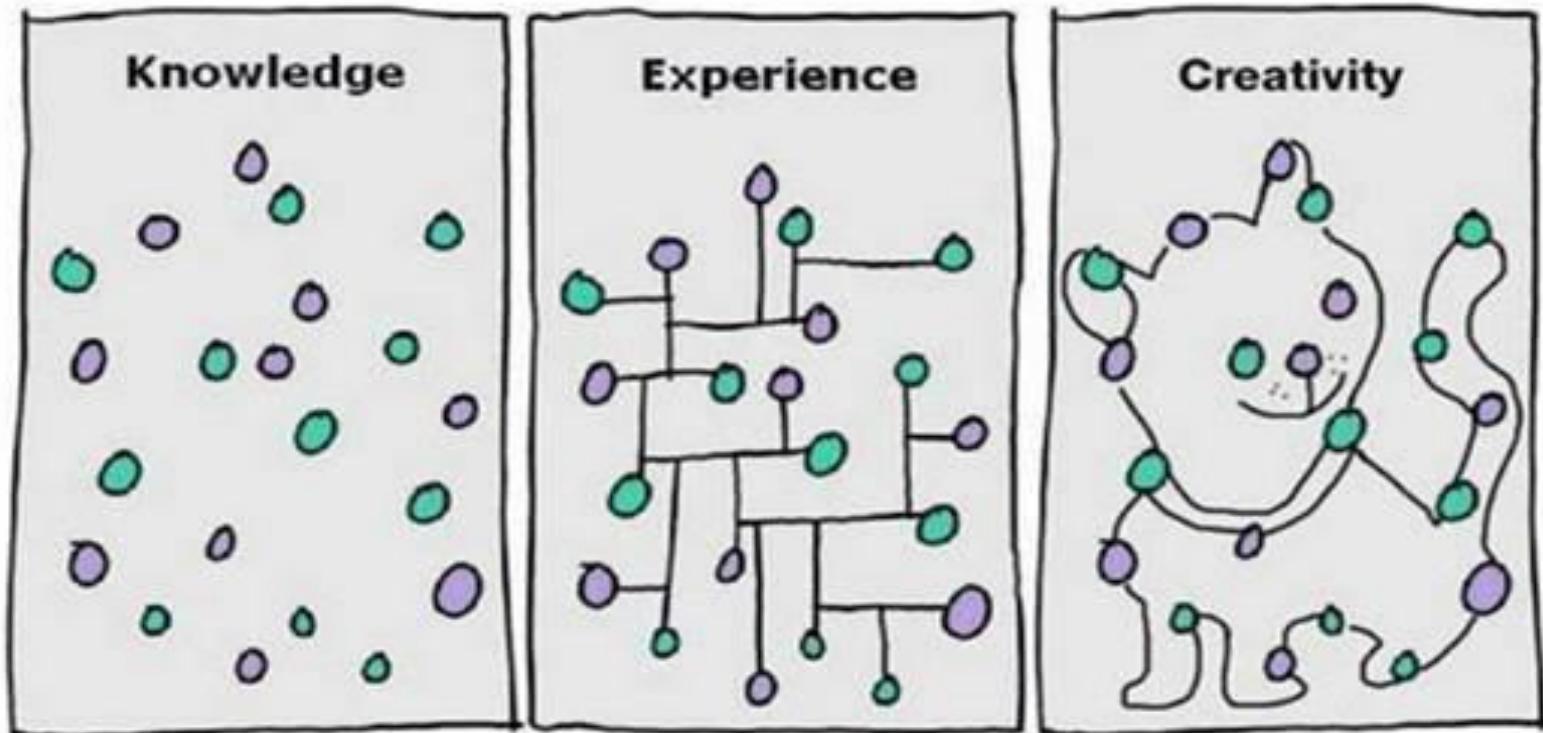
Can be widely dispersed in gas, liquid and solid forms and may easily afflict others than the intended targets. *Nerve gas, tear gas, pepper spray, sulfur mustard (mustard gas)*



# **State of Modern Chemistry**

- **Highly interdisciplinary science**
- **Major branches of Chemistry**
  - Analytical Chemistry
  - Biochemistry
  - Inorganic Chemistry
  - Organic Chemistry
  - Physical Chemistry
  - Agrochemistry
  - Computational Chemistry
  - Materials Chemistry
  - Nuclear Chemistry
  - Polymer Chemistry etc.

# Your Journey *through* Chemistry:



# Course outline

## Physical Chemistry

- Essential concepts and definitions in Thermodynamics
- Revision: heat, work & energy; Real gas
- First Law of Thermodynamics
- The Second Law of Thermodynamics
- Entropy
- Gibbs Free Energy
- The Chemical Potential
- Phase and Reaction Equilibria
- Chemical Kinetics

# Thermodynamics

- The study of the transformations of energy (work, heat, energy and their effect on the state of the system). Concerned with equilibrium positions of systems.
- Provides a framework of relating the *macroscopic* properties of a system to one another.
- Our discussions will be restricted to equilibrium thermodynamics which deals with systems in equilibrium.

# SOME BASIC CONCEPTS:

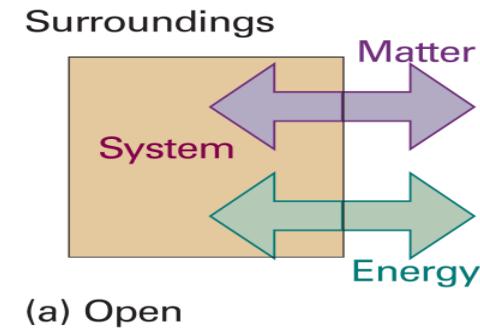
□ Thermodynamic System – Open, Closed, Isolated

□ Surroundings

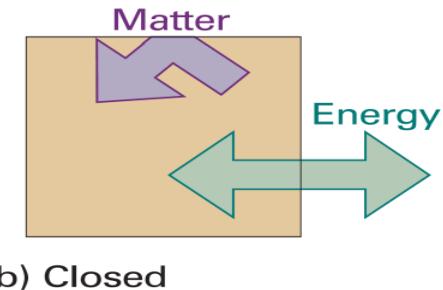
□ Boundary / Wall

- Rigid and Nonrigid (movable)
- Permeable and Impermeable  
(no matter is allowed to pass through it)
- Adiabatic and Nonadiabatic  
(diathermic boundary –  
permits the passage of energy as heat )

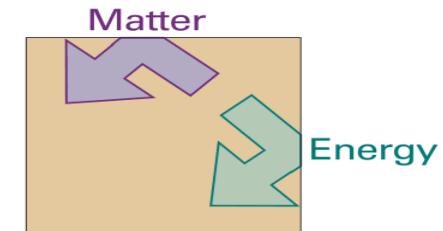
A system surrounded by a rigid,  
impermeable, adiabatic wall –  
**Isolated system**



(a) Open



(b) Closed



(c) Isolated

**Fig. 2.1** (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

# Thermodynamic Equilibrium

For Isolated system:

Macroscopic properties do not change with time

For Non-isolated system:

- Macroscopic properties do not change with time
- Removal of the system from contact with its surroundings causes no change in the properties of the system

- Mechanical Equilibrium
- Thermal Equilibrium
- Material Equilibrium

LECTURES

2,3

CY11001  
Spring 2016

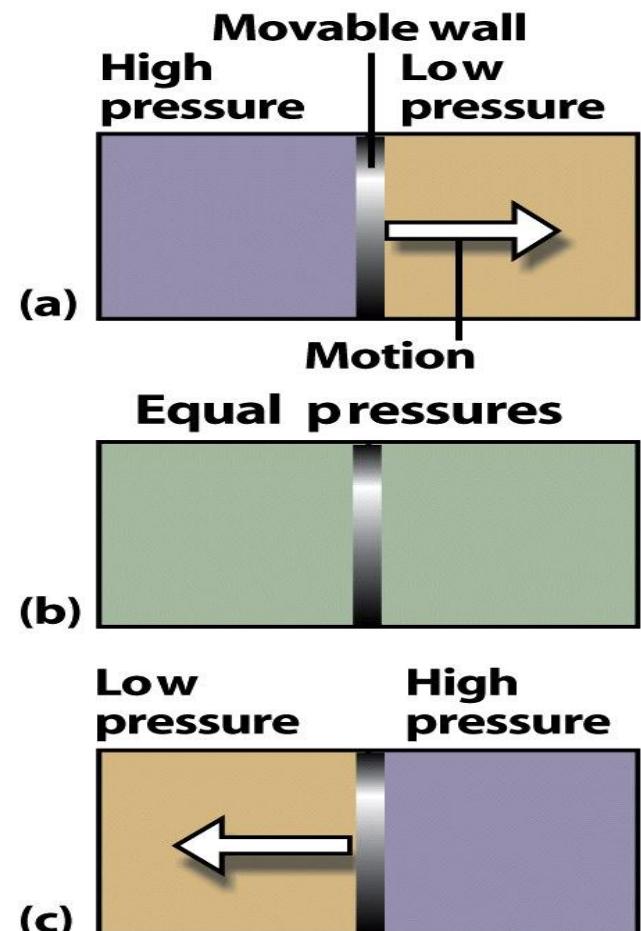


Department of Chemistry  
Indian Institute of Technology  
Kharagpur

# Mechanical equilibrium

the condition of equality of pressure on either side of a movable wall.

**No unbalanced forces** act on or within the system – system does not undergo acceleration or no turbulence inside the system



**Figure 1-1**  
*Atkins Physical Chemistry, Eighth Edition*  
© 2006 Peter Atkins and Julio de Paula

# Thermal equilibrium

between system and the surroundings, is a condition in which no change in the properties of the system or surroundings when they are separated by a thermally conducting wall.

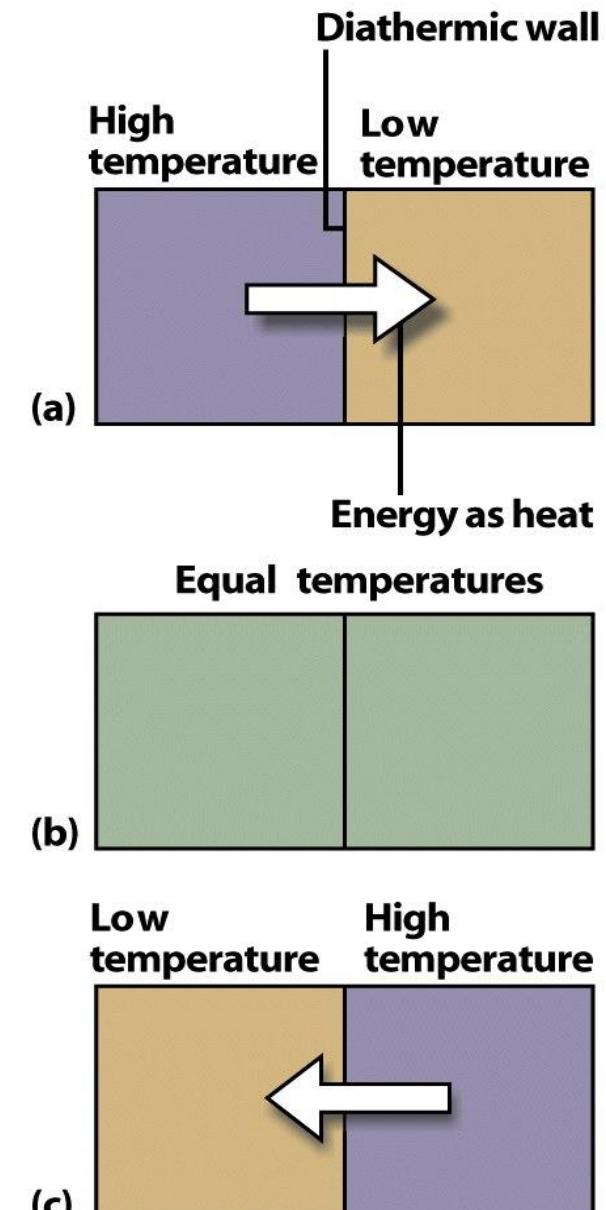


Figure 1-2  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

# Material equilibrium

Concentrations of the chemical species in the various parts of the system are constant with time

- a) No net chemical reactions are occurring in the system
- b) There is no net transfer of matter from one part (phase) of the system to another or between the system and its surroundings

**For thermodynamic equilibrium, all three kinds of equilibrium must be present**

# Thermodynamic Properties:

Intensive properties (do not depend on the size of the system, density, pressure)

Extensive properties (they do. Ex: mass, volume)

If each intensive property is constant throughout the system,

Homogeneous system

Heterogeneous system

a homogeneous part of a system is called a phase

# How do we define a system? State of a System

**Macroscopic state** of a system can be specified by the values of a small number of macroscopic Properties/Parameters/Physical characteristics or attributes of a system - **Thermodynamic variables**

**Thermodynamic variables** which are experimentally measurable

- Composition – mass of each chemical species that is present in each phase,
- pressure ( $p$  or  $P$ ), volume ( $V$ ), Temperature ( $T$ ), density, etc.
- field strength, if magnetic/electrical field act on the system
- gravitational field

If the value of every thermodynamic property in system A is same as in system B – same thermodynamic state

Microscopic state of a system needs description about each molecules – a very complicated picture

# Thermodynamic Processes:

When one or more of the thermodynamic properties of a system changes, the state of the system also changes and system is undergoing a process

Isothermal (constant  $T$ ),

Isobaric (constant  $p$ ),

Isochoric (constant  $V$ )

Adiabatic

Exothermic & Endothermic

Cyclic

Reversible & Irreversible

## Reversible process:

- *Ideal*
- Change must occur in *successive stages of infinitesimal quantities*
- *Infinite duration*
- *Virtual thermodynamic equilibrium*, at each of the small stages.
- Backward changes of the thermodynamic quantities in different stages will be the *same as in the forward direction but opposite in sign with respect to the forward direction*

## Irreversible Process:

- **Real / Spontaneous**
- Occurs suddenly or spontaneously without the restriction of occurring in *successive stages of infinitesimal quantities*.
- Does not remain in the *virtual equilibrium* during the transition.
- The work in the *forward and backward processes* can be *unequal*.

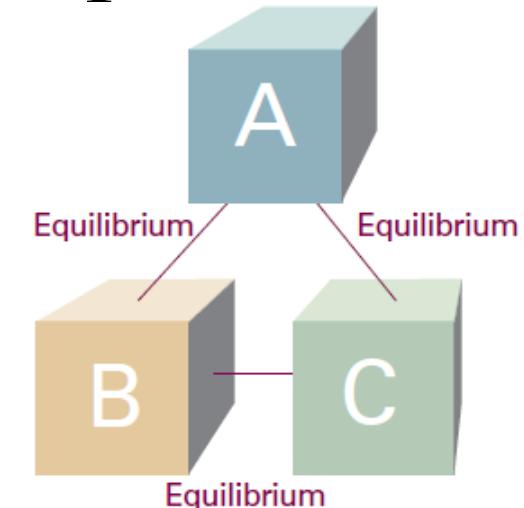
# Zeroth Law of Thermodynamics – Temperature

(Flower, 1931)

**Temperature** is a property associated with random motion of many particles.

Introduction of the concept of temperature in thermodynamics is based on the **the zeroth law of thermodynamics**:

A well-defined quantity called **temperature** exists such that two systems will be in thermal equilibrium if and only if both have the same temperature.



**Fig. 1.3** The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

Application of Zeroth Law of Thermodynamics: Thermometer

# The Equation of State

An equation that relates macroscopic variables (e.g.,  $p$ ,  $V$ , and  $T$ ) for a given substance *in thermodynamic equilibrium*.

$$p = f(V, T, n)$$

- Equation of state is not a theoretical deduction *from* thermodynamics, rather an experimental addition *to* it. An equation of state is as accurate as the experiments that led to its formulation. It holds *only* within the range of measurement.

perfect/ideal gas equation,  $pV = nRT$ .

perfect/ideal gas, a gas that obeys  $pV = nRT$  exactly under all conditions.

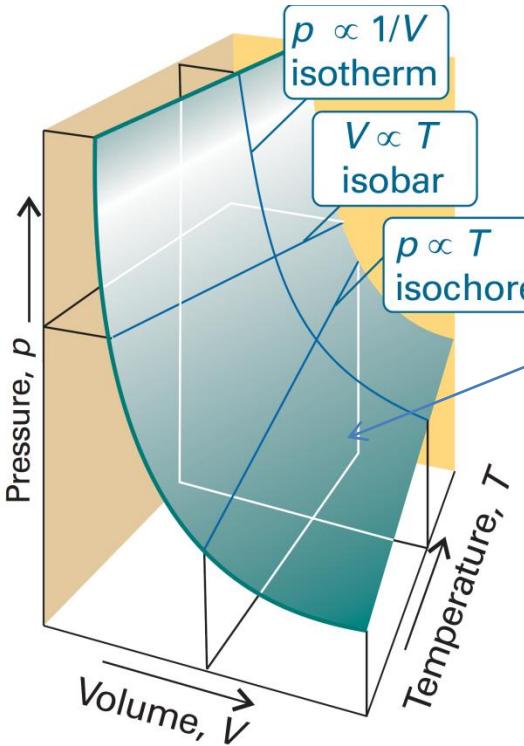
**gas constant**,  $R$  (with  $R = N_A k$ , where  $N_A$  is Avogadro's constant and  $k$  is Boltzmann's constant).

**Table 1.2** The gas constant

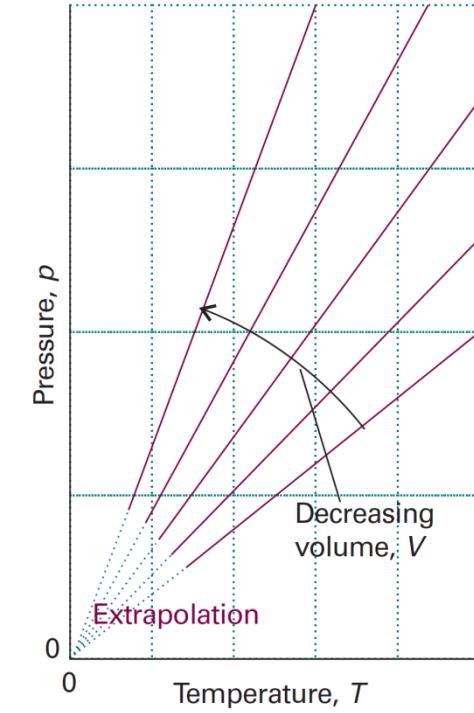
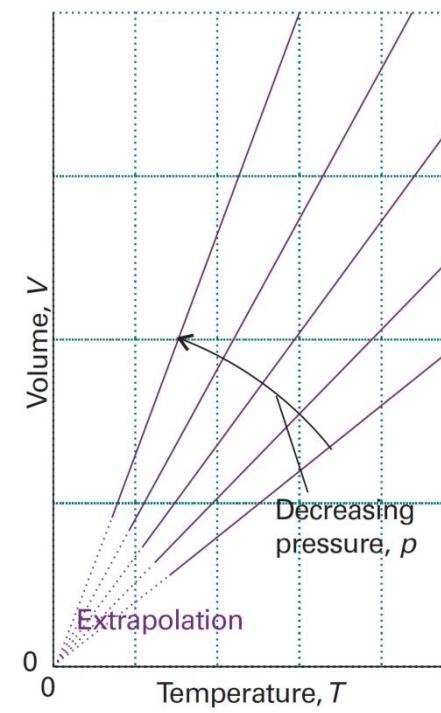
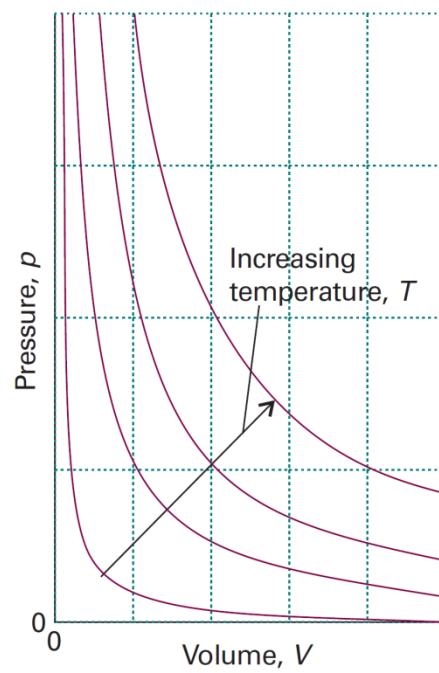
**R**

8.314 47	$\text{J K}^{-1} \text{mol}^{-1}$
$8.205\ 74 \times 10^{-2}$	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
$8.314\ 47 \times 10^{-2}$	$\text{dm}^3 \text{bar K}^{-1} \text{mol}^{-1}$
8.314 47	$\text{Pa m}^3 \text{K}^{-1} \text{mol}^{-1}$
1 62.364	$\text{dm}^3 \text{Torr K}^{-1} \text{mol}^{-1}$
1.987 21	$\text{cal K}^{-1} \text{mol}^{-1}$

# The Equation of State (Ideal Gas)



Surface of possible states



# Mixture of Gases

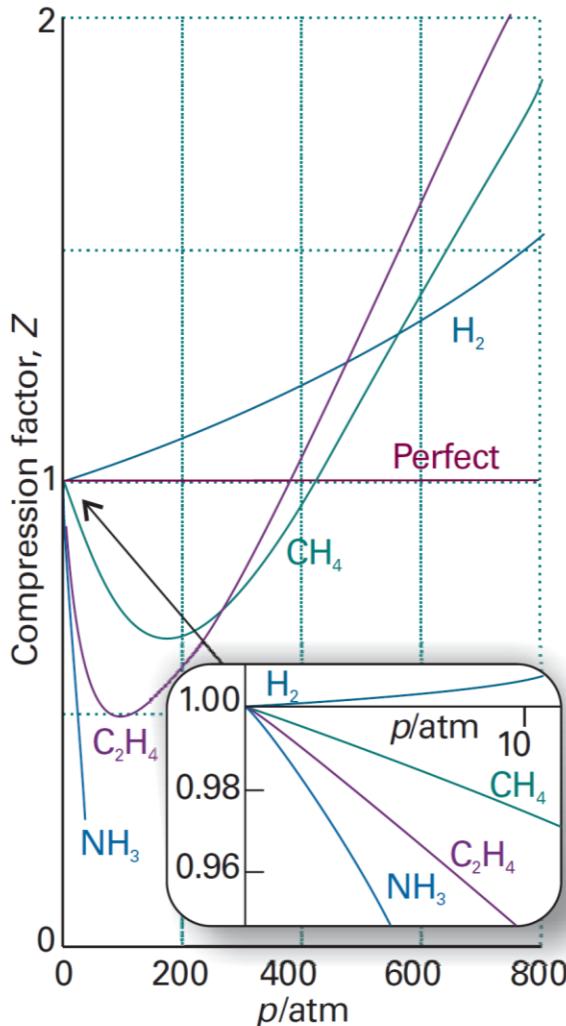
- **Partial pressure:** of a gas ( $i$ ), in a mixture of any gases

$p_i = x_i p$ ,     $x_i$ =Mole fraction of the component.

- **Dalton's law:** The pressure exerted by a mixture of (ideal) gases is the sum of the partial pressures that each one would exert if it occupied the container alone.

$$p = \sum_i p_i$$

- **vapour pressure,** the pressure of a vapour in equilibrium with its condensed phase.



**Fig. 1.14** The variation of the compression factor,  $Z$ , with pressure for several gases at  $0^\circ\text{C}$ . A perfect gas has  $Z = 1$  at all pressures. Notice that, although the curves approach 1 as  $p \rightarrow 0$ , they do so with different slopes.

## Deviation from ideality: REAL GAS

Compression/compressibility factor:

$$Z(p, T) = V_m / V_{m\text{,ideal}}$$

$$Z(p, T) = pV_m / RT$$

- At very low pressure and high temp.;  $Z \sim 1$  (Perfect gas behavior)
- At high  $p$ , molecular volume significant, repulsion dominates  
 $V_m > V_{m\text{,ideal}} \rightarrow Z > 1$
- At intermediate  $p$ , (& low temp), insignificant molecular volume; attraction dominates  
 $V_m < V_{m\text{,ideal}} \rightarrow Z < 1$

# The Equation of State for Real Gases

## Virial Equation of State

At very low pressure, real gases behave ideally. Hence, let the ideal gas law be the first term in a series in powers of a variable ( $p$  or  $1/V_m$ )

$$pV_m = RT (1 + B' p + C' p^2 \dots)$$

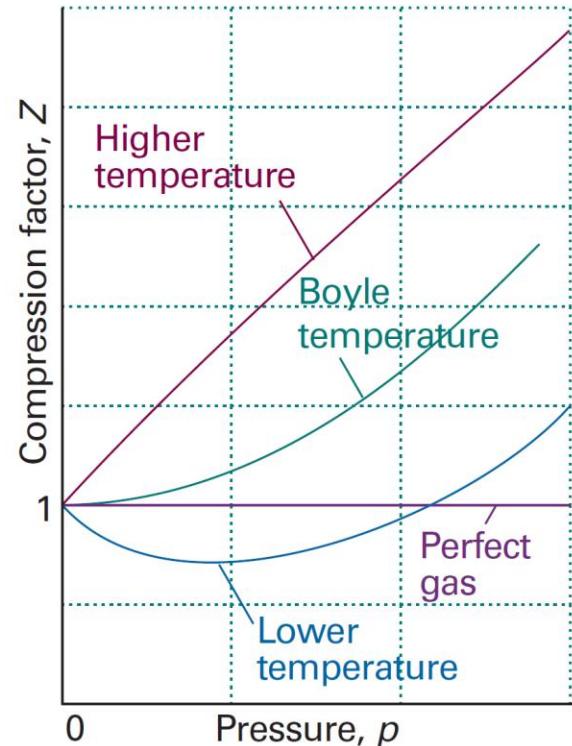
$$pV_m = RT (1 + B/V_m + C/V_m^2 \dots)$$

$B'$  and  $C'$  are 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients (at temp T)

As,  $p \rightarrow 0$ , virial equation reproduces ideal gas equation.

$$Z = (1 + B' p + C' p^2) = (1 + B/V_m + C/V_m^2)$$

The properties of real gases *do not always coincide with the perfect gas values at low pressures.*



**Fig. 1.16** The compression factor,  $Z$ , approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

# Condensation of a real gas

## Critical Constants ( $T_c$ ; $p_c$ ; $V_c$ ):

Temperature at and above which the separation of liquid and gas surface ceases to exist.

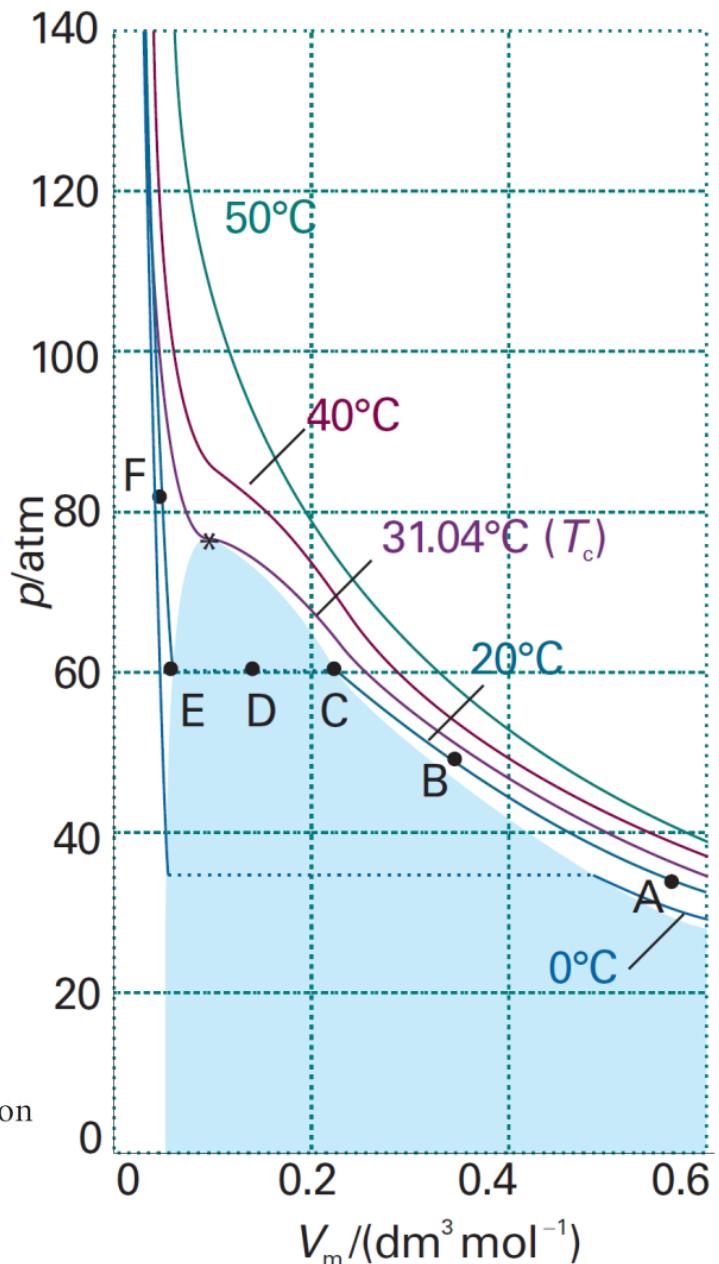
At the critical point,

$$\frac{dp}{dV_m} = 0 \text{ and } \frac{d^2 p}{dV_m^2} = 0$$

$T_c$ : Highest  $T$  at which condensation of a gas is possible.

$p_c$ : Highest  $p$  at which a liquid boils when heated.

**Fig. 1.15** Experimental isotherms of carbon dioxide at several temperatures. The ‘critical isotherm’, the isotherm at the critical temperature, is at  $31.04^\circ\text{C}$ . The critical point is marked with a star.



# The Principle of Corresponding States

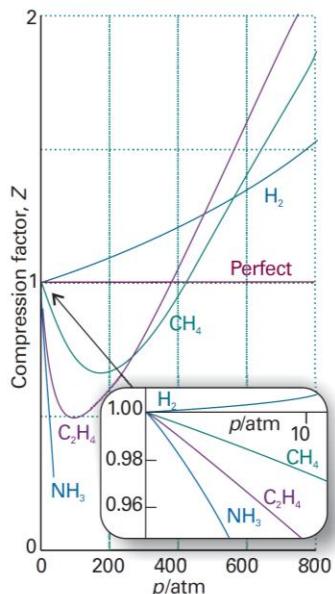
Real gases at same reduced volume and reduced temperature exert same reduced pressure and have same compressibility factor.

## Reduced Variables:

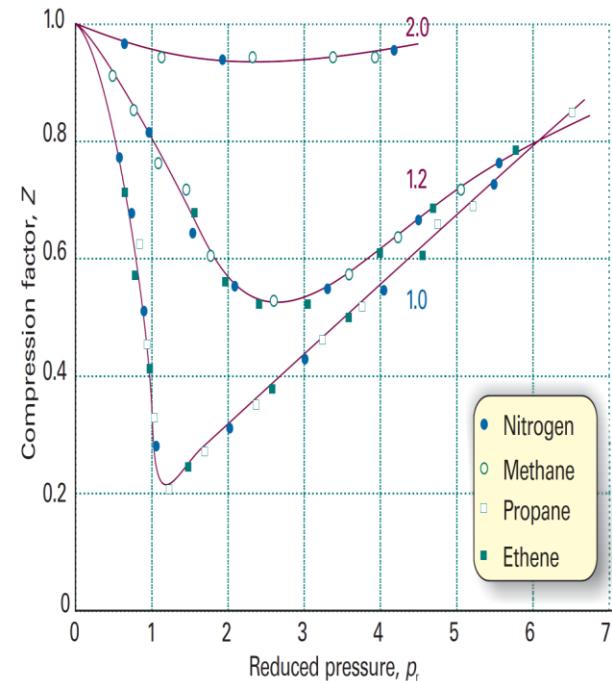
$$V_r = V_m/V_c$$

$$T_r = T/T_c$$

$$p_r = p/p_c$$

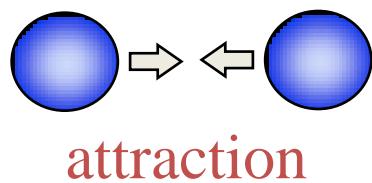
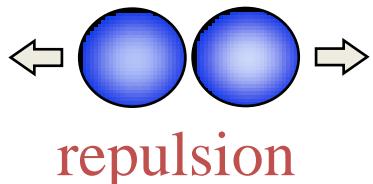


Limitations:  
Polar or non-spherical molecules.



**Fig. 1.19** The compression factors of four of the gases shown in Fig. 1.14 plotted using reduced variables. The curves are labelled with the reduced temperature  $T_r = T/T_c$ . The use of reduced variables organizes the data on to single curves.

# The van der Waals model of real gases



$$V_{eff} = V - nb$$

$$p = \frac{nRT}{V} \quad (\text{Ideal gas equation})$$

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$\left( p + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

The van der Waals equation of state for real gases

- At high temperature and large volume, vdW equation reduces to ideal gas law.
- Liquid and gases coexist when attractive and repulsive forces balance
- Critical Constants and vdW parameters:  $V_c=3b$ ,  $p_c=a/27b^2$ ,  $T_c=8a/27Rb$ ,  $Z_c=p_cV_c/RT_c=3/8$  (the critical compression factor)

$$\frac{dp}{dV_m} = 0 \text{ and } \frac{d^2p}{dV_m^2} = 0$$

# Assignment 1

1. Which of the following are intensive property?  
Concentration , Number of moles, Viscosity, Momentum, Melting point
2. The relative humidity of air is 50% at a temperature of  $20^{\circ}\text{C}$ . If the atmospheric pressure is 1 bar, what is the mole fraction of water in the air? The vapor pressure of water at  $20^{\circ}\text{C}$  is 2330 Pa. Assume the gas mixture behaves as an ideal gas.
3. Derive the expressions for the molar volume, temperature, and pressure at the critical point in terms of the van der Waals constants.
4. What is the molar volume of n-hexane at 660 K and 91 bar according to (a) the ideal gas law and (b) the van der Waals equation? For n-hexane,  $T_c = 507.7\text{ K}$  and  $p_c = 30.3\text{ bar}$ .
5. Show that for a van der Waals gas, the Boyle's temperature  $T_B = a/bR$ . (Use  $1/(1-x) = 1 + x + x^2 + \dots$  for  $x \ll 1$ ).

LECTURE

# 4

CY11001  
Spring 2016



Department of Chemistry  
Indian Institute of Technology  
Kharagpur

# The First Law of Thermodynamics:

- There exists an extensive state function  $E$  such that for any closed system,  $\Delta E = q + w$
- In absence of any external field acting on the system and the system at rest,  $\Delta E = \Delta U$  ( $K=V=0$ )

$$\Delta U = q + w$$

$$dU = dq + dw = \delta q + \delta w = dq + dw$$

- $w$ , work done on the system by the surroundings
- $q$ , heat absorbed by the system from the surroundings
- The conventions for the signs of  $q$  and  $w$  are set from the system's perspective

- For isolated system,  $dU = 0$
- For adiabatic process,  $q=0$ ;  $dU = w$
- For cyclic process,  $\oint dU = 0$ ;  $q = -w$

# Energy

$$E = K + V + U$$

- $K$  and  $V$  are the macroscopic (not molecular) kinetic and potential energies of the body, together represent the mechanical energy
- $U$  is the internal energy of the body (due to molecular motions and intermolecular interactions)

**Internal Energy,  $U$ , is the total energy within a system. ( $E=U$ , as  $K=V=0$ )**

- Extensive property
- $U_m = U/n$  (molar internal energy)
- It is a state function, independent of path
- $dU$  is a perfect (exact) differential
- For cyclic process  $\oint dU = 0$

## Molecular Interpretation of Internal Energy:

$$U_m = U_{tr,m} + U_{rot,m} + U_{vib,m} + U_{el,m} + U_{\text{intermol},m}$$

$$U_{tr,m} = f(T) = \frac{3}{2} RT$$

$$U_{rot,m} = 0 \text{ (monoatomic)}$$

$$U_{rot,m} = RT \text{ (linear molecules)}$$

$$U_{rot,m} = \frac{3}{2} RT \text{ (nonlinear molecules)}$$

$$U_{\text{intermol},m} = f(T, p \text{ (or } V))$$

= 0 (for ideal gas)

$U_{el,m}$  = constant if temp is not extremely high and no chemical reaction

$$U_{vib,m} = 0 \text{ for monoatomic}$$

$$U_{vib,m} = f(T)$$

Small in magnitude and nearly constant for diatomic and light molecules at low to moderate temperature.

### For Ideal Gas

$$U_m = \frac{3}{2} RT + \text{const. (monoatomic)}$$

$$U_m = \frac{3}{2} RT + \frac{3}{2} RT \text{ (or } RT) + U_{vib,m}(T) + \text{const.}$$

- Internal energy of ideal gas increases linearly with  $T$
- Internal energy of ideal gas is independent of  $V$

# Heat

- Heat is that which is transferred between a system and surrounding by virtue of a *temperature difference only*.
- Heat is not a state function (path dependent).
- Heat can be transferred reversibly or irreversibly. A reversible transfer of heat requires the *temperature difference* between two bodies be *infinitesimal*.

# Work:

- **expansion work**, work of expansion (or compression)
- **non-expansion / additional work**: any other work

## Expansion Work:

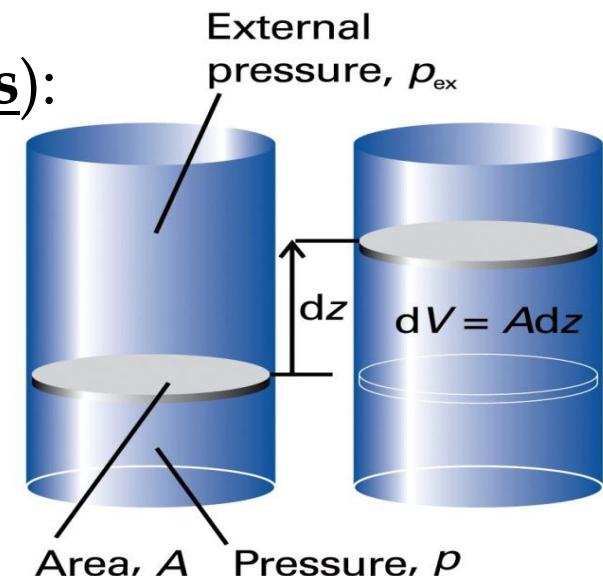
General expression of work (reversible process):

$p_{\text{ex}}$  = external pressure

$A$  = piston area

$dz$  = displacement

$dV = A dz$  = volume change for the gas



Work is required to move an object a distance  $dz$  against an opposing force  $F$ . Total work done,

$$w = - \int F dz = - \int (p_{\text{ex}} A) dz = - \int_{V_i}^{V_f} p_{\text{ex}} dV = - \int_{V_i}^{V_f} pdV$$

Figure 2-6  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

Only for reversible process

$dV$  = change in the volume of the system

# Expansion against *constant* pressure

Chemical example: expansion of a gas formed in a chemical reaction in a container that can expand

$$w = - \int_{V_i}^{V_f} p_{ex} dV = -p_{ex}(V_f - V_i) = -p_{ex}\Delta V$$

Expansion against constant final pressure:

$$w = -p_f(V_f - V_i)$$

Free expansion:

Expansion against zero opposing force

$$w = 0$$

Expansion, i.e.,  $V_f > V_i$ ,  $w < 0$  (work done by the system on surrounding)

Compression, i.e.,  $V_f < V_i$ ,  $w > 0$  (work done on the system by surrounding)

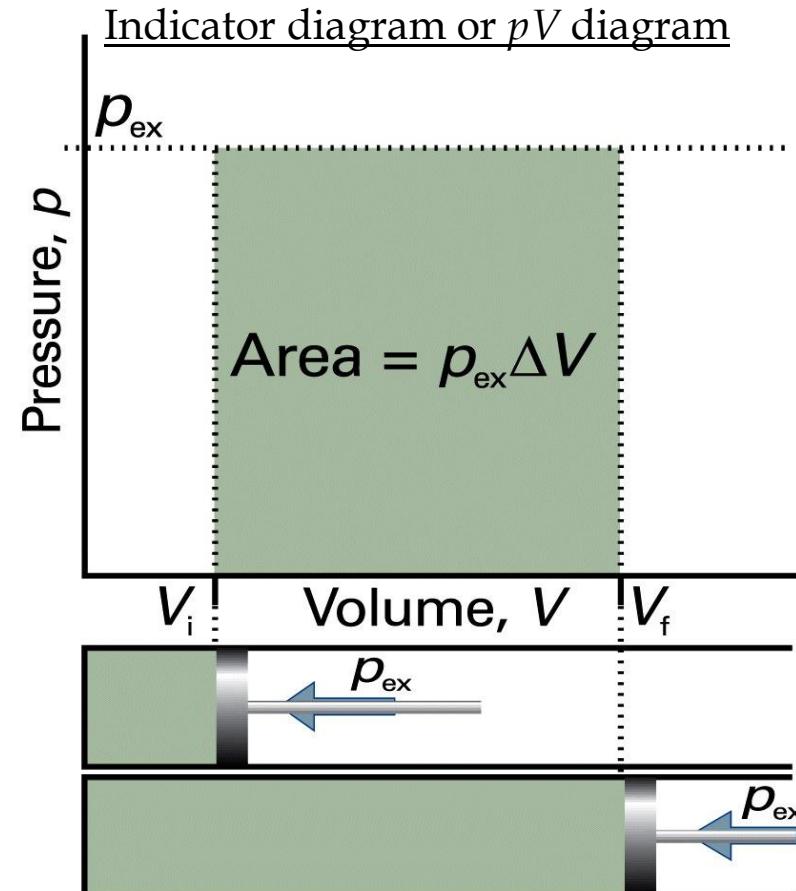


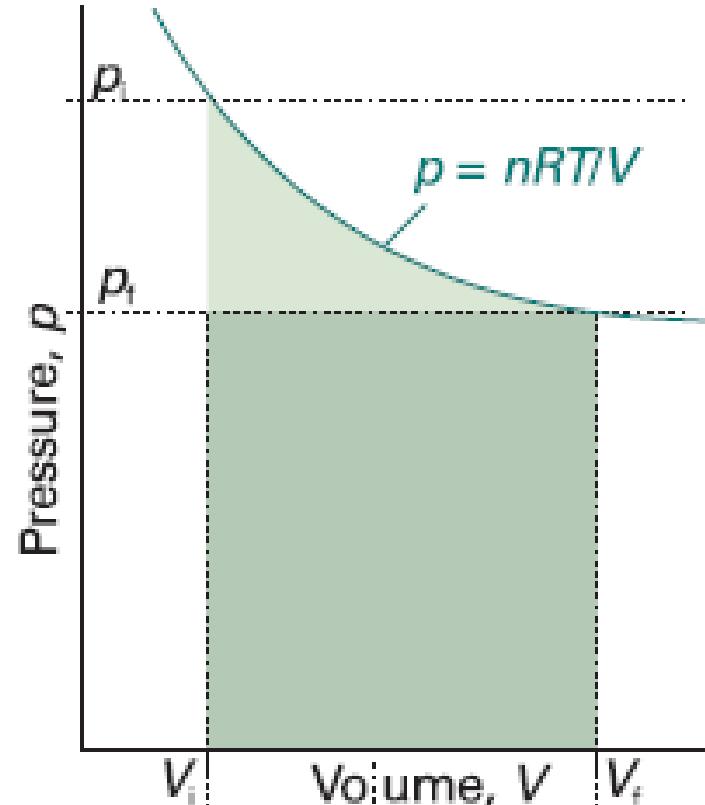
Figure 2-7  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

# Isothermal expansion (ideal gas):

Reversible

$$w = - \int_{V_i}^{V_f} pdV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

- At higher  $T$ , work done is more for same expansion of volume.



Work against constant final pressure

Irreversible

$$w = -p_f(V_f - V_i) = -p_f \Delta V$$

$$|w_{\text{rev}}| > |w_{\text{irrev}}|$$

Maximum work is obtained when expansion is reversible.

# Adiabatic Reversible Process for ideal gas, ( $C_V$ independent of Temp)

$$dU = dw + dq = dw$$

For ideal gas,  $C_V dT = -pdV$

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V}$$

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

$$\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^{nR} = \left(\frac{V_1}{V_2}\right)^{C_p - C_V}$$

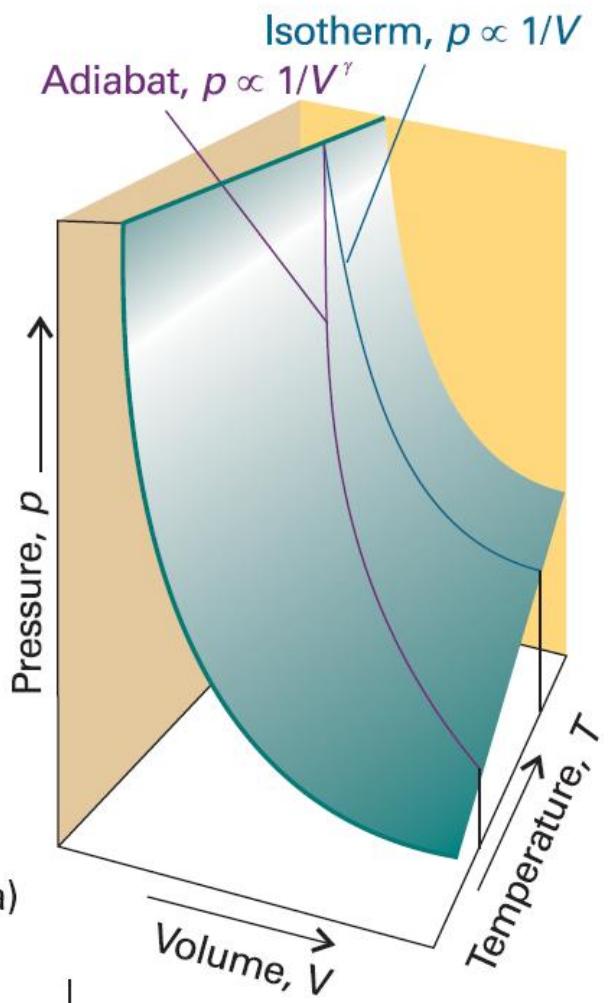
$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad \text{where} \quad \gamma = \frac{C_{p,m}}{C_{V,m}}$$

$$TV^{\gamma-1} = \text{constant}$$

$$PV^\gamma = \text{constant}$$

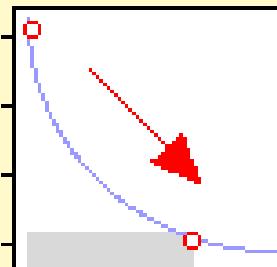
$$VT^c = \text{constant}$$

$$T^\gamma P^{1-\gamma} = \text{constant}$$



2.24L, 10 atm  $\longleftrightarrow$  22.4 L, 1 atm

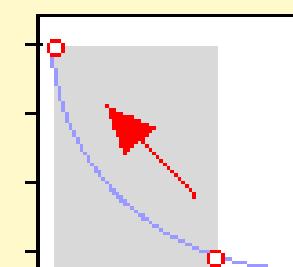
### Expansion



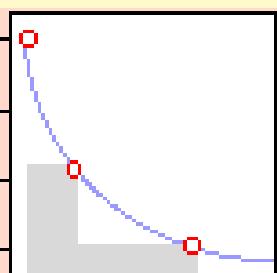
1 stage

-20 L-atm

### Compression

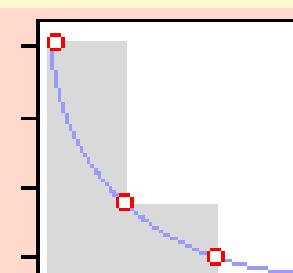


+202 L-atm

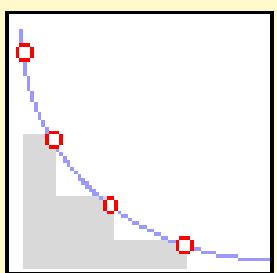


2 stages

-28 L-atm

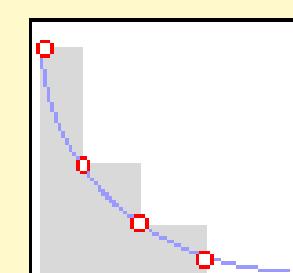


+119 L-atm



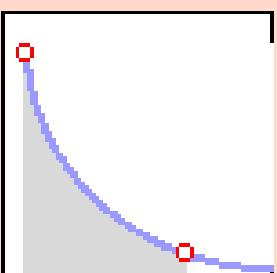
3 stages

-33 L-atm



+85 L-atm

P

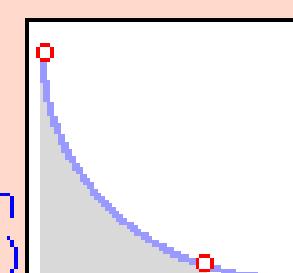


infinite stages  
(reversible)

-52 L-atm

(maximum work)

P



+52 L-atm

(minimum work)

V

$$|w_{\text{rev}}(\text{compression})| = |w_{\text{rev}}(\text{expansion})|$$

V

**Work is path dependent:**

**Ideal gas, closed system, reversible process**

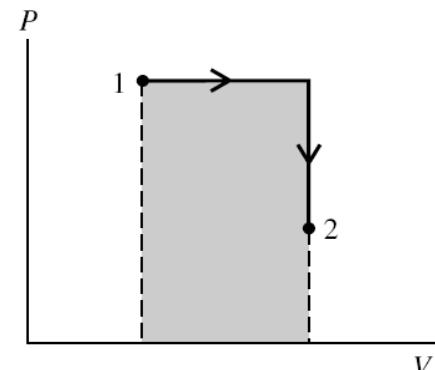
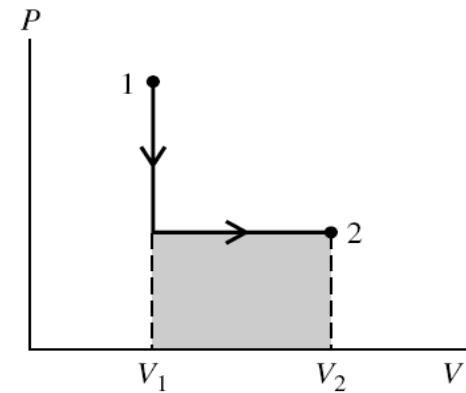
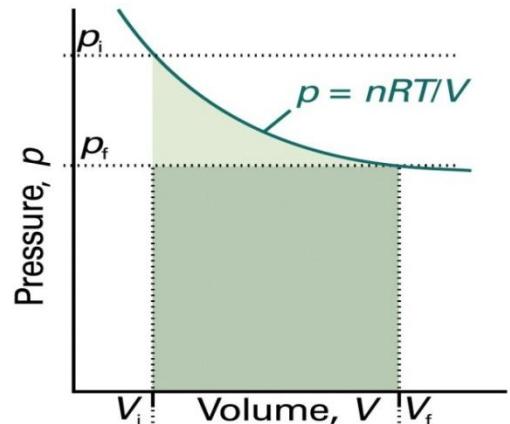
Calculate  $w_f$  and  $w_b$

- 10 Pa, 1 m<sup>3</sup>,  $T \xrightarrow{\text{isothermal}} 1 \text{ Pa}, 10 \text{ m}^3, T$

- 10 Pa, 1 m<sup>3</sup>,  $T \xrightarrow{\text{isochoric}} 1 \text{ Pa}, 1 \text{ m}^3, T_2 \xrightarrow{\text{isobaric}} 1 \text{ Pa}, 10 \text{ m}^3, T$

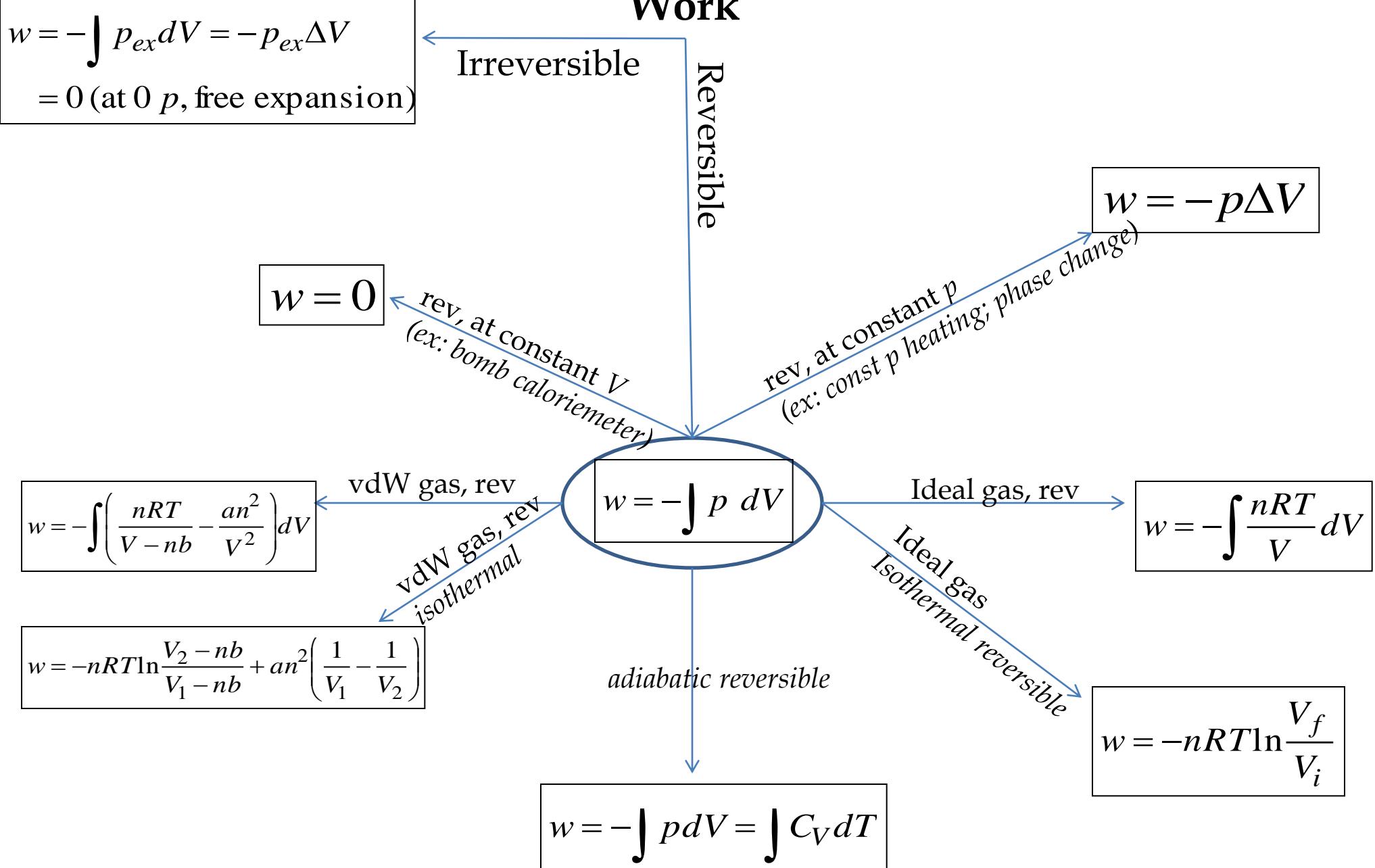
- 10 Pa, 1 m<sup>3</sup>,  $T \xrightarrow{\text{isobaric}} 10 \text{ Pa}, 10 \text{ m}^3, T_3 \xrightarrow{\text{isochoric}} 1 \text{ Pa}, 10 \text{ m}^3, T$

$w_{\text{rev}}$  depends on the path used to go from 1 to 2, and  $w_{\text{rev}}$  can have *any* positive or negative value for a given change of state



Homework

# Work



LECTURES

5,6

CY11001  
Spring 2016



Department of Chemistry  
Indian Institute of Technology  
Kharagpur

# Heat Transactions and Heat Capacity:

In general change in the internal energy of a closed system is given by

$$dU = dq + dw_{\text{exp}} + dw_{\text{add}}$$

- For  $dV = 0$ ;  $dw_{\text{exp}} = 0$  and if  $dw_{\text{add}} = 0$ , then

$$dU = dq \text{ (constant volume, no additional work)} = dq_V$$

For a measurable change  $\Delta U = q_V$

- **heat capacity**,  $C$ , the ratio of the heat supplied to the temperature rise it causes.  $C = dq/dT$ ;  $C = q/\Delta T$

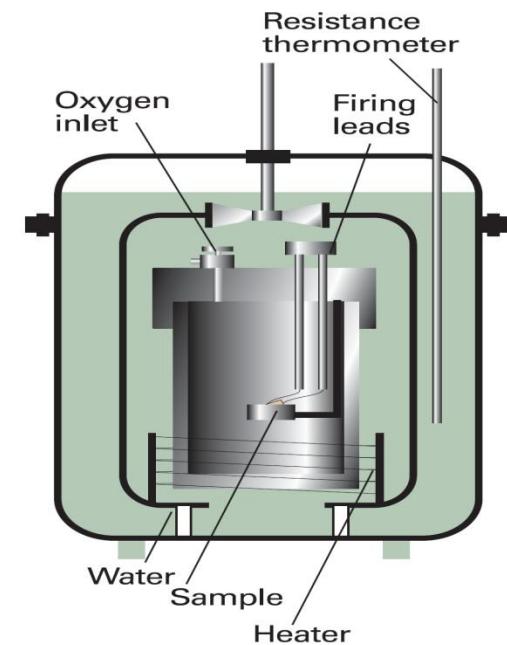
- **heat capacity at constant volume**,  $C_V = (\partial U / \partial T)_V$

- **molar heat capacity**, the heat capacity divided by the amount of substance,  $C_m = C/n$ .

- **specific heat capacity**, the heat capacity divided by the mass,  $C_s = C/m$

The measurement of internal energy change

- *Adiabatic bomb calorimeter*



# Heat Capacity at Constant Pressure:

$$dU = dq + dw_{\text{exp}} + dw_{\text{add}}$$

For  $dV \neq 0$ ;  $dw_{\text{exp}} \neq 0$       Even if  $dw_{\text{add}} = 0$ ,       $dU \neq dq$

Define  $H = U + pV$

$$dH = dU + pdV + Vdp = dU - w \text{ (at const } p) = dq_p$$

**heat capacity at constant pressure**,  $C_p = (\partial H / \partial T)_p$

Empirical expression,  $C_{p,m} = a + bT + c/T^2$

For ideal gas; **relation between  $\Delta U$  and  $\Delta H$** ,

$$\Delta H = \Delta U + \Delta n_g RT.$$

Show that for a perfect gas,  $C_p - C_V = nR$

(home work)

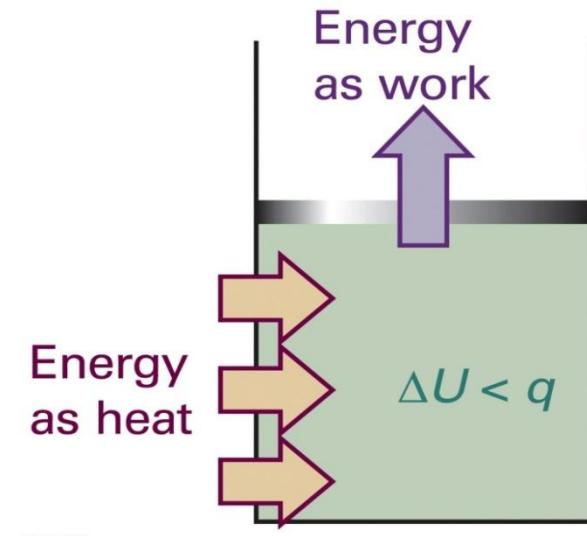


Figure 2-12  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

The measurement of enthalpic change

- *isobaric calorimeter*
- *differential scanning calorimeter*
- *adiabatic flame calorimeter*

- For most cases,  $C_p > C_V$

# Partial differentiation:

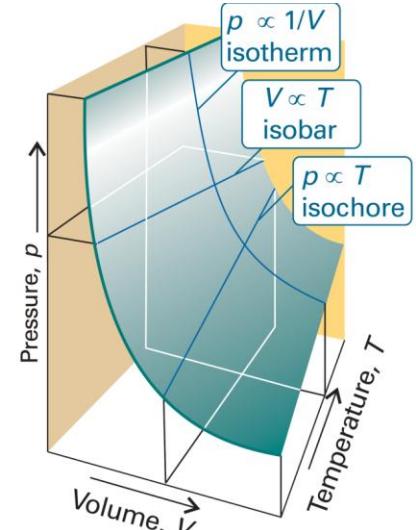
Consider a function of two variables  $\rightarrow z = f(x, y)$

A **partial derivative** of one of the variables: the rate of change of the function *wrt* that variable with all other variables kept fixed.

**Example:** For  $z = f(x, y)$ ,

$$\left( \frac{\partial z}{\partial x} \right)_y = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}$$

$$\left( \frac{\partial z}{\partial y} \right)_x = \lim_{\Delta y \rightarrow 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}$$



Total differential of  $z(x, y)$ :

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

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

Clairaut's theorem

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

Cyclic Rule

# Partial derivatives of $p$ , $V_m$ , and $T$ with respect to each other:

$$V_m = f(p, T); \quad p = f(V_m, T); \quad T = f(p, V_m)$$

$$dT = \left( \frac{\partial T}{\partial p} \right)_{V_m} dp + \left( \frac{\partial T}{\partial V_m} \right)_p dV_m$$

$$dp = \left( \frac{\partial p}{\partial T} \right)_{V_m} dT + \left( \frac{\partial p}{\partial V_m} \right)_T dV_m$$

$$dV_m = \left( \frac{\partial V_m}{\partial T} \right)_p dT + \left( \frac{\partial V_m}{\partial p} \right)_T dp$$

$$\left( \frac{\partial p}{\partial V_m} \right)_T \left( \frac{\partial V_m}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_{V_m} = -1$$

$$\frac{\partial^2 T}{\partial p \partial V_m} = \frac{\partial^2 T}{\partial V_m \partial p} \left( = \frac{1}{R} \text{ for ideal gas} \right)$$

$$\alpha(T, p) = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_p$$

$$\kappa(T, p) = - \frac{1}{V_m} \left( \frac{\partial V_m}{\partial p} \right)_T$$

Expansion coefficient

Isothermal compressibility

$$\left( \frac{\partial p}{\partial T} \right)_{V_m} = - \frac{\left( \frac{\partial V_m}{\partial T} \right)_p}{\left( \frac{\partial V_m}{\partial p} \right)_T} = \frac{\alpha(T, p)}{\kappa(T, p)}$$

- How fast the (fraction of) volume increases with temperature and decreases with pressure
- For ideal gas,  $\alpha = 1/T$  and  $\kappa = 1/p$

# Variation of internal energy with $T$ and $V$

$$U = f(V, T)$$

$$U = f(p, T)$$

$$U = f(p, V)$$

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

$$\pi_T = \left( \frac{\partial U}{\partial V} \right)_T$$

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

Internal pressure

Heat capacity

$$dU = \pi_T dV + C_V dT$$

Constant  $V$  process

$$dU_V = C_V dT$$

Constant  $T$  process

$$dU_T = \pi_T dV$$

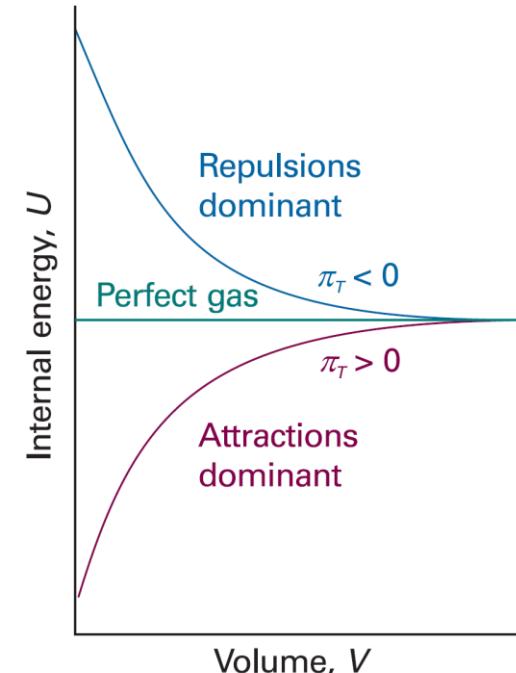
Special case: Ideal gas

For ideal gas

$$\pi_T = \left( \frac{\partial U}{\partial V} \right)_T = 0$$

$$\left( \frac{\partial U}{\partial p} \right)_T = 0$$

$$dU = C_V dT \quad \text{for ideal gas}$$



**Fig. 2.25** For a perfect gas, the internal energy is independent of the volume (at constant temperature). If attractions are dominant in a real gas, the internal energy increases with volume because the molecules become farther apart on average. If repulsions are dominant, the internal energy decreases as the gas expands.

# Variation of enthalpy with $T$ and $p$

$$H = f(p, T)$$

$$dH = \left( \frac{\partial H}{\partial p} \right)_T dp + \left( \frac{\partial H}{\partial T} \right)_p dT$$

$$= \left( \frac{\partial H}{\partial p} \right)_T dp + C_p dT$$

Constant  $p$  process

$$dH_p = C_p dT$$

Constant  $T$  process

$$dH_T = \left( \frac{\partial H}{\partial p} \right)_T dp$$

Special case: Ideal gas

For ideal gas

$$\left( \frac{\partial H}{\partial p} \right)_T = 0$$

$$\left( \frac{\partial H}{\partial V} \right)_T = 0$$

$$dH = C_p dT \quad \text{for ideal gas}$$

# Joule's Experiment (1843)

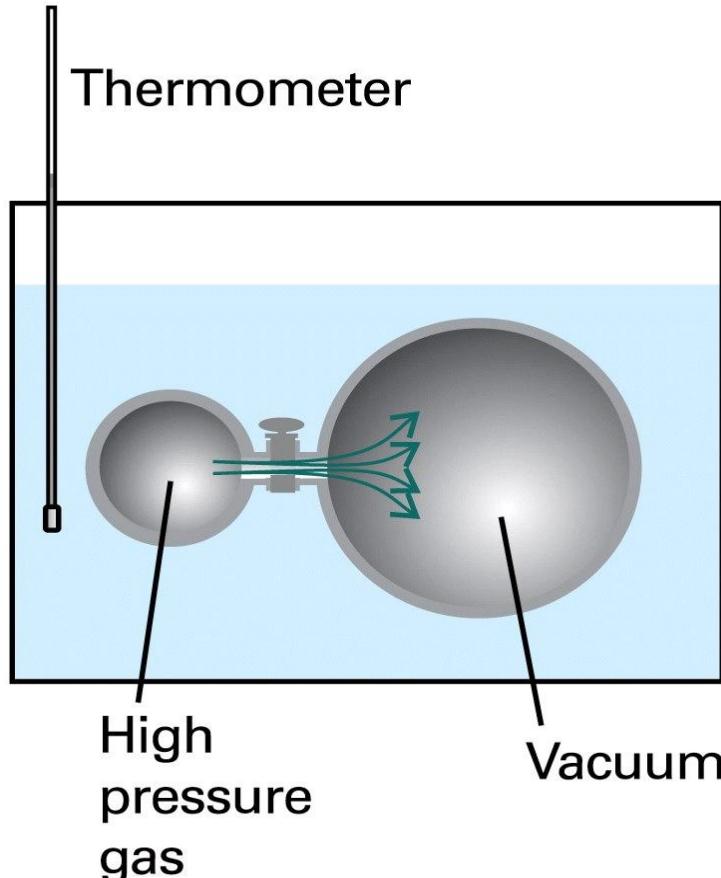


Figure 2-26  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

Purpose is to determine  $\pi_T$ ,

$$\left( \frac{\partial U}{\partial V} \right)_T$$

whether or not gases cool on expansion, and if so how much.

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

- In this experiment, observed  $dT = 0$
- Heat change,  $q$ , for the system (gas) = 0
- no work done for free expansion,  $w = 0$

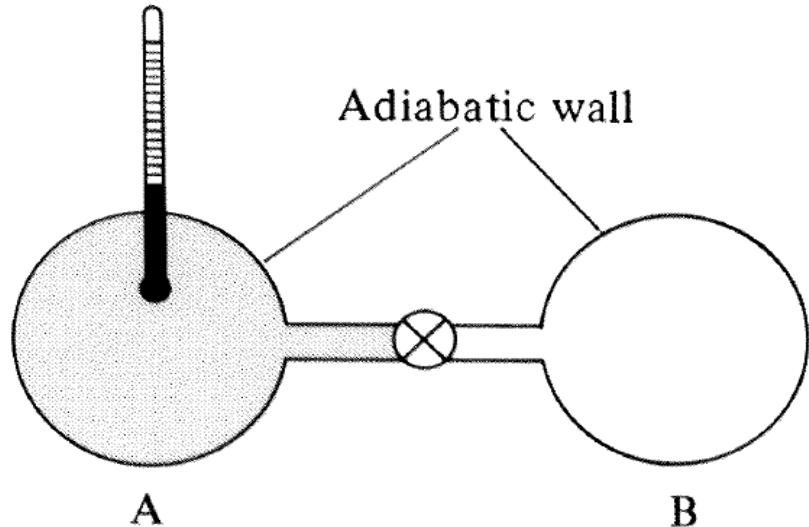
hence  $dU = 0$ , and,

$$\text{as } dV \neq 0, \left( \frac{\partial U}{\partial V} \right)_T = 0$$

Actually this is only valid for ideal gas

In reality,  $dT \neq 0$ , Joule's apparatus was not sensitive to find out the small value of  $dT$

# Keyes-Sears modification (1924)



$$dU = \pi_T dV + C_V dT$$

$$dU = -C_V \mu_J dV + C_V dT$$

- Heat change,  $q$ , for the system (gas) = 0
- no work done for free expansion,  $w = 0$   
hence  $dU = 0$ ,

Constant-energy process,  $U$  constant

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

$$\approx \frac{\Delta T}{\Delta V}$$

Joule Coefficient,  
 $\mu_J$

$$\left( \frac{\partial T}{\partial U} \right)_V \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_U = -1$$

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

# Joule-Thompson Experiment:

$$\left( \frac{\partial H}{\partial p} \right)_T$$

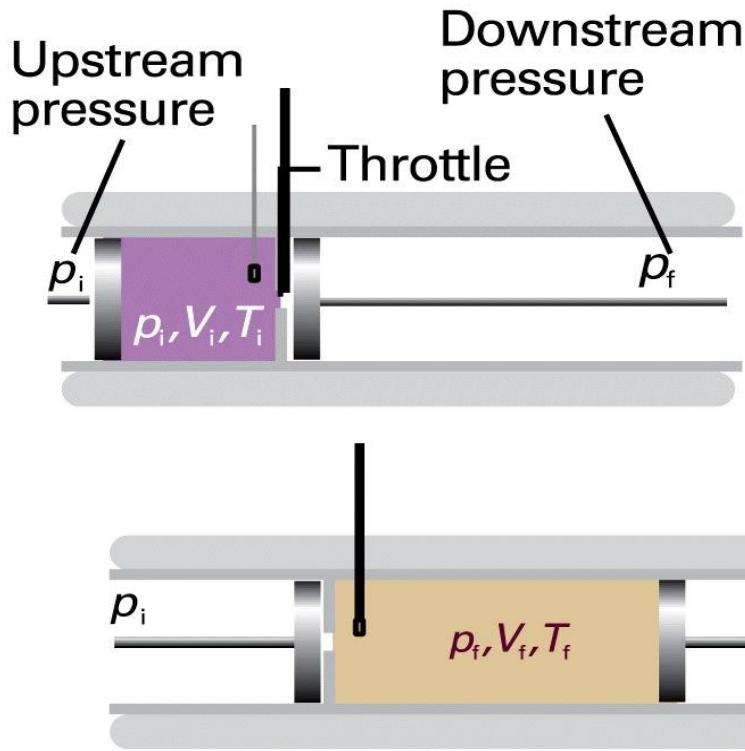


Figure 2-28  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

## Joule-Thompson Coefficient,

$$\mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H \approx \left( \frac{\Delta T}{\Delta p} \right)$$

Ratio of change in  $T$  to the  $p$  when a gas expands under constant  $H$ .

Purpose is to determine

In this experiment

$$q = 0 \quad w = -p_f(V_f - 0) - p_i(0 - V_i) = p_iV_i - p_fV_f$$

$$\Delta U = U_f - U_i = q + w = -p_fV_f + p_iV_i$$

$$U_f + p_fV_f = U_i + p_iV_i \quad \text{Isenthalpic process}$$

$$H_f = H_i, \Delta H = 0 \quad (\text{Constant } H)$$

$$H = f(p, T); \quad dH = \left( \frac{\partial H}{\partial p} \right)_T dp + \left( \frac{\partial H}{\partial T} \right)_p dT$$

$$\left( \frac{\partial H}{\partial p} \right)_T = - \left( \frac{\partial H}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_H = -C_p \times \mu_{JT}$$

$$dH = -\mu_{JT} C_p dp + C_p dT$$

# Inversion Temperature and Cooling of gases with JT expansion:

$$\mu_J = \left( \frac{\partial T}{\partial V} \right)_U \quad \mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H \quad \mu_T = \left( \frac{\partial H}{\partial p} \right)_T = -C_p \mu_{JT}$$

Isothermal Joule-Thomson  
Coefficient

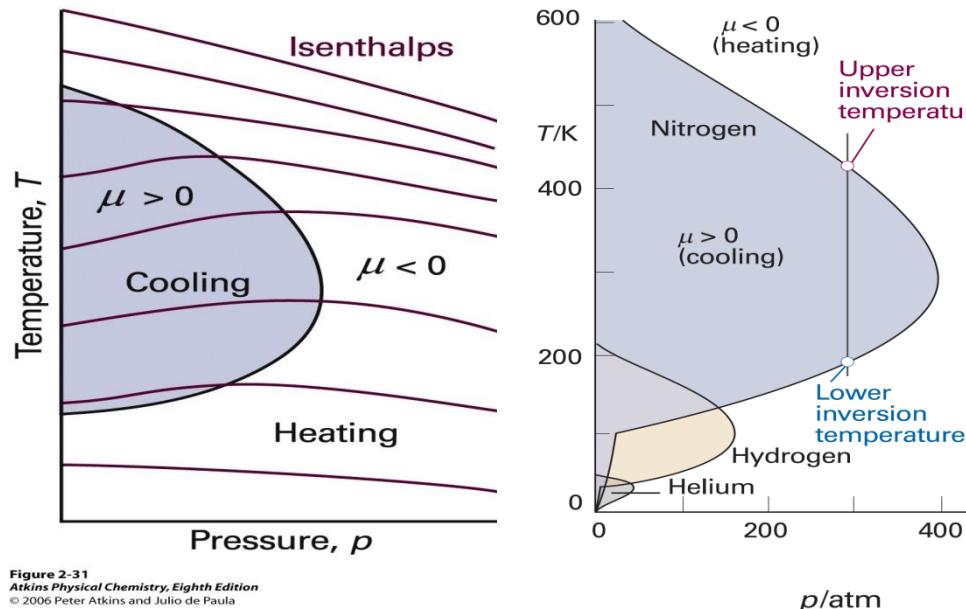
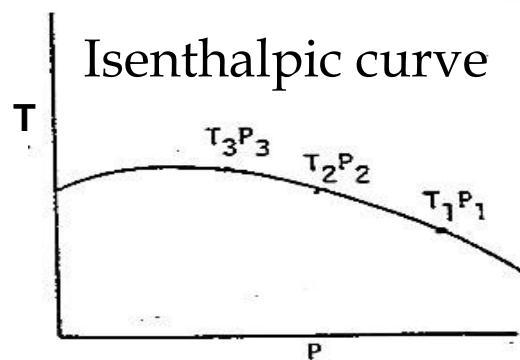


Figure 2-31  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

At room temperature and 1 atm, N<sub>2</sub> and O<sub>2</sub> will cool upon expansion while He and Ne will warm upon expansion.

## Sign of $\mu_{JT}$

For ideal gas  $\mu_{JT} = 0$

For real gas  $\mu_{JT} \neq 0$

Some inversion  
temperatures are  
(at 1 atm):

He	40 K
Ne	231 K
N <sub>2</sub>	621 K
O <sub>2</sub>	764 K

# Calculation of thermodynamic functions for various processes

	reversible phase change at const. $T, p$	const $p$ heating, no phase change	const $V$ heating, no phase change
$w$	$-\int p \, dV = -p\Delta V$	$-\int p \, dV = -p\Delta V$	0
$q$	latent heat	$q_p = \Delta H$	$q_V = \Delta U$
$\Delta U$	$q + w$	$q + w$	$= \int C_V(T) dT$
$\Delta H$	$q (=q_p)$	$= \int C_p(T) dT$	$\Delta U + V\Delta p$

# Calculation of thermodynamic function for various processes for ideal gas

state 1 - state 2, no phase change				rev, isothermal	rev, adiabatic
w	rev $- \int p dV$	rev, const ext. $p$ $- p_{ex} \Delta V$	irrev, const final $p$ $- p_f \Delta V$	$- nRT \ln \frac{V_2}{V_1}$	$= \int C_V(T) dT$
q	$\Delta U - w$			$nRT \ln \frac{V_2}{V_1}$	0
$\Delta U$	$= \int C_V(T) dT$			0	$= \int C_V(T) dT$
$\Delta H$	$= \int C_p(T) dT$			0	$= \int C_p(T) dT$

Adiabatic expansion of a perfect gas into vacuum

$$q = 0 \quad \Delta U = 0 \quad w = 0 \quad \Delta H = 0$$

# Assignment 2

1. Calculate  $(\partial P/\partial V)_T$  and  $(\partial P/\partial T)_V$  for a van der Waals gas with  $a = 0$ .
2. (a) The surface tension of water at 25 °C is 0.072 N/m. How much work is required to form a surface of 100 m by 100 m? (b) A mole of electrons is transported across a potential difference of 1V from the positive electrode to the negative electrode. How much work is required?
3. Express  $(\partial C_V/\partial V)_T$  as a second derivative of  $U$  and find its relation to  $(\partial U/\partial V)_T$  and show that  $(\partial C_V/\partial V)_T = 0$  for ideal gas.
4. Show that (a)  $(\partial H/\partial p)_T = -\mu C_p$ ; (b)  $(\partial U/\partial T)_p = \alpha \pi_T V + C_V$ ; (c)  $C_p - C_V = \alpha^2 T V / \kappa_T$
5. Show that the work done in a reversible adiabatic expansion of an ideal gas is given by  
 $w = (p_2 V_2 - p_1 V_1) / (\gamma - 1)$
6. 2 mol of an ideal gas undergoes isothermal expansion along three different paths. (1) reversible expansion from  $p_i = 25$  bar and  $V_i = 4.5$  L to  $p_f = 4.5$  bar, (2) a single step irreversible expansion against a constant external pressure of 4.5 bar, and (3) a two-step irreversible expansion consisting initially of an expansion against a constant external pressure of 11 bar until  $P = P_{\text{external}}$ , followed by an expansion against a constant external pressure of 4.5 bar until  $P = P_{\text{external}}$ . Calculate the work for each of these processes.

LECTURE

# 7

CY11001  
Spring 2016



Department of Chemistry  
Indian Institute of Technology  
Kharagpur

## Limitations of the First Law of Thermodynamics

The first law assures us that the total energy of system plus surroundings remains constant during the reaction. Energy can be transferred/transformed, keeping the total energy fixed.

$$dU_{\text{universe}} = dU_{\text{system}} + dU_{\text{surrounding}} = 0$$

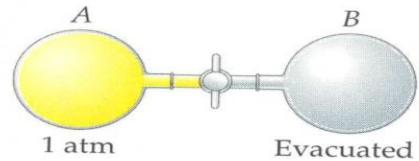
Does not say:

Whether energy will get transferred / transformed?

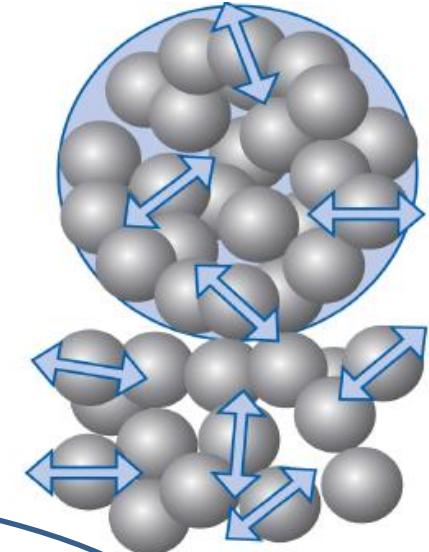
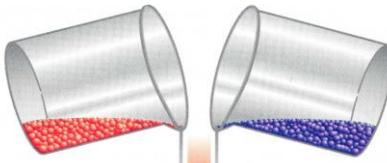
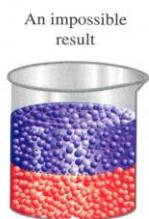
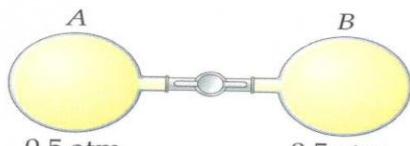
If yes, in which direction?

If yes, how long?

If yes, how fast?



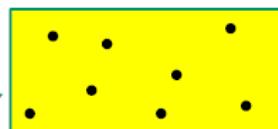
Spontaneous ↓  
↑ Not spontaneous



In all the cases first law allows either outcomes, but we observe only one outcome **spontaneously**.

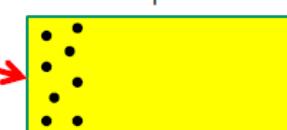


Gas expands to fill volume



Gas remains in partitioned section

Remove the partition



The two configurations have the same energy.  
We gain no stability by choosing 1 or 2.

Heat flows



$T_{hot}$   $T_{cold}$

$T_{hot}$   $T_{cold}$

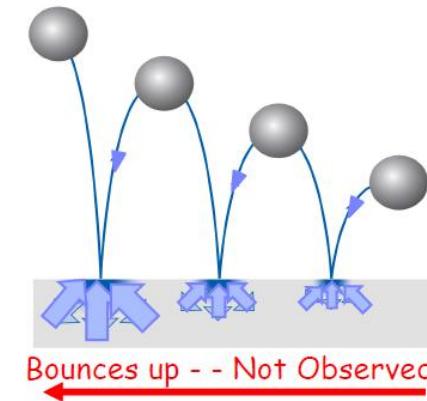
$T_{hot}$   $T_{cold}$

Never observed

heat

heat

Always observed



## **Spontaneity:**

A spontaneous process occurs naturally and needs no external source of work. A non-spontaneous process, although allowed by first law of TD, requires an external source of work to drive it.

**Who drives, a spontaneous process?**

# Entropy

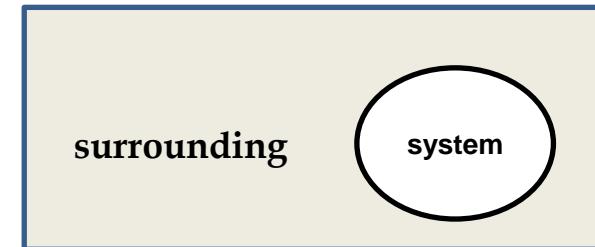
- The thermodynamic property of a system that is related to its degree of randomness or disorder is called **entropy (S)**.
- The **entropy S** and the **entropy change  $\Delta S = S_2 - S_1$**  are **state functions**.
- The **entropy S** has a unique value, once the pressure **p**, the temperature **T** and the composition **n** of the system are specified,  $S=S(p,T,n)$ .
- The **entropy is an extensive property**, i.e., increases with the amount of matter in the system.  $S_m = S/n$  (molar entropy).

# Thermodynamic definition of entropy

$dS_{\text{syst}}$  = Change in entropy that occurs during a chemical or physical process

=  $dq_{\text{rev}} / T$  ( $q_{\text{rev}}$  is the heat supplied reversibly)

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev}}}{T}$$



For surroundings,

$$dS_{\text{surr}} = - dq / T_{\text{surr}}$$

$$\Delta S_{\text{surr}} = \frac{-q}{T_{\text{surr}}}$$

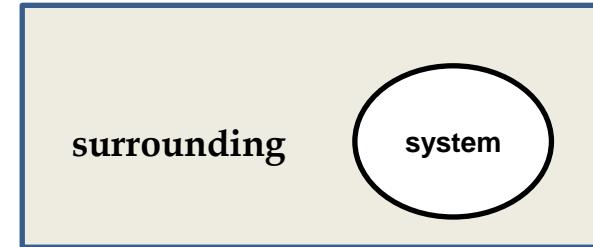
Large change in entropy occurs when heat is dissipated to surrounding at low temperature.

# How do you calculate entropy change?

For surrounding

$$dS_{surr} = - dq / T_{surr}$$

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



Calculate the actual  $q$  for the process from state 1 to state 2 and apply the above formula

For system

- Find out state 1 and state 2
- Construct reversible pathway(s) from state 1 and state 2
- Apply the formula

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

- Calculate the entropy change in the surroundings when 1.0 mole of  $\text{H}_2\text{O(l)}$  is formed from its elements under standard conditions at  $25^\circ \text{C}$  (298.15 K).  
 $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{H}_2\text{O(l)}$   $\Delta_f H = -286 \text{ kJ/mol}$ .

## Calculation of Entropy Changes (A few special cases)

1. Cyclic Process  $\Delta S_{\text{sys}} = 0$  ( $S$  is a state function)

2. Reversible adiabatic process  $\Delta S_{\text{sys}} = 0$  ( $dq_{\text{rev}} = 0$ )

3. Reversible phase-change at constant  $p$  and  $T$

$$\Delta S_{\text{sys}} = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T}$$

4. Constant  $p$  heating (reversibly) with no phase change:

$$dq_{\text{rev}} = dq_p = C_p dT$$

$$\Delta S_{\text{sys}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right)$$

5. Reversible isothermal process:

$$\Delta S_{\text{sys}} = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

6. For ideal gas:

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{dU - w_{\text{rev}}}{T} = \frac{C_V dT + p dV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V}$$

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

$$\Delta S = C_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\boxed{\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev}}}{T}}$$

# Calculation of Entropy at any temperature

Heating at constant pressure/Volume

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

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

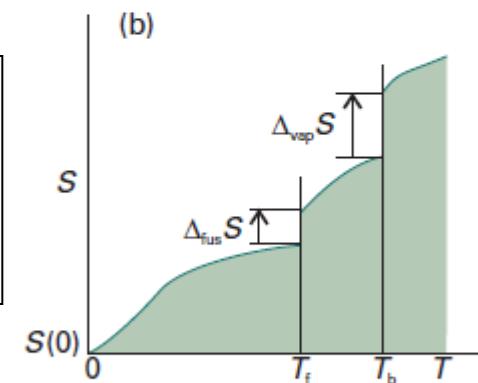
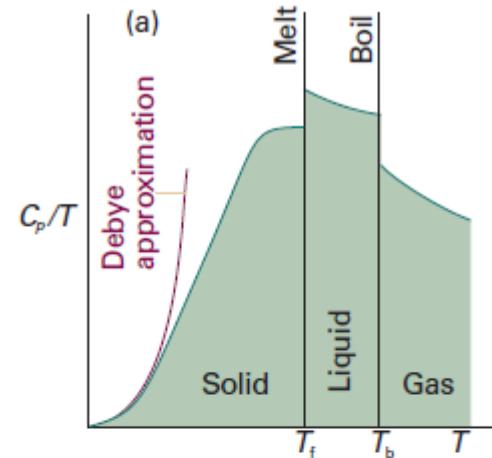
Entropy at any temperature,

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

Debye Extrapolation: At low  $T$ ,  $C_p \propto T^3$

Trouton's Rule

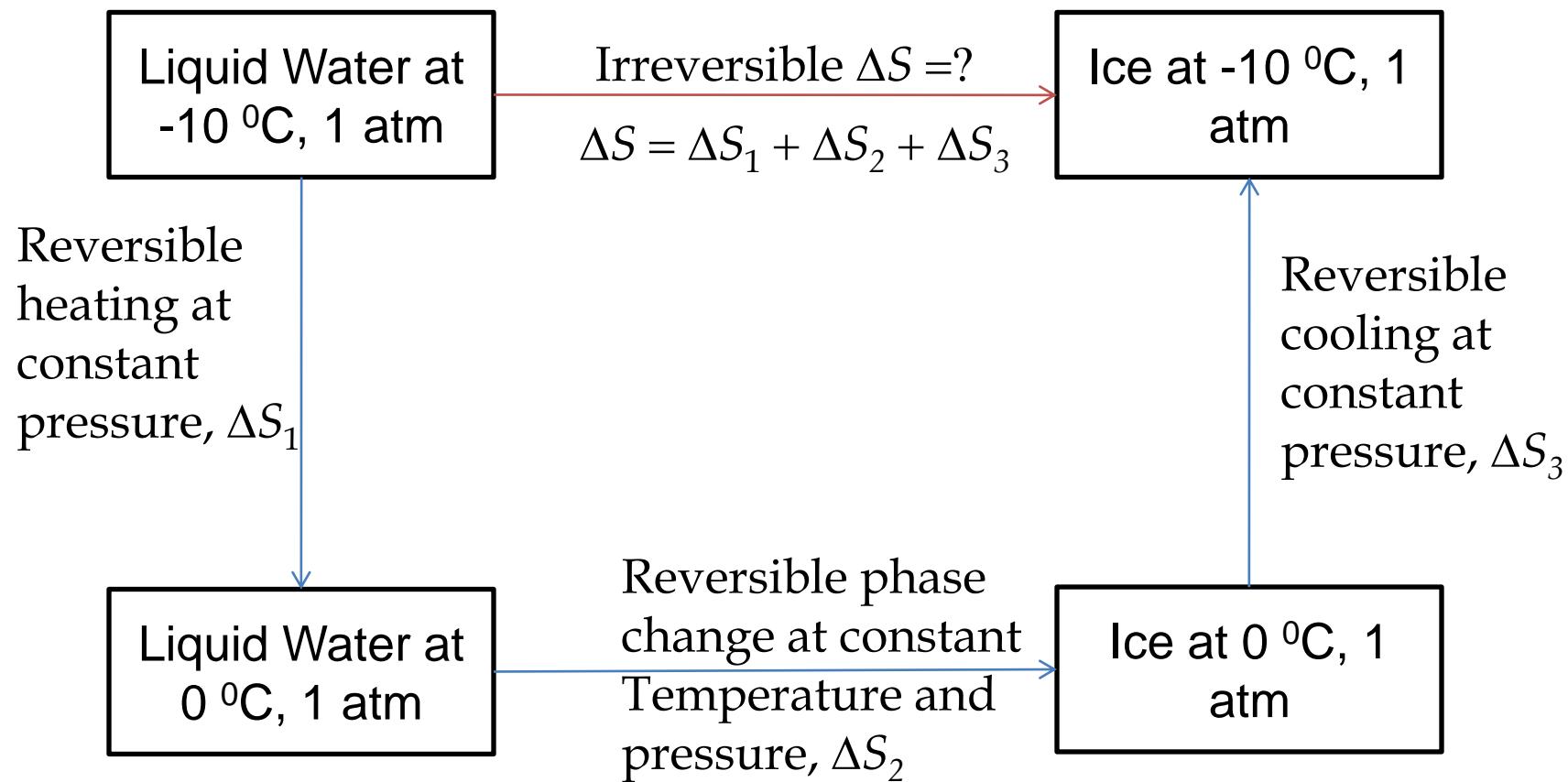
A wide range of liquid give approx. the same standard entropy of vaporization  $\sim 85 \text{ J K}^{-1} \text{ mol}^{-1}$ . Exception: water, it is  $109 \text{ J/K/mol}$



**Fig. 3.14** The calculation of entropy from heat capacity data. (a) The variation of  $C_p/T$  with the temperature for a sample. (b) The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

# Construction of Reversible Steps to Describe an Irreversible Process:

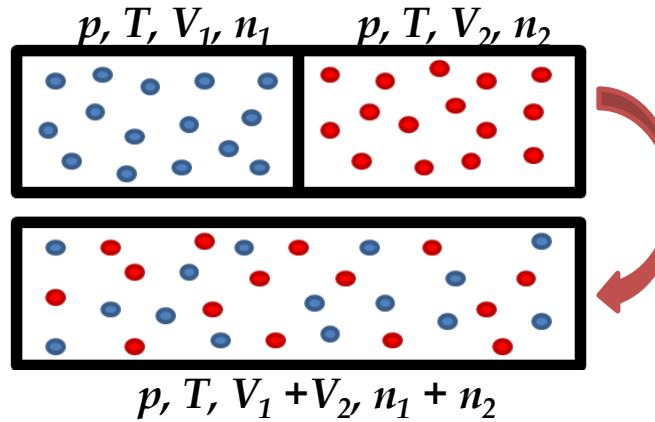
Example 1:



Entropy is an extensive property.  $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

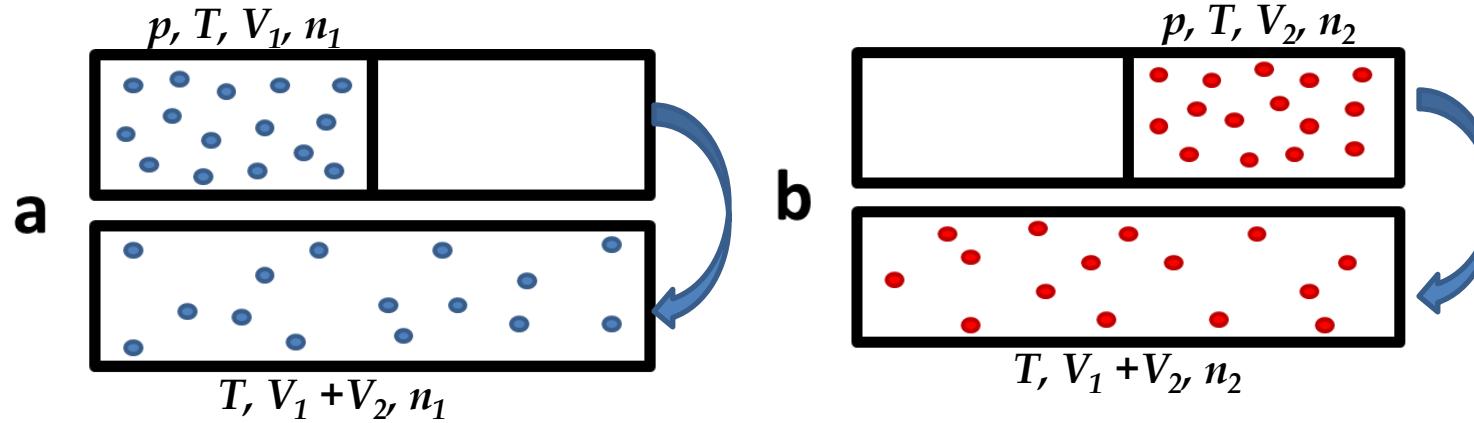
# Construction of Reversible Steps to Describe an Irreversible Process:

Example 2: Entropy of Mixing of ideal gases



$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2$$

Irreversible mixing  
of gases  $\Delta S=?$



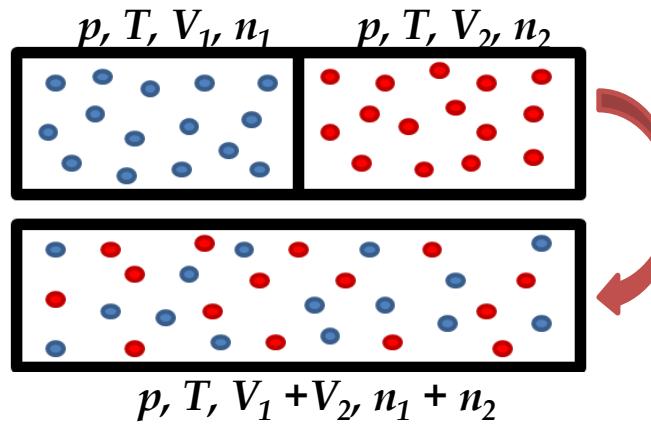
$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}$$

$$\Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

Reversible,  
isothermal  
expansion

# Construction of Reversible Steps to Describe an Irreversible Process:

## Example 2: Entropy of Mixing of ideal gases



Irreversible mixing  
of gases

$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}, \Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2}$$

$$\frac{n_1 R T}{V_1 + V_2}$$

$$\frac{V_1}{V_1 + V_2} = \frac{p}{n_1 R T + n_2 R T} = \frac{p}{p + p} = \frac{n_1}{n_1 + n_2} = X_1$$

$$\begin{aligned}\Delta S_{\text{mix}} &= -n_1 R \ln X_1 - n_2 R \ln X_2 \\ &= -n R(X_1 \ln X_1 + X_2 \ln X_2)\end{aligned}$$

\*Find out  $X_1$  for  
which  $\Delta S_{\text{mix}}$  is  
maximum.

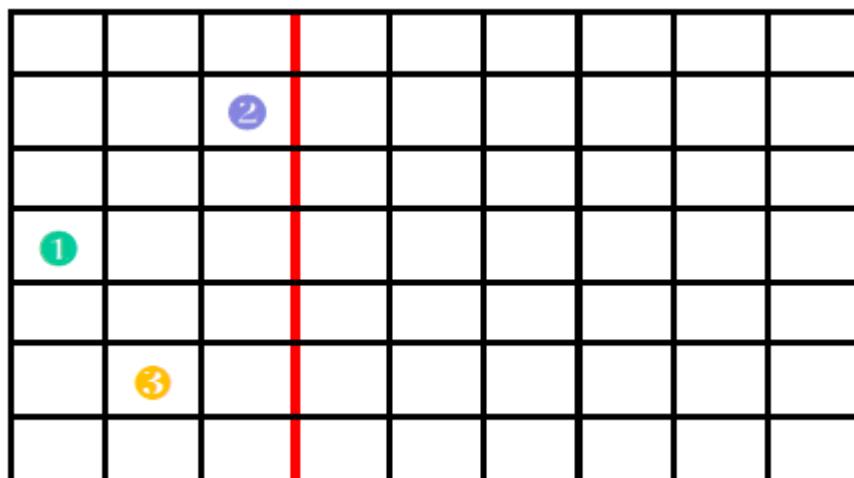
# Statistical View of Entropy

The equilibrium thermodynamic state of an isolated system is the most probable state.

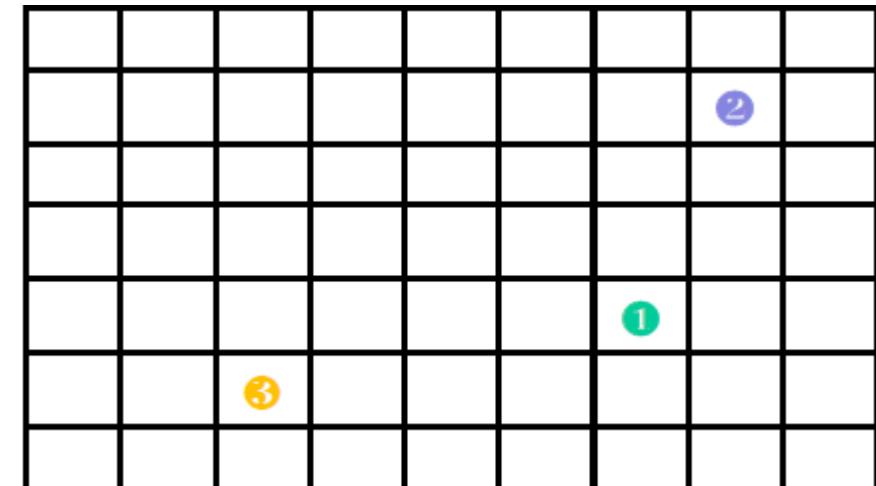
$$S = k_B \ln W$$

$k_B$  is Boltzmann's constant

$W$  is number of different ways in which the energy of the system can be arranged (number of microstates)



$$W = 21 \times 20 \times 19 = 7,980$$



$$W = 63 \times 62 \times 61 = 2,38,266$$

# The Clausius Inequality:

$$dS = dq_{rev} / T$$

$$dS_{surr} = -dq / T_{surr}$$

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

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

$$|dw_{rev}| > |dw|$$

$$-dw_{rev} > -dw$$

$$dw - dw_{rev} \geq 0$$

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

$$dq_{rev} \geq dq$$

$$dq_{rev}/T \geq dq/T$$

$$dS \geq dq/T$$

$$TdS - dq \geq 0$$

The Clausius Inequality

For a closed system,

$$dq = dU - dw$$

$$TdS \geq dU - dw$$

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

Entropy can not decrease when a spontaneous change occurs in an isolated system ( $dq = 0$ )

# Entropy and Reversibility

- Reversible process:

Reversible heat transfer between system and surrounding must occur with no finite temperature difference.

$$T_{syst} = T_{surr} \Rightarrow dS_{univ} = dS_{syst} + dS_{surr} = \frac{dq_{rev}}{T_{syst}} - \frac{dq}{T_{surr}} = 0$$

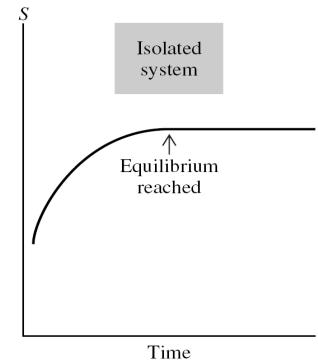
- Irreversible process (spontaneous):

The system + surrounding = universe, can be considered an isolated system. For any isolated system,  $dS_{univ} = dS_{syst} + dS_{surr} > 0$

$$\Delta S_{univ} \geq 0$$

# Entropy and Equilibrium

- For an isolated system, spontaneous changes will occur until the entropy is maximized. This leads to equilibrium.



- For a closed system (heat and work exchange with surrounding is allowed), spontaneous changes will occur until the entropy of system plus surrounding, is maximized. This leads to equilibrium.

$$dS_{total} = dS_{sys} + dS_{surr} > 0$$

Spontaneous process

$$dS_{total} = dS_{sys} + dS_{surr} = 0$$

Equilibrium process

$$dS_{total} = dS_{sys} + dS_{surr} < 0$$

Impossible process

For any process

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

“=” for reversible, equilibrium

“>” spontaneous (irreversible) (real)

LECTURES

8,9

CY11001  
Spring 2016



Department of Chemistry  
Indian Institute of Technology  
Kharagpur

$$dS \geq \frac{dq}{T} \quad (\text{Clausius Inequality})$$

$$TdS - dq \geq 0$$

$$TdS - dU + dw \geq 0$$

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

# Conditions for Spontaneity

For a closed system  $dU - TdS - dw_{pV} - dw_{\text{non } pV} \leq 0$  Condition for spontaneity

Const. V

Const. T

$$dw_{pV} = 0$$

$$A = U - TS$$

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

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

$$\text{for } dw_{\text{non } pV} = 0$$

$$dA \leq dw_{\text{tot}}$$

$$dU - TdS \leq 0$$

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

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

Const. T

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

$$d(U - TS) \leq 0$$

$$A = U - TS$$

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

Helmholtz's energy /  
Helmholtz's free energy /  
Helmholtz's function/  
Maximum Work Function

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

For a closed system at constant T and V, the state function  $A = U - TS$  decreases during the spontaneous irreversible process

# Conditions for Spontaneity

For a closed system

$$dU - TdS + pdV - dw_{\text{non } pV} \leq 0$$

Condition for spontaneity

Const.  $p$ ,

$$dH = dU + pdV + Vdp$$

$$dH - TdS - dw_{\text{non } pV} \leq 0$$

$$dH - TdS - dw_{\text{non } pV} \leq 0$$

for  $dw_{\text{non } pV} = 0$

$$dH - TdS \leq 0$$

$$dH_{S,p, \text{ no non } pV \text{ work}} \leq 0$$

Const.  $T$

$$dS_{H,p, \text{ no non } pV \text{ work}} \geq 0$$

$$d(H-TS) \leq 0$$

$$G = H - TS$$

$$dG_{p,T, \text{ no non } pV \text{ work}} \leq 0$$

Gibbs's energy / Gibbs's free energy / Gibbs's function

$$-dG_{p,T} \geq (-dw_{\text{non } pV})$$

$$-dG_{p,T} = (-dw_{\text{non } pV})_{\max}$$

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

# Criteria for spontaneity

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

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

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

$$dS_{U,V} \geq 0$$

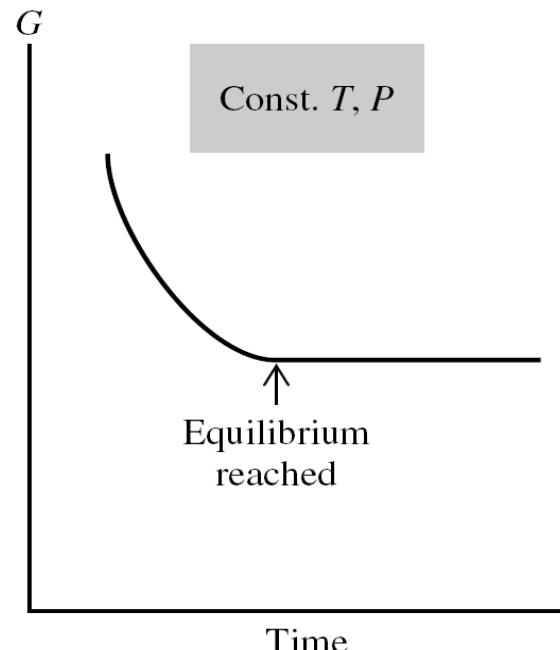
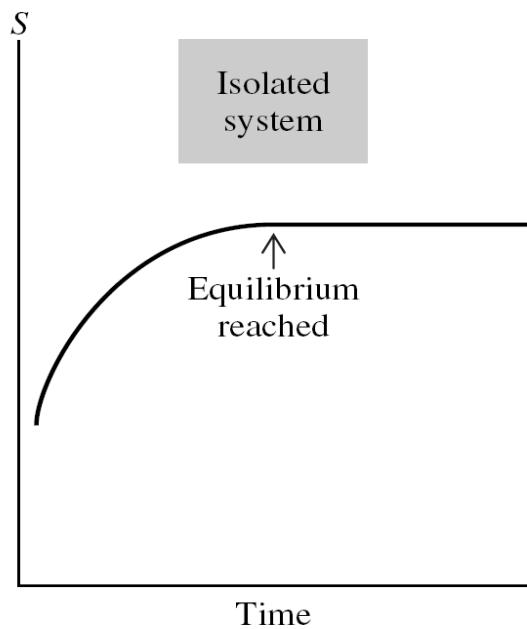
$$dH_{S,p} \leq 0$$

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

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

$$dG_{p,T} \leq 0$$

Reversible processes carry equal sign.



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

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

$$\oint dS = 0$$

$$dS \geq dq/T$$

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

$$A = U - TS$$

$$(-dA)_{T,V} = (-dw_{tot})_{\max}$$

$$G = H - TS$$

$$-dG_{p,T} = (-dw_{non\,pV})_{\max}$$

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

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

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

$$dS_{U,V} \geq 0$$

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

$$dG_{p,T} \leq 0$$

Thermodynamic definition of entropy.

Entropy is a state function. Change in entropy for a cyclic process is zero.

The Clausius inequality relation.

2<sup>nd</sup> law of thermodynamics. Total entropy increases for spontaneous processes.

Helmholtz free energy corresponds to total work function (at const  $T$  and  $V$ ) and Gibbs free energy corresponds to total non- $pV$  work (at constant  $p$  and  $T$ ).

Spontaneity of processes. Equality holds good for reversible processes or system in equilibrium.

# Combination of First and Second Laws of Thermodynamics:

$$dU = dw + dq$$

True for any path

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

$$dS \geq dq/T$$

$$dS = dq_{\text{rev}}/T$$

$$dU = -pdV + TdS$$

$$dA = d(U - TS)$$

$$= dU - TdS - SdT$$

$$= -pdV + TdS - TdS - SdT$$

$$= -pdV - SdT$$

The Fundamental Equation of Thermodynamics

Applicable to both reversible and irreversible processes!

$$dH = TdS + Vdp$$

$$dG = Vdp - SdT$$

The Fundamental Equation of Chemical Thermodynamics

# Combination of First and Second Laws of Thermodynamics: *(The Gibbs Equations)*

$$dU = -pdV + TdS$$

$$dA = -pdV - SdT$$

$$dH = TdS + Vdp$$

$$dG = Vdp - SdT$$

A closed system (constant composition/change in composition reversibly), only  $pV$  work

# The Maxwell Relations

$$dG = Vdp - SdT$$

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

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

$$dA = -pdV - SdT$$

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

$$dH = Vdp + TdS$$

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

if,  $df = gdx + hdy$

$$\text{then } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

The Euler Reciprocity Relation.

Isothermal variation of entropy with pressure and volume

# Variation of Gibbs free energy with $T$ and $p$

$$dG = Vdp - SdT$$

The Fundamental Equation of Chemical Thermodynamics

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

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

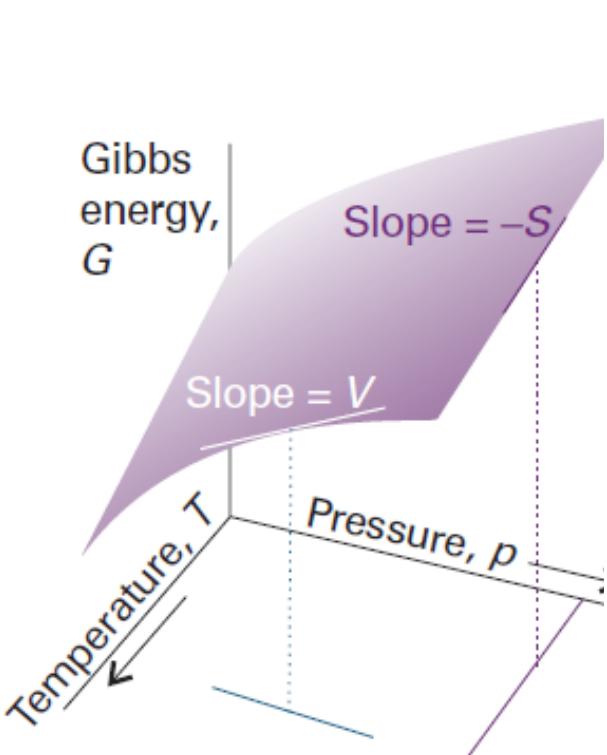


Figure 3-19  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

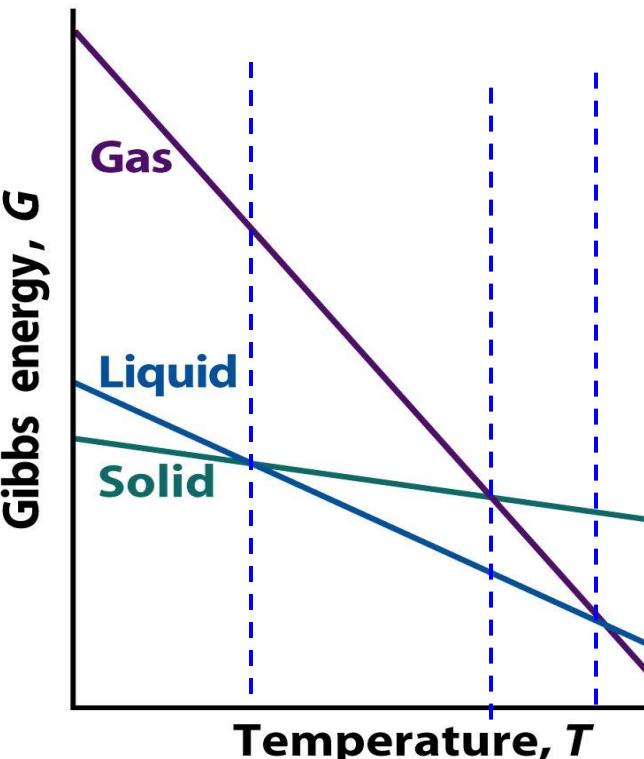
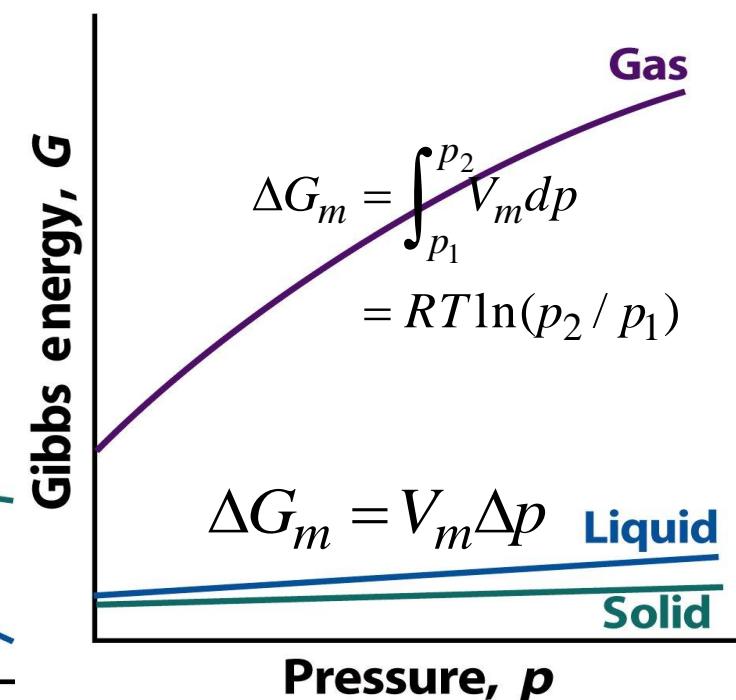


Figure 3-20  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula



# Temperature dependence of Gibbs Energy Or Gibbs-Helmholtz Equation:

$$G = H - TS$$

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

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = ?$$

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

Show that (home work)

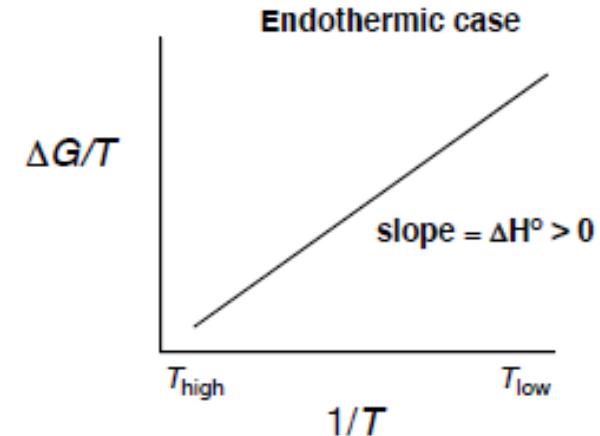
$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

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

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

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

Gibbs-Helmholtz Equations



If we know  $\Delta H$  of a process, we can know how  $\Delta G/T$  varies with  $T$ .

Show that,  $\Delta G/T = -\Delta S_{univ}$

# Prove the following relations:

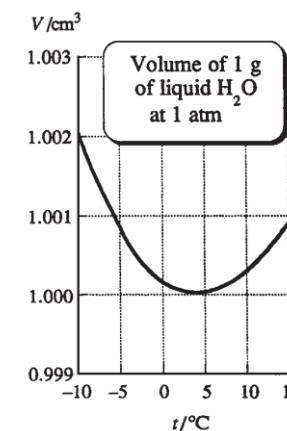
$$\left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{\alpha T}{\kappa} - p \right) = 0 \text{ (for ideal gas)} = an^2/V^2 \text{ (for vdW gas)}$$

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

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

$$\mu_{JT} = \frac{V}{C_p} (\alpha T - 1) = ? \text{ (for ideal gas)} = ? \text{ (for vdW gas)}$$

$$C_p - C_V = \frac{TV\alpha^2}{\kappa} = nR \text{ (for ideal gas)}$$



What is the relation between  $C_p$  and  $C_V$  of water at  $3.98^{\circ}\text{C}$ ?

## Variation of entropy with temperature at constant $p$ or constant $V$

$$dU = -pdV + TdS$$

$$dH = VdP + TdS$$

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

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

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

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

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

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

## Variation of entropy with temperature and pressure

$$dS = \left( \frac{\partial S}{\partial T} \right)_p dT + \left( \frac{\partial S}{\partial p} \right)_T dp$$

$$\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p = -\alpha V$$

$$dS = \frac{C_p}{T} dT - \alpha V dp$$

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

From Maxwell relation

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

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad \left( \frac{\partial U}{\partial T} \right)_V = C_V \quad \left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{\alpha T}{\kappa} - p \right)$$

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

$$dH = \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial p} \right)_T dp \quad C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \left( \frac{\partial H}{\partial p} \right)_T = V(1 - \alpha T)$$

$$\Delta H = \int C_p dT + \int (V - TV\alpha) dp$$

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

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

# Heat Engine

An engine is a device (system) that converts energy to work.

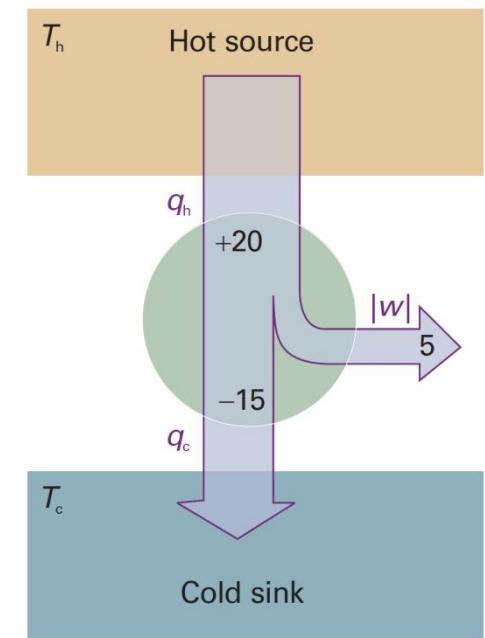
A heat engine draws heat from a hot reservoir, converts some heat to work, and releases some heat to a cold reservoir.

The engine itself is a system that undergoes a cyclical process

Experiments suggested:

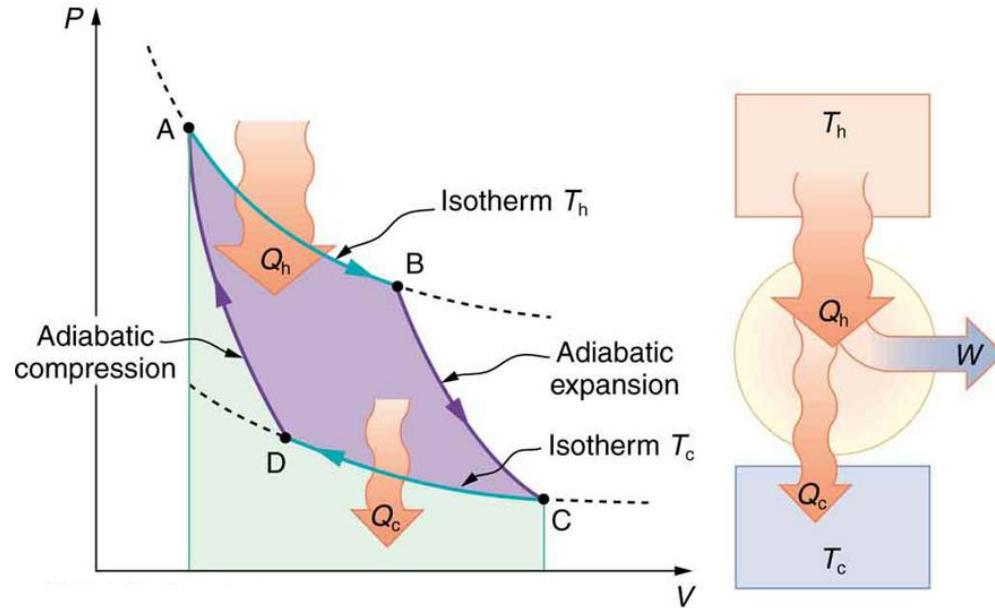
**(Clausius)** An engine does not exist whose sole effect is to transfer heat from a **cold body to a hot body**.

**(Kelvin)** An engine does not exist that operates in a cycle and performs work by exchanging heat with only one reservoir!



**Fig. 3.7** Suppose an energy  $q_h$  (for example, 20 kJ) is supplied to the engine and  $q_c$  is lost from the engine (for example,  $q_c = -15$  kJ) and discarded into the cold reservoir. The work done by the engine is equal to  $q_h + q_c$  (for example,  $20\text{ kJ} + (-15\text{ kJ}) = 5\text{ kJ}$ ). The efficiency is the work done divided by the energy supplied as heat from the hot source.

# Carnot Engine (1825, Sadi Carnot)



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

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

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

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

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

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

# Efficiency of Carnot cycle

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from source}}$$

$$\eta = \frac{-w_{\text{tot}}}{q} = \frac{nR(T_h - T_c) \ln(V_B/V_A)}{nRT_h \ln(V_B/V_A)}$$

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

$$\eta = 1 - \frac{T_c}{T_h} = 1 + \frac{q_c}{q_h}$$

All reversible engines have same efficiency regardless of their construction

The total change in entropy during a Carnot cycle:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

Entropy change around any closed path is 0.  
Entropy is a state function.

# Assignment 3

- Calculate  $\Delta S$  when 1 mol of water goes from 300 K at 1 atm to 310 K at 40 atm? Obtain  $C_p$  and  $\alpha$  from thermodynamic table and assume they do not change with temperature.
- Show that  $dq = dU + pdV = C_V dT + RT d \ln V$  does not satisfy Clairut's theorem, but  $dq/T = C_V d \ln T + R d \ln V$  does.
- Prove the following relations:

$$(a) \left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{\alpha T}{\kappa} - p \right) = 0 \text{ (for ideal gas)} = an^2/V^2 \text{ (for vdW gas)} \quad (e) C_p - C_V = \frac{TV\alpha^2}{\kappa} = nR \text{ (for ideal gas)}$$

$$(b) \left( \frac{\partial H}{\partial p} \right)_T = V(1 - \alpha T) = 0 \text{ (for ideal gas)} = ? \text{ (for vdW gas)} \quad (f) \left( \frac{\partial(G/T)}{\partial(1/T)} \right)_p = H$$

$$(c) \left( \frac{\partial S}{\partial p} \right)_T = -\alpha V; \left( \frac{\partial S}{\partial V} \right)_T = \frac{\alpha}{\kappa}; \left( \frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T}; \left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \quad (g) \left( \frac{\partial(G/T)}{\partial T} \right)_p = -\frac{H}{T^2}$$

$$(d) \mu_{JT} = \frac{V}{C_p} (\alpha T - 1) = ? \text{ (for ideal gas)} = ? \text{ (for vdW gas)}$$

- A van der Waals gas with  $a=0$  undergoes Joule Thompson expansion. What would happen to its temperature? (rises/falls/remains const)

LECTURE  
**10**

CY11001  
Spring 2016

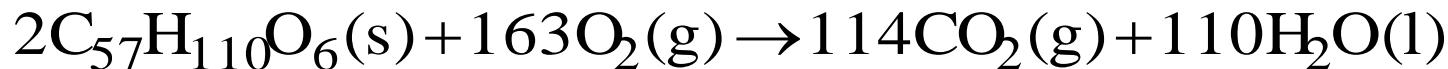


Department of Chemistry  
Indian Institute of Technology  
Kharagpur

# Thermochemistry

## Application of Thermodynamics to Chemistry - Thermochemistry

- Make a cold drink (put ice to water!)
- Burn fuel to drive a car
- Burn fat by doing exercise
- Hot packs and cold packs
- Equipment cooling



The decrease in volume at 25 °C is about 600 ml for the consumption of 1 g of fat!

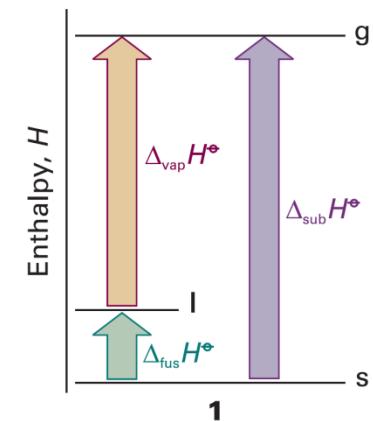
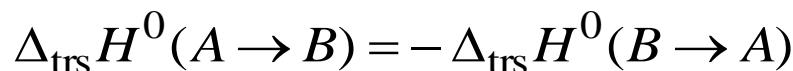
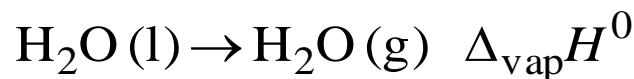
# Application of Thermodynamics to Chemistry - Thermochemistry

A chemical reaction involves transfer of heat and exchange of energy between system (reaction vessel) and surrounding. Hence the laws of thermodynamics are applicable to chemical reactions.

$\Delta H > 0$  (endothermic);  $\Delta H < 0$  (exothermic);

## Enthalpies During Physical Changes

A physical change is accompanied by a standard enthalpy of transition  $\Delta_{trs}H^0$



## Standard States:

For Solid and Liquid – pure form at 1 bar pressure and at the temperature of interest (T).

For gas – pure form at 1 bar pressure and temperature of interest (T) and the gas behaves as an ideal gas.

Conventionally, the thermodynamic data are reported for standard states at 298.15 K.

Enthalpy is a state function

# Examples of various enthalpies of transition

**Table 2.4** Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase $\beta$	$\Delta_{trs}H$
Fusion	s $\rightarrow$ l	$\Delta_{fus}H$
Vaporization	l $\rightarrow$ g	$\Delta_{vap}H$
Sublimation	s $\rightarrow$ g	$\Delta_{sub}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{mix}H$
Solution	Solute $\rightarrow$ solution	$\Delta_{sol}H$
Hydration	$X^\pm(g) \rightarrow X^\pm(aq)$	$\Delta_{hyd}H$
Atomization	Species(s, l, g) $\rightarrow$ atoms(g)	$\Delta_{at}H$
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{eg}H$
Reaction	Reactants $\rightarrow$ products	$\Delta_rH$
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_cH$
Formation	Elements $\rightarrow$ compound	$\Delta_fH$
Activation	Reactants $\rightarrow$ activated complex	$\Delta^\ddagger H$

\* IUPAC recommendations. In common usage, the transition subscript is often attached to  $\Delta H$ , as in  $\Delta H_{trs}$ .

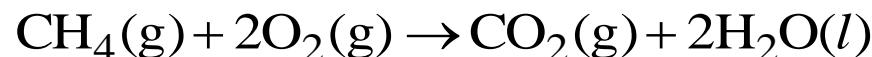
Enthalpy of vaporization of water is 44 kJ/mol at 298 K. What is the enthalpy of condensation of water vapor at the same temperature?

## Enthalpies During Chemical Changes

$aA + bB \rightarrow cC + dD$  The standard enthalpy change,

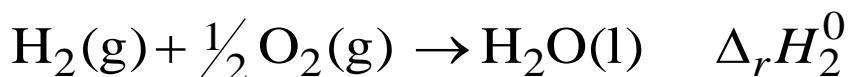
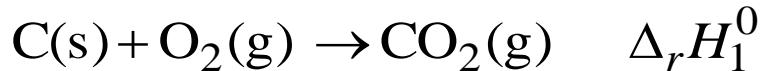
$$\begin{aligned}\Delta_r H^0 &= \sum_{\text{products}} vH_m^0 - \sum_{\text{reactants}} vH_m^0 \\ &= cH_m^0(C) + dH_m^0(D) - aH_m^0(A) - bH_m^0(B)\end{aligned}$$

The change in standard enthalpy during a chemical reaction is the change in enthalpy when reactants in their standard states change to products in their standard states.



$$\Delta_r H^0 = 2H_m^0(\text{H}_2\text{O(l)}) + H_m^0(\text{CO}_2(\text{g})) - H_m^0(\text{CH}_4(\text{g})) - 2H_m^0(\text{O}_2(\text{g}))$$

For the combustion of methane, the standard reaction enthalpy refers to the reaction where 1 mol of pure methane gas at 1 bar reacts with 2 mol of pure oxygen gas at 1 bar to form 1 mol of pure CO<sub>2</sub> gas at 1 bar and 2 mol of pure liquid water at 1 bar.



$$\text{Rxn (1)} + 2 \text{Rxn (2)} - \text{Rxn(3)}$$

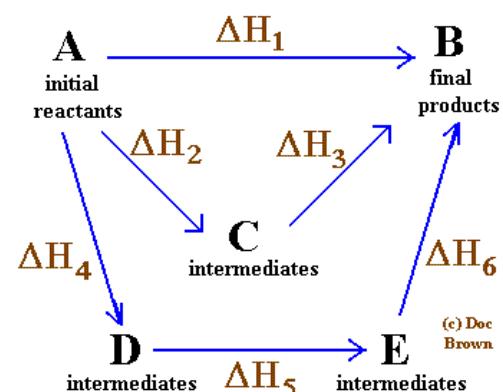
$$\Delta_r H^0 = \Delta_r H_1^0 + 2\Delta_r H_2^0 - \Delta_r H_3^0$$

## Hess's law

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.



Germain Hess



$$\begin{aligned}\Delta_r H_1^0 &= \Delta_r H_2^0 + \Delta_r H_3^0 \\ &= \Delta_r H_4^0 + \Delta_r H_5^0 + \Delta_r H_6^0\end{aligned}$$

# Standard Enthalpies of Formation ( $\Delta_f H^0$ )

The standard reaction enthalpy for the formation of the compound from its elements in their reference state (the most stable state at 1 bar pressure and the specified temperature).

For example -

At 298 K, the reference state of

$N_2$  -  $N_2$  gas at 1 bar, *Mercury* - liquid Mercury at 1 bar,  
*Carbon* - graphite at 1 bar.

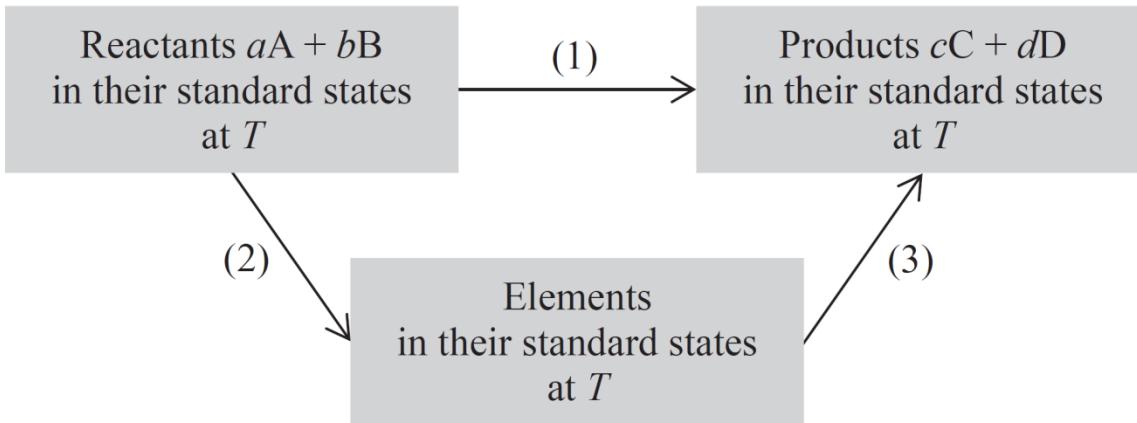
**Standard enthalpy of formation of  $H_2CO(g)$  at 307 K:**



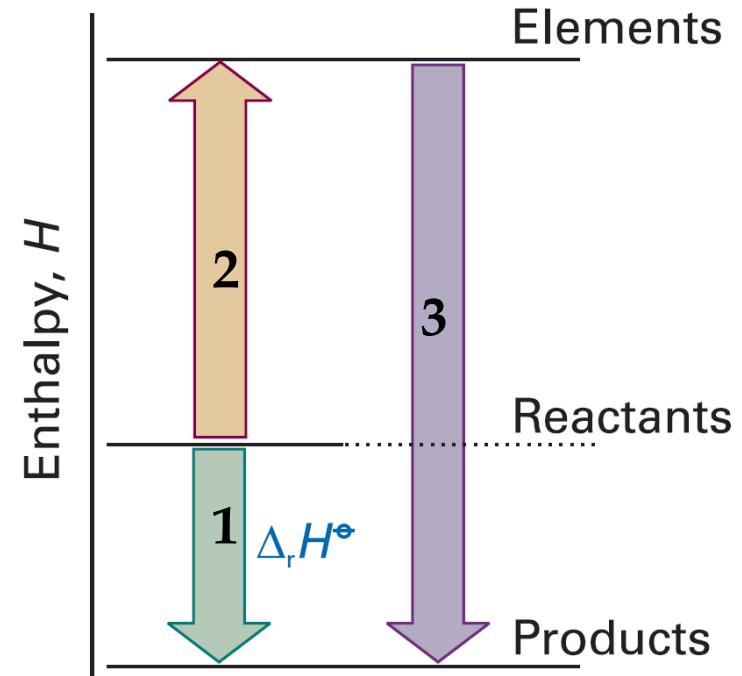
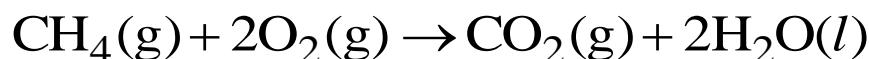
All elements in their reference states (oxygen gas, solid carbon in the form of graphite, etc.) have a standard enthalpy of formation of zero, as there is no change involved in their formation.

	$\Delta_f H^0$ (kJ/mol) at 298 K
$H_2O(l)$	-285.8
$H_2O(g)$	-241.8
$NH_3(g)$	-46.1
$NO_2(g)$	+33.2
$C_6H_6(l)$	+49.0
$CH_4(g)$	-74.8
$CO_2(g)$	-393.5

# Enthalpy of Reaction from Standard Enthalpies of Formation ( $\Delta_f H^0$ )



$$\Delta_r H^0 = \sum_{\text{products}} v \Delta_f H^0 - \sum_{\text{reactants}} v \Delta_f H^0$$



$$\Delta_r H^0 = 2\Delta_f H^0(\text{H}_2\text{O}(l)) + \Delta_f H^0(\text{CO}_2(g)) - \Delta_f H^0(\text{CH}_4(g)) - 2\Delta_f H^0(\text{O}_2(g))$$

$$\Delta_r H^0 = 2(-285.83) + (-393.5) - (-74.8) - 2(0) \text{ kJ/mol} = -890.36 \text{ kJ/mol}$$

# Temperature Dependence of $\Delta H$

$$\left( \frac{dH}{dT} \right)_p = C_p$$

$$\frac{d\Delta_r H^0}{dT} = \Delta_r C_p^0 = C_p^0(\text{product}) - C_p^0(\text{reactant})$$

$$\Delta_r H^0(T_2) - \Delta_r H^0(T_1) = \int_{T_1}^{T_2} \Delta_r C_p^0 dT$$

## Kirchhoff's Law

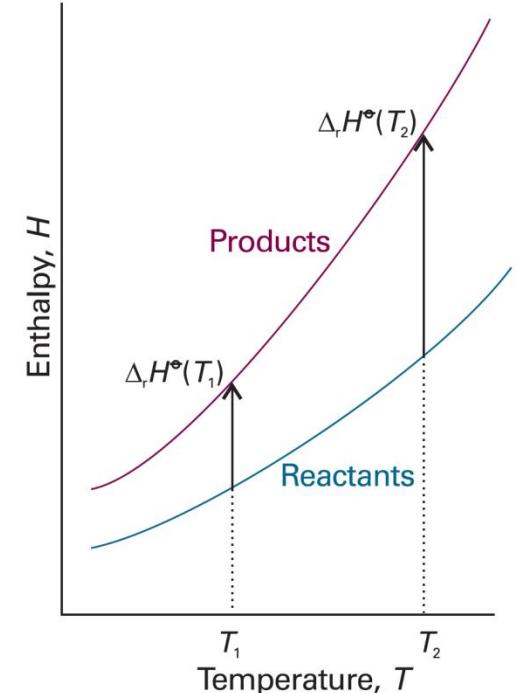
If  $\Delta C_p$  does not change over a small temperature range,

$$\Delta_r H^0(T_2) - \Delta_r H^0(T_1) = \Delta_r C_p^0(T_2 - T_1)$$

### Problem:

Find out  $\Delta_r H^0$  for the reaction :  $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$  at 1200 K. Assume  $\Delta C_p$  is independent of T.

$\Delta_f H^0$  of  $\text{CO}_2\text{(g)}$ , and  $\text{CO(g)}$  at 298 K are -393.5 and -110.5 kJ/mol, respectively.  $C_p^0$  of  $\text{CO}_2\text{(g)}$ ,  $\text{CO(g)}$ , and  $\text{O}_2\text{(g)}$  at 298 K are 37.11, 29.11, and 29.35 J/mol-K, respectively.



**Fig. 2.19** An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

## Determine $\Delta U^0$ from $\Delta H^0$

$$\Delta H = \Delta U + \Delta(pV)$$

$$\Delta_r H^0 = \Delta_r U^0 + p^0 \Delta_r V^0 \text{ (at constant pressure)}$$

The change in volume of a reaction can be obtained from the change in volume of the gaseous components of the reaction (molar volume of gas > molar volume of solid/liquid)

$$p^0 \Delta_r V^0 = \Delta_r n_g RT$$

$$\Delta_r H^0 = \Delta_r U^0 + (\Delta n_g)RT$$



$$P^0 \Delta_r V^0 = \Delta_r n_g RT = -2RT$$

$$\Delta_r U^0 = \Delta_r H^0 - 2RT$$

$RT = 2.5 \text{ kJ/mol}$  at  $300 \text{ K}$  and  $8.3 \text{ kJ/mol}$  at  $1000 \text{ K}$ !

For reactions not involving gases,  $\Delta_r n_g = 0$ . Hence  $\Delta_r H^0 = \Delta_r U^0$

# Determination of $\Delta_r G^0$ and $\Delta_r S^0$

$$\Delta_r H^0 = \sum_{\text{products}} v \Delta_f H^0 - \sum_{\text{reactants}} v \Delta_f H^0$$

$$\Delta_r S^0 = \sum_{\text{products}} v S_m^0 - \sum_{\text{reactants}} v S_m^0$$

$$\Delta_r G^0 = \sum_{\text{products}} v \Delta_f G^0 - \sum_{\text{reactants}} v \Delta_f G^0$$

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

# An example snapshot of thermodynamic table

	$M/(g\ mol^{-1})$	$\Delta_f H^\circ/(kJ\ mol^{-1})$	$\Delta_f G^\circ/(kJ\ mol^{-1})$	$S_m^\circ/(J\ K^{-1}\ mol^{-1})\dagger$	$C_{p,m}^\circ/(J\ K^{-1}\ mol^{-1})$
<b>Neon</b>					
Ne(g)	20.18	0	0	146.33	20.786
<b>Nitrogen</b>					
N <sub>2</sub> (g)	28.013	0	0	191.61	29.125
N(g)	14.007	+472.70	+455.56	153.30	20.786
NO(g)	30.01	+90.25	+86.55	210.76	29.844
N <sub>2</sub> O(g)	44.01	+82.05	+104.20	219.85	38.45
NO <sub>2</sub> (g)	46.01	+33.18	+51.31	240.06	37.20
N <sub>2</sub> O <sub>4</sub> (g)	92.1	+9.16	+97.89	304.29	77.28
N <sub>2</sub> O <sub>5</sub> (s)	108.01	-43.1	+113.9	178.2	143.1
N <sub>2</sub> O <sub>5</sub> (g)	108.01	+11.3	+115.1	355.7	84.5
HNO <sub>3</sub> (l)	63.01	-174.10	-80.71	155.60	109.87
HNO <sub>3</sub> (aq)	63.01	-207.36	-111.25	146.4	-86.6
NO <sub>3</sub> <sup>-</sup> (aq)	62.01	-205.0	-108.74	+146.4	-86.6

At 298 K

**LECTURES**

**11, 12**

*CY11001  
Spring 2016*



Department of Chemistry  
Indian Institute of Technology  
Kharagpur

# Limitations of the Fundamental Equation of Chemical Thermodynamics:

$$dG = Vdp - SdT$$

Does not apply

- When composition is changing due to exchange of matter with surroundings (open system)
- Irreversible chemical reaction
- Irreversible inter-phase transport of matter

**For one phase and multi-component system, in thermal and mechanical equilibrium but not in material equilibrium,  $G = f(T, p, n_1, n_2, \dots)$ ,**

$$(T, p, n_1, n_2, \dots) \xrightarrow{\text{Irreversible}} (T+dT, p+dp, n_1+dn_1, n_2+dn_2, \dots)$$

$$dG = \left( \frac{\partial G}{\partial p} \right)_{T, n_i} dp + \left( \frac{\partial G}{\partial T} \right)_{p, n_i} dT + \left( \frac{\partial G}{\partial n_1} \right)_{T, p, n_j \neq n_1} dn_1 + \dots + \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq n_i} dn_i$$

$$dG = Vdp - SdT + \sum_i \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq n_i} dn_i$$

$G$  is state function,  $dG$  is same if the process was reversible

# Chemical Potential

$$dG = Vdp - SdT + \sum_i \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq n_i} dn_i$$

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

$$\mu_i = f(T, p, n_1, n_2, \dots)$$

Applicable to single phase, multi component system at thermal and mechanical equilibrium but *not material equilibrium.*

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

$$dG_{p,T} = \sum_i \mu_i dn_i$$

$$dw_{\text{add,max}} = \sum_i \mu_i dn_i$$

For pure substance

$$\mu \text{ (Chemical Potential)} = G_m = G/n$$

Maximum additional work that can arise from changing the components of the system.

# Fundamental Equations of Thermodynamics or Gibbs Equations - Revisited

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

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

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

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

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

Applicable  
to single  
phase multi-  
component  
open system  
in thermal  
and  
mechanical  
equilibrium  
and  $pV$   
work only.

## Multi-phase Multi-Component System:

$$dG^\alpha = V^\alpha dp - S^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$

For one phase ( $\alpha$ ) system,  
in thermal and mechanical  
equilibrium  $pV$  work only

For multiple phases

$$dG = \sum_\alpha dG^\alpha = \sum_\alpha V^\alpha dp - \sum_\alpha S^\alpha dT + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha$$
$$\mu_i^\alpha = \left( \frac{\partial G^\alpha}{\partial n_i^\alpha} \right)_{p, T, n_{j \neq i}^\alpha}$$

Since,  $S$  and  $V$  are extensive properties,

$$dG = Vdp - SdT + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha$$

Thermal and mechanical  
equilibrium.  $pV$  work only

# Material Equilibrium

$$dG = Vdp - SdT + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha}$$

Thermal and mechanical equilibrium.  $p$ - $V$  work only

For a liquid and vapor mixture of water and acetone,

$$dG = Vdp - SdT + \mu_w^v dn_w^v + \mu_{ac}^v dn_{ac}^v + \mu_w^l dn_w^l + \mu_{ac}^l dn_{ac}^l$$

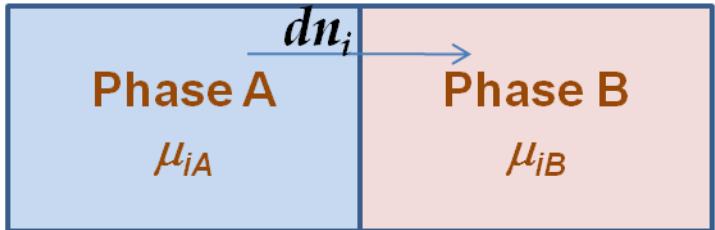
$$dG_{p,T} = \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha}$$

Thermal and mechanical equilibrium and constant  $T$  and  $p$ .  $p$ - $V$  work only

At complete equilibrium (thermal, mechanical, and material) at constant  $T$  and  $p$ ,  $pV$  work only,  $dG = 0$ .

$$\sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} = 0$$

# Chemical Potential and Phase Equilibrium



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

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

Change taking place  
at constant  $T, p$

If  $\mu_{i,A} > \mu_{i,B}$ , then  $dG < 0$

If  $\mu_{i,A} < \mu_{i,B}$ , then  $dG > 0$

If  $\mu_{i,A} = \mu_{i,B}$ , then  $dG = 0$

- Spontaneous transport of  $i$  from phase  $A$  to phase  $B$
- Spontaneous transport of  $i$  from phase  $B$  to phase  $A$
- Phase Equilibrium

- Substance  $i$  flows spontaneously from a phase with higher chemical potential to a phase with lower chemical potential .

# Gibbs-Duhem Equation

$$G_{p,T} = n_1\mu_1 + n_2\mu_2 + \dots = \sum_i n_i \mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i$$

At thermal and mechanical equilibrium.

At constant  $p$  and  $T$

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

**Gibbs-Duhem Equation**

For a binary mixture,  $n_1 d\mu_1 + n_2 d\mu_2 = 0$

Hence,  $d\mu_1 = - (n_2/n_1) d\mu_2$

If  $n_2 > n_1$ , a small change in  $\mu_2$  causes a large change in  $\mu_1$

Chemical potential of one component of a mixture can not change independently of the chemical potentials of other components.

# Chemical Potential and Phase Equilibrium

Chemical potential for a component in a mixture:  $\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j}$

$\mu$  (Chemical Potential) for pure substance =  $G_m = G/n$

Chemical potential for substance  
in the phases that are in  
equilibrium

$$\mu_i^\alpha(p, T) = \mu_i^\beta(p, T)$$

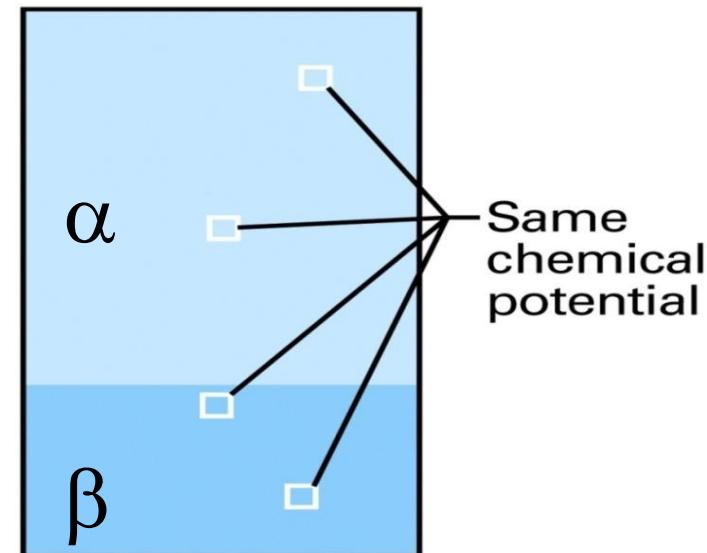
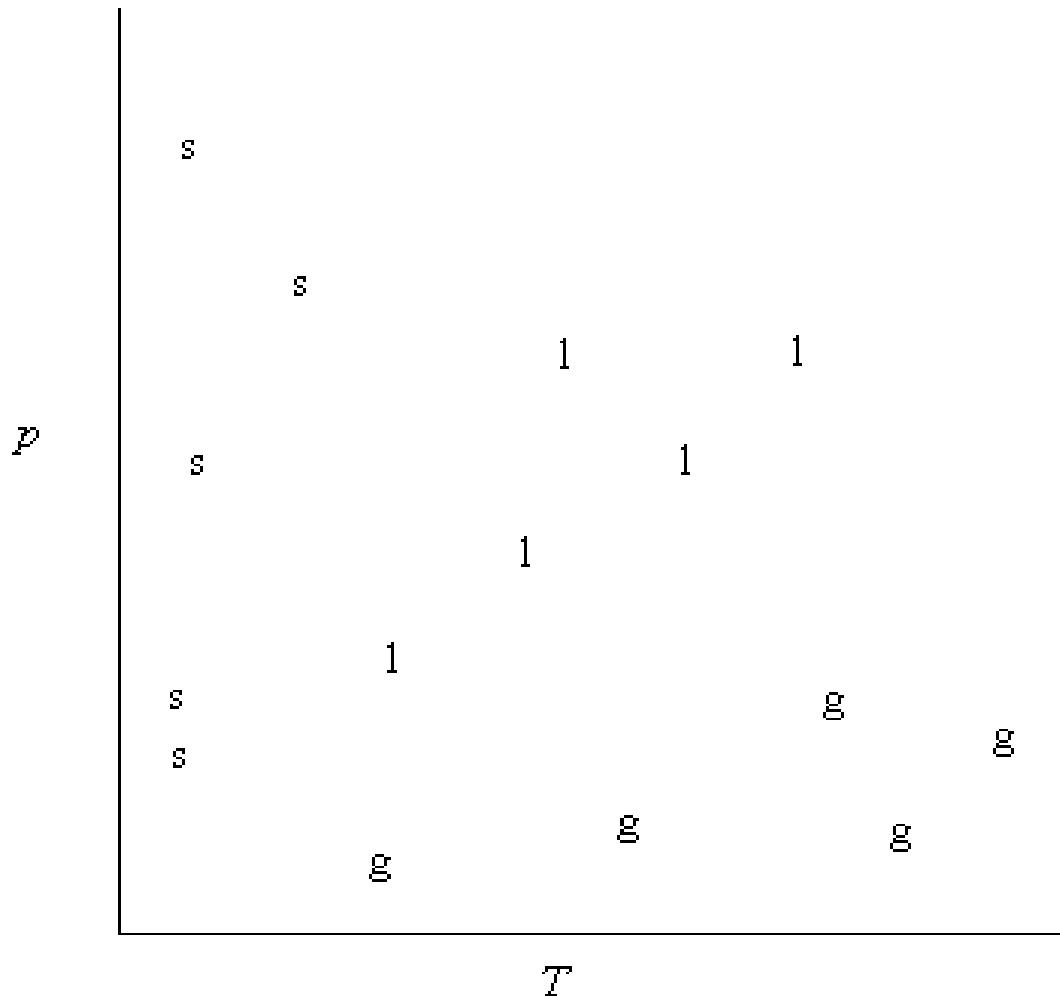


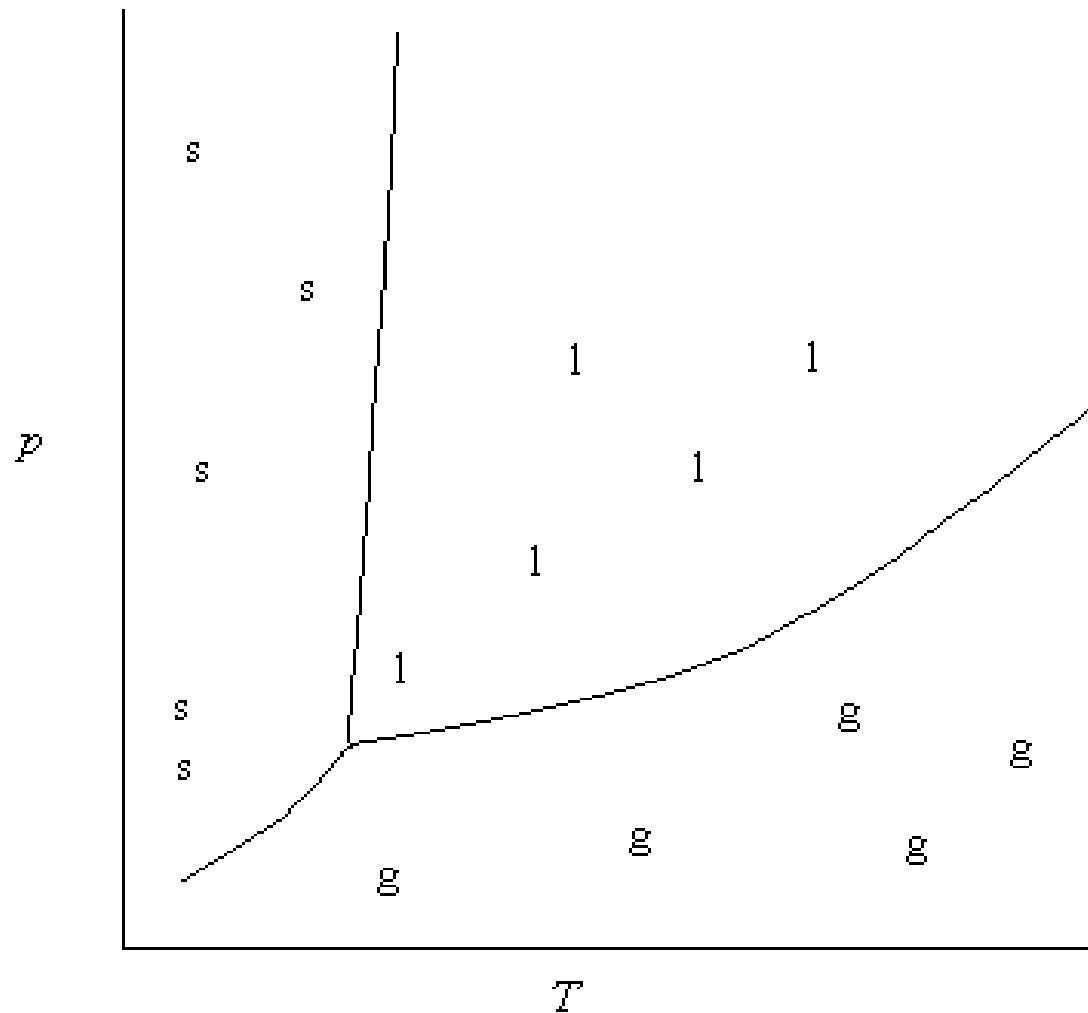
Figure 4-8  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

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

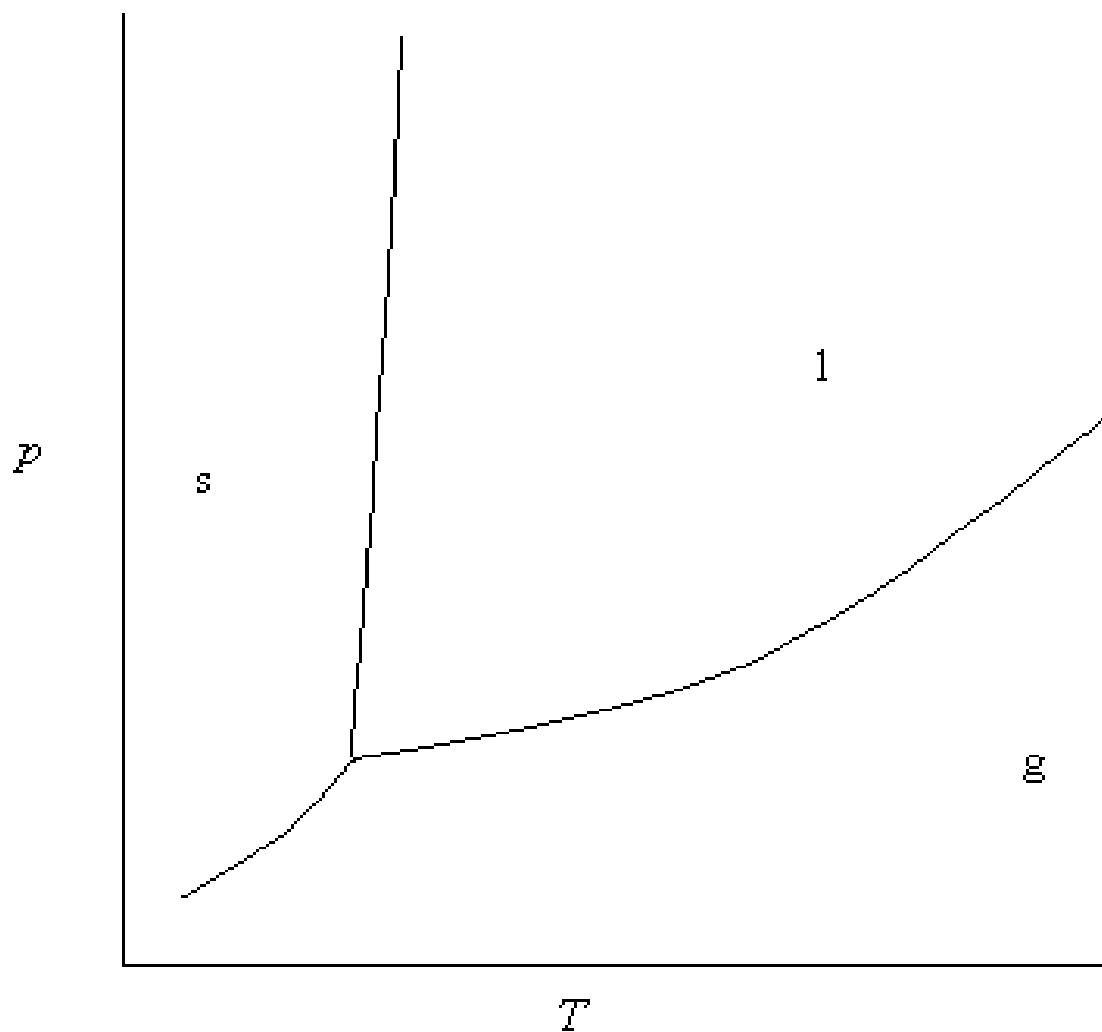
# How to construct one-component phase diagrams



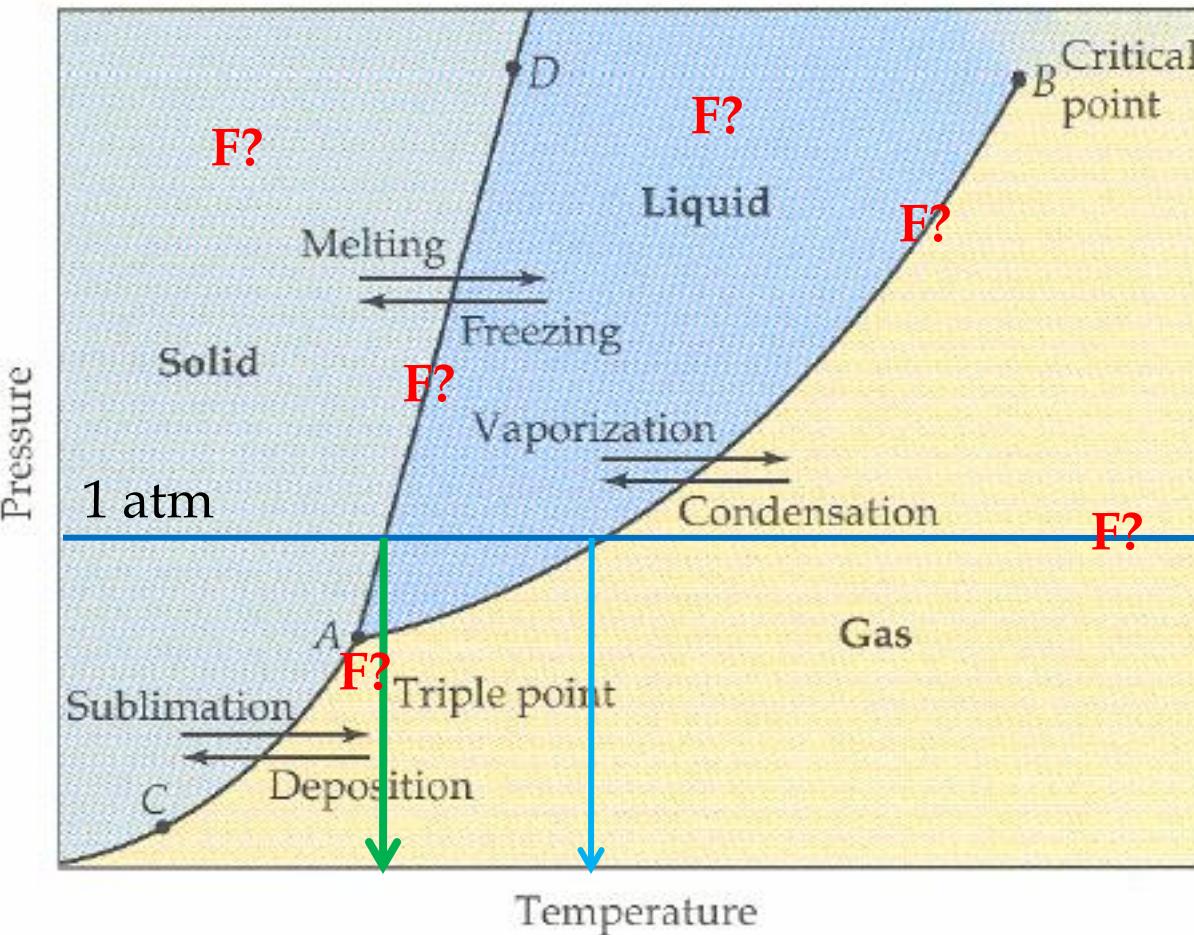
# How to construct one-component phase diagrams



# How to construct one-component phase diagrams



# A typical phase diagram



Phase Rule:  $F = C - P + 2$

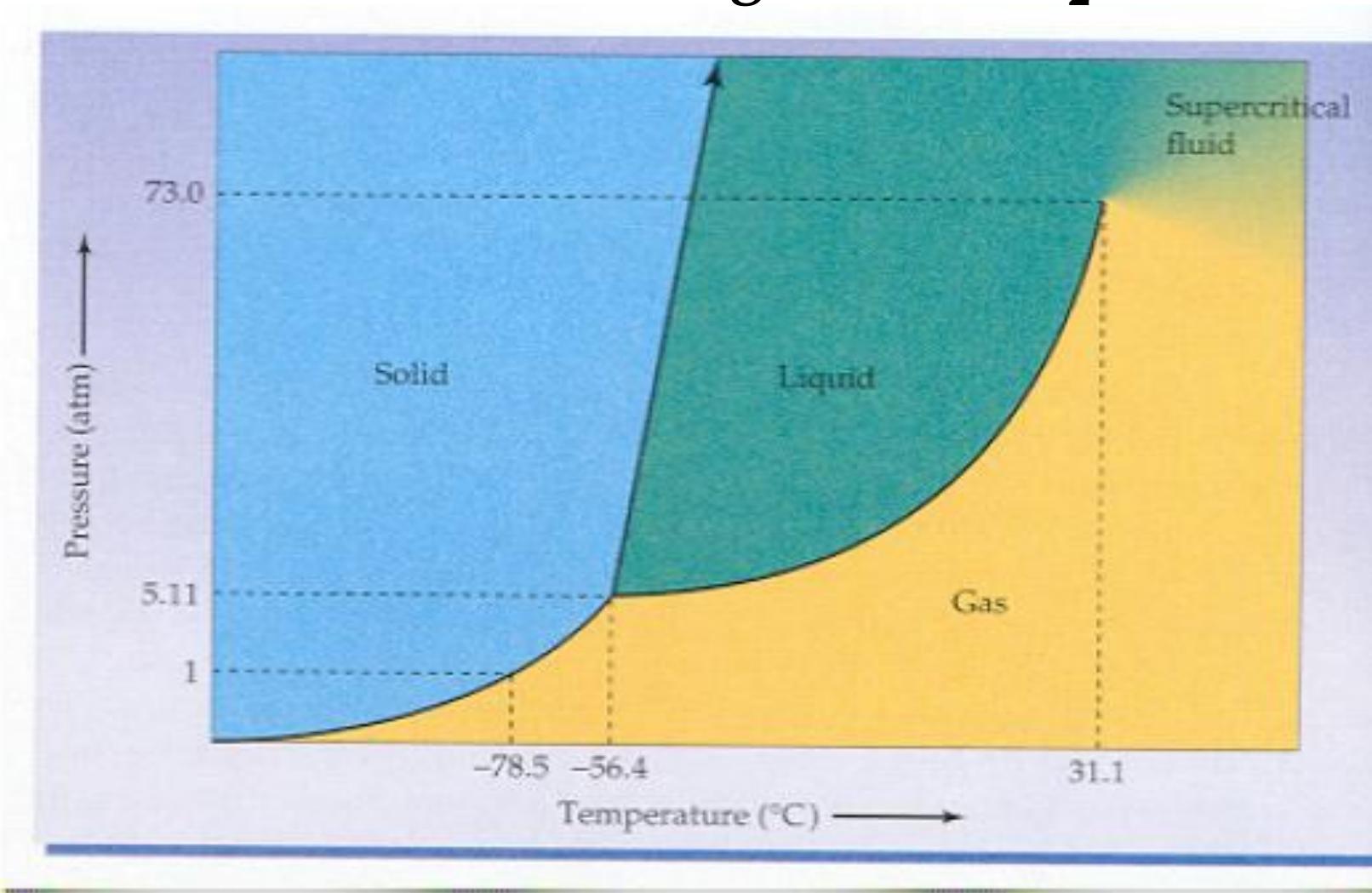
C: # of components

P: # of phases

F: # of parameters that can be varied independently

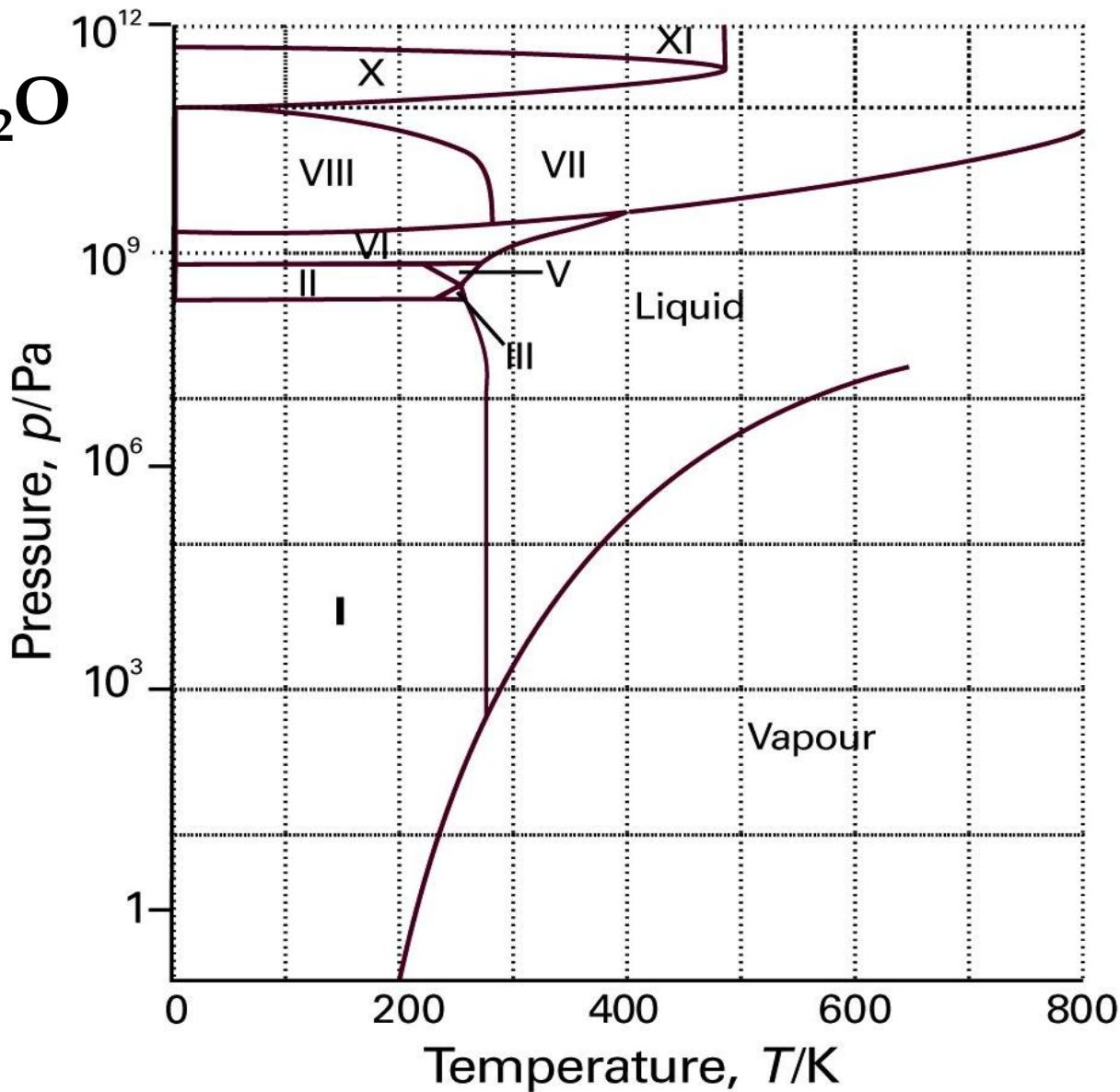
- Thermodynamic stability
- Metastable states
- Phase boundary / Coexistence curves
- Boiling / melting point
- Normal boiling / normal melting point (1 atm)
- Standard boiling / standard melting point (1 bar)
- Triple point
- Critical temperature
- Vapor pressure / Sublimation vapor pressure

# Phase Diagram of CO<sub>2</sub>



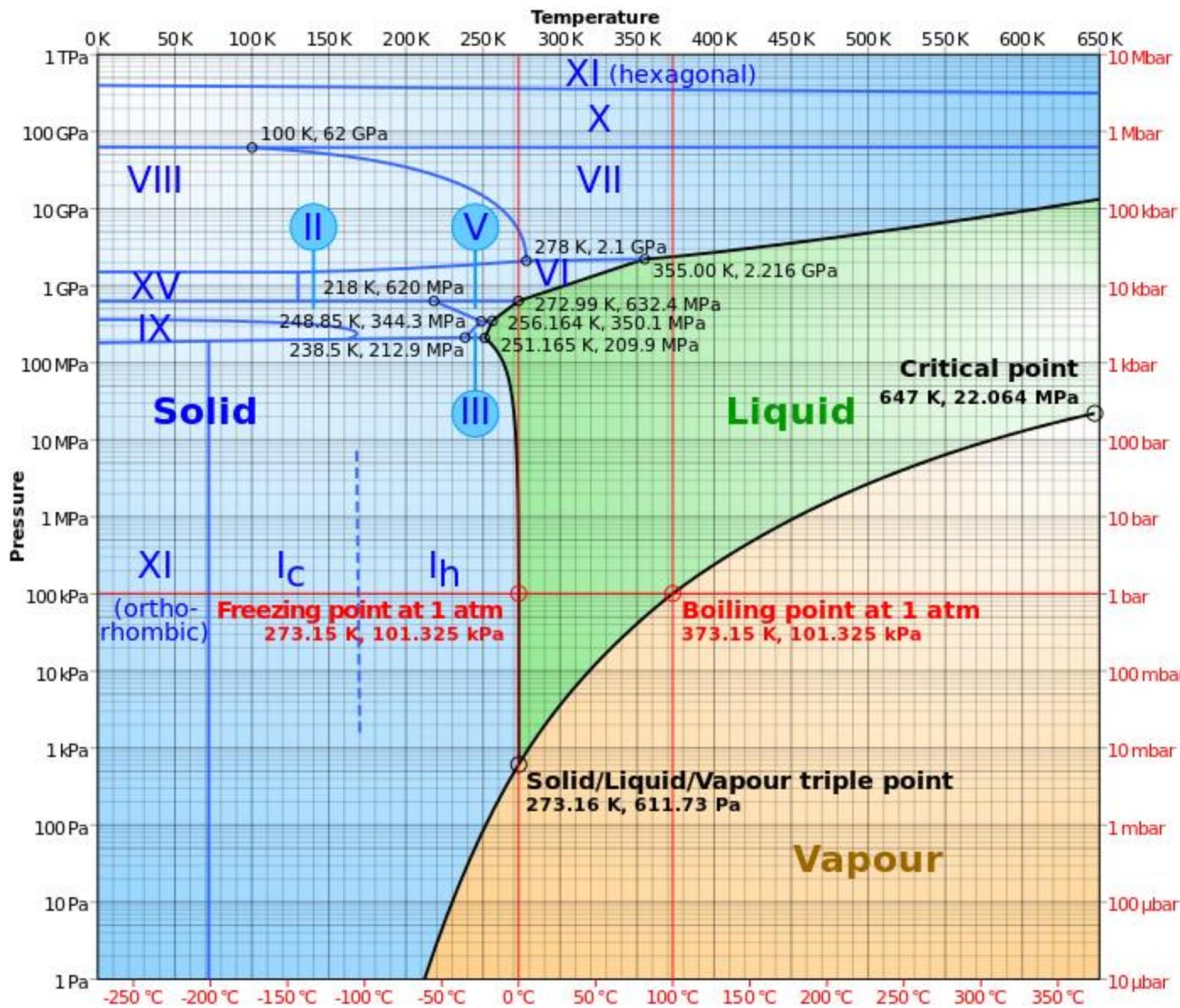
Melting point of solid CO<sub>2</sub> rises with pressure  
At normal atmospheric pressure, CO<sub>2</sub> can not be liquefied (dry ice).

# Phase Diagram of $\text{H}_2\text{O}$



**Figure 4-5**  
*Atkins Physical Chemistry, Eighth Edition*  
© 2006 Peter Atkins and Julio de Paula

# Phase Diagram of H<sub>2</sub>O



# Location and shape of phase boundary

One component (pure) system

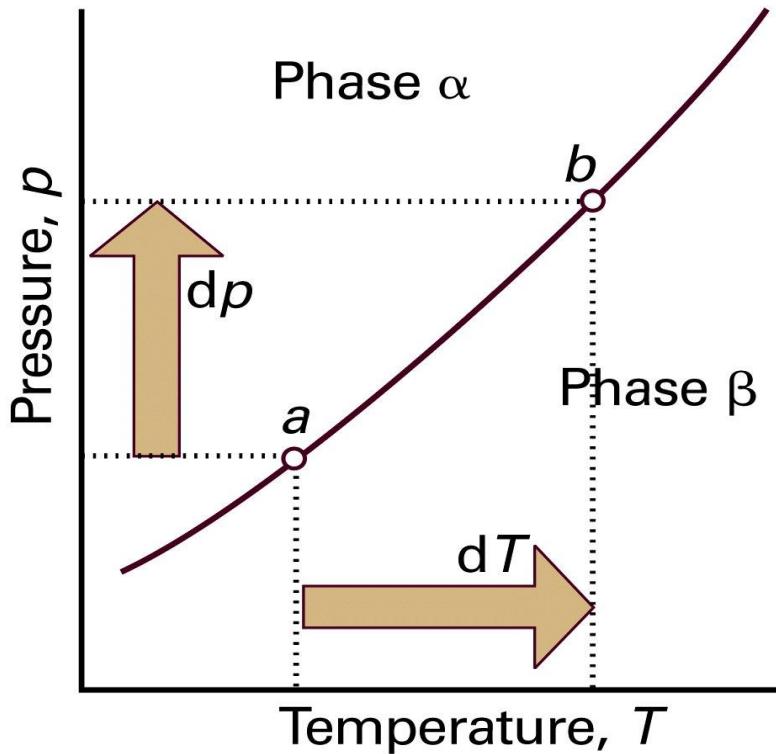


Figure 4-12  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

For point "a"

$$\mu^\alpha(p, T) = \mu^\beta(p, T)$$

For point "b"

$$\mu^\alpha(p+dp, T+dT) = \mu^\beta(p+dp, T+dT)$$

$$\mu^\alpha(p, T) + d\mu^\alpha = \mu^\beta(p, T) + d\mu^\beta$$

$$d\mu^\alpha = d\mu^\beta$$

$$d\mu = V_m dp - S_m dT$$

$$V_m^\alpha dp - S_m^\alpha dT = V_m^\beta dp - S_m^\beta dT$$

$$dp/dT = (S_m^\alpha - S_m^\beta) / (V_m^\alpha - V_m^\beta)$$

$$dp/dT = \Delta S_{m,\text{trs}} / \Delta V_{m,\text{trs}}$$

$$dT/dp = \Delta V_{\text{trs}} / \Delta S_{\text{trs}}$$

$$dp/dT = \Delta S_{\text{trs}} / \Delta V_{\text{trs}}$$

**The Clapeyron Equation**  
Applies to any phase equilibrium of any pure substance.

# (i) Solid to Liquid Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta S_{trs}}{\Delta V_{trs}} = \frac{\Delta H_{fus}}{T_{fus}\Delta V_{fus}}$$

If  $T_1$  is melting point at  $p_1$ , and  $T_2$  at  $p_2$

$$\int_{p_1}^{p_2} dp = \frac{\Delta H_{fus}}{\Delta V_{fus}} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta p = \frac{\Delta H_{fus}}{\Delta V_{fus}} \ln \frac{T_2}{T_1}$$

$$\text{for, } T_2 \approx T_1, \ln \frac{T_2}{T_1} = \ln(1 + \frac{T_2 - T_1}{T_1}) \approx \frac{T_2 - T_1}{T_1} = \frac{\Delta T}{T_1}$$

$$\Delta p = \frac{\Delta H_{fus}}{T_1 \Delta V_{fus}} \Delta T$$

$$\Delta T = \frac{T_1 \Delta V_{fus}}{\Delta H_{fus}} \Delta p$$

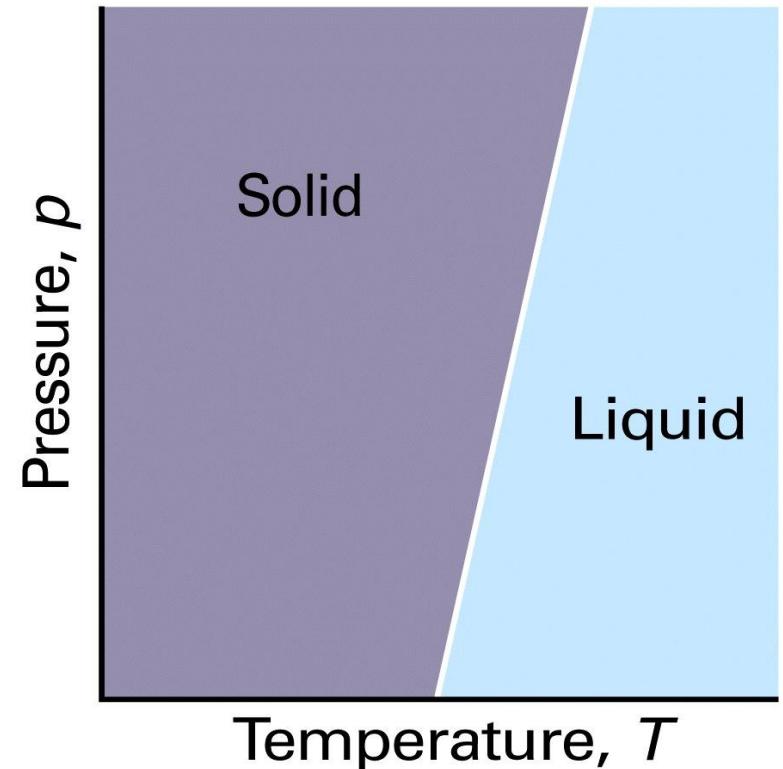


Figure 4-13  
*Atkins Physical Chemistry, Eighth Edition*  
© 2006 Peter Atkins and Julio de Paula

Melting point (linearly) rises with pressure

## (ii) Liquid to Vapor Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta S_{trs}}{\Delta V_{trs}} = \frac{\Delta H_{vap}}{T_{vap}\Delta V_{vap}}$$

$$\Delta V_{vap} = V_m(g) - V_m(l) \cong V_m(g) = RT/p \text{ (for ideal gas)}$$

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{TV_m} = \frac{\Delta H_{vap}}{T(RT)/p} \quad \text{(for ideal gas)}$$

$$\frac{dp}{p} \frac{1}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

$$\boxed{\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}}$$

**Clausius -Clapeyron Equation**

$$\int_{\ln p_1}^{\ln p_2} d \ln p = \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\boxed{\ln \frac{p_2}{p_1} = -\frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$p_2 = p_1 \exp(-\xi), \xi = \frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

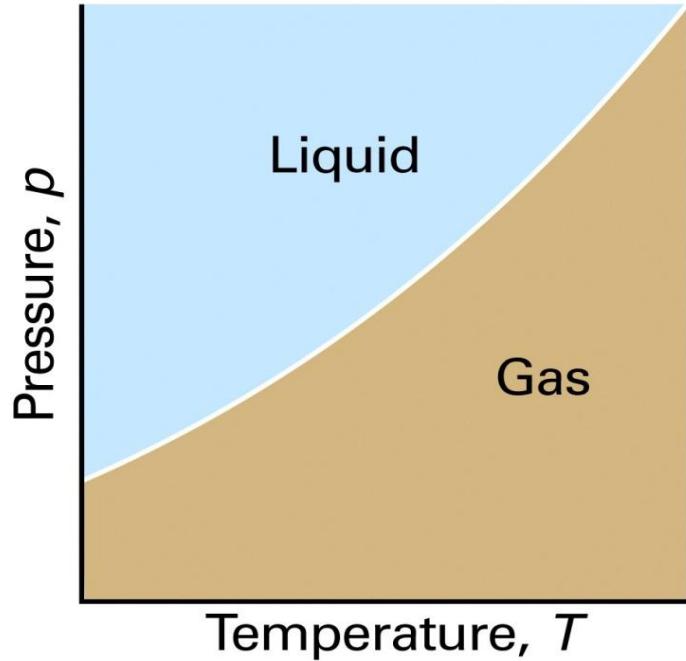


Figure 4-14  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

### (iii) Solid to Vapor Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta S_{trs}}{\Delta V_{trs}} = \frac{\Delta H_{sub}}{T_{sub}\Delta V_{sub}}$$

$$\Delta V_{sub} = V_m(g) - V_m(s) \cong V_m(g) = RT/p \text{ (for ideal gas)}$$

$$\frac{d \ln p}{dT} = \frac{\Delta H_{sub}}{RT^2}$$

$$\ln \frac{p_2}{p_1} = -\frac{\Delta H_{sub}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$p_2 = p_1 \exp(-\xi),$$

$$\xi = \frac{\Delta H_{sub}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$= \frac{\Delta H_{fus} + \Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

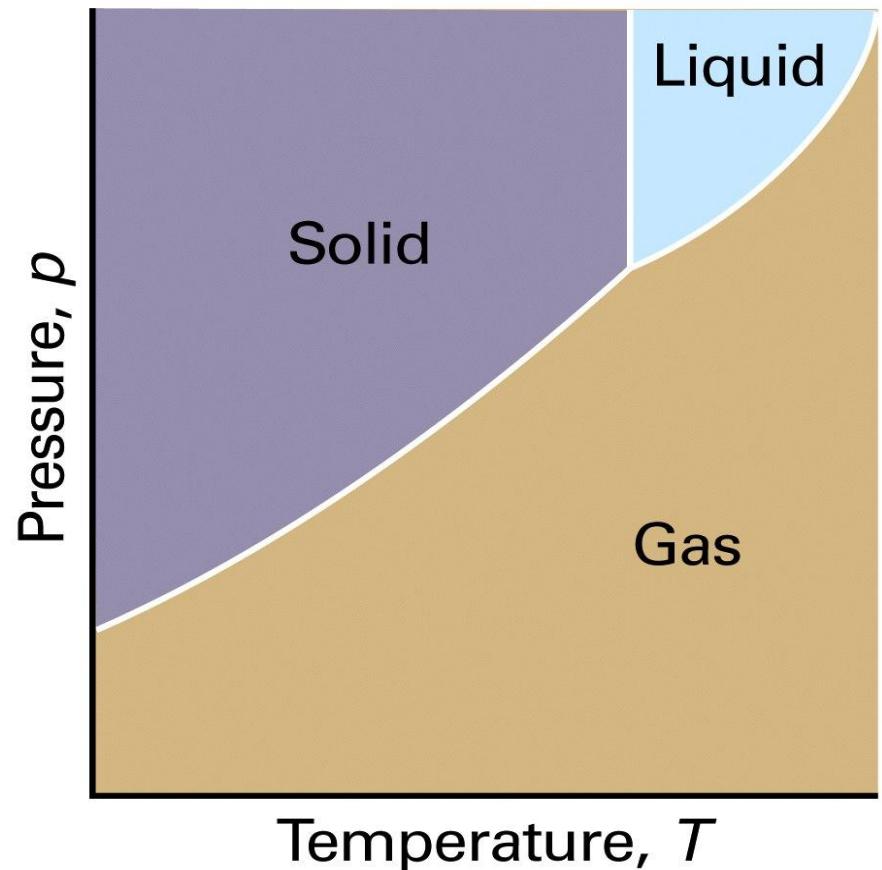


Figure 4-15  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

# Location and shape of phase boundary

One component (pure) system

Clapeyron Equation

$$dT/dp = \Delta V_{trs} / \Delta S_{trs}$$

Solid to Liquid Phase Boundary

$$\Delta T = \frac{T_1 \Delta V_{fus}}{\Delta H_{fus}} \Delta p$$

Liquid to Vapor Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{TV_m} = \frac{\Delta H_{vap}}{T(RT)/p}$$

**Clausius -Clapeyron Equation**

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

For Solid to Vapor

$$\frac{d \ln p}{dT} = \frac{\Delta H_{sub}}{RT^2} = \frac{\Delta H_{fus} + \Delta H_{vap}}{RT^2}$$

# Temperature Dependence of Chemical Potential:

$$dG = Vdp - SdT$$

$$d\mu = V_m dP - S_m dT$$

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

$$S_m(\text{solid}) < S_m(\text{liquid}) \ll S_m(\text{gas})$$

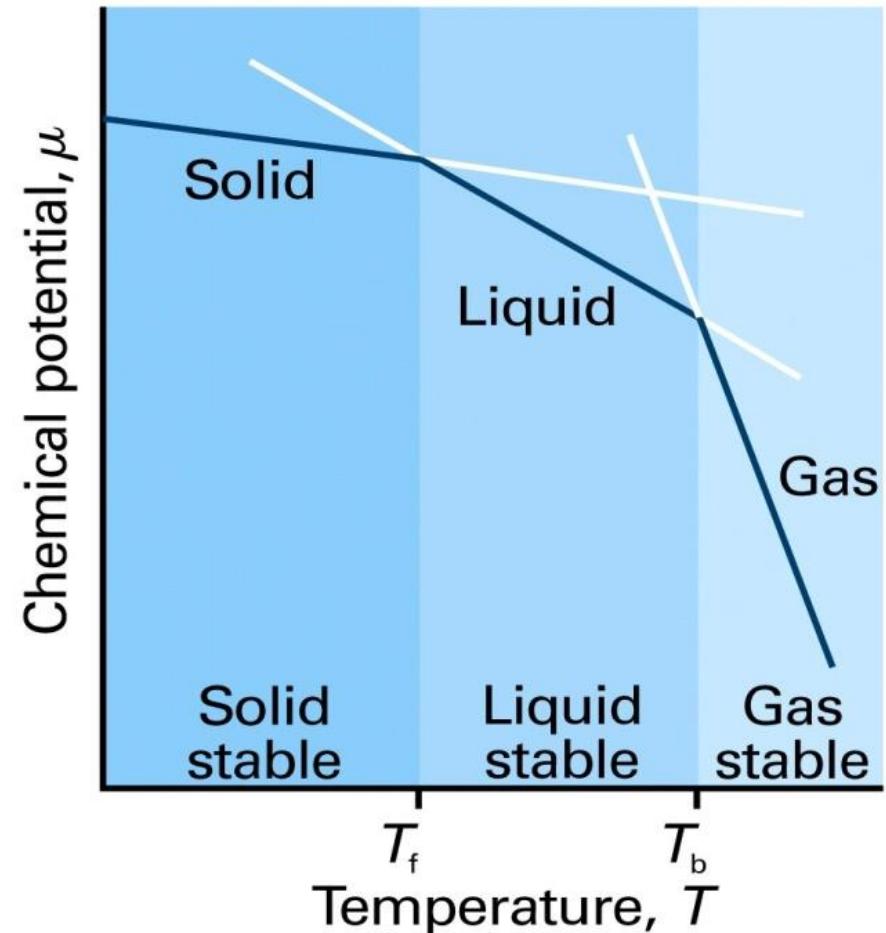
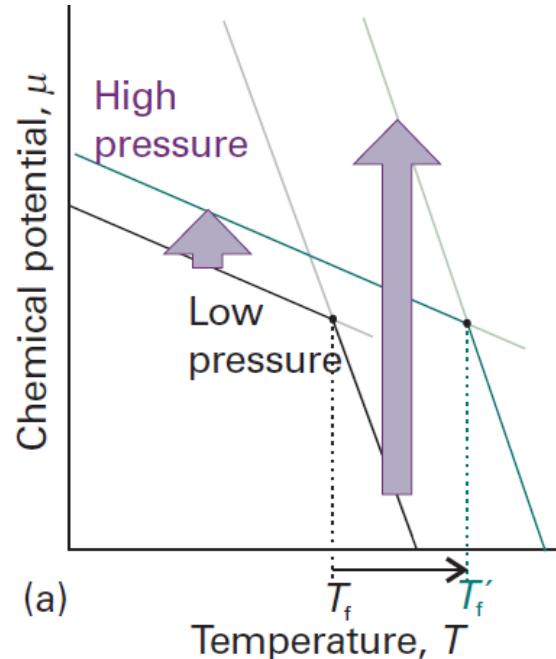


Figure 4-9  
*Atkins Physical Chemistry, Eighth Edition*  
© 2006 Peter Atkins and Julio de Paula

# Effect of pressure on Melting/Boiling Point

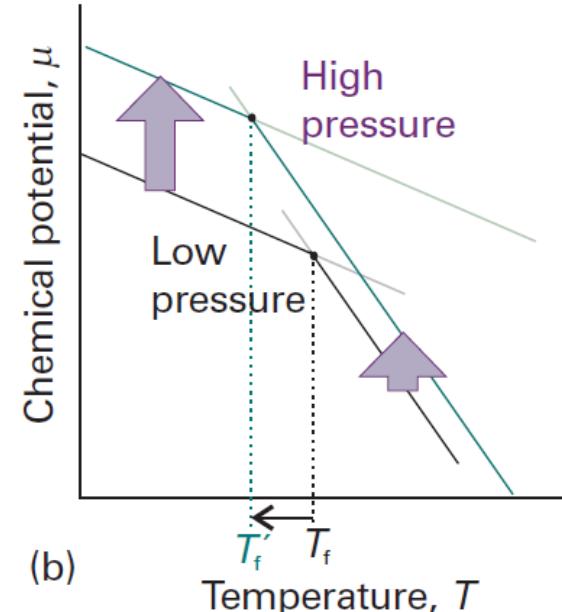
$$\left( \frac{\partial \mu}{\partial p} \right)_T = V_m$$

$$V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$



Melting point increases with pressure when  $V_m(l) > V_m(s)$

$$dG = Vdp - SdT$$
$$d\mu = V_m dP - S_m dT$$



Melting point decreases with pressure when  $V_m(l) < V_m(s)$

# (isothermal) Pressure dependence of Chemical Potential

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

$$\int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} V dp$$

$$G_2 = G_1 + \int_{p_1}^{p_2} V dp$$

for one component system,  $\mu_2(T) = \mu_1(T) + \int_{p_1}^{p_2} V_m dp$

Case 1: liquid or solid;  $V$  weakly dependent on  $p$

$$\mu_2(T) = \mu_1(T) + V_m(p_2 - p_1)$$

for one component system

Case 2: ideal gas;  $V$  is dependent on  $p$ ,

$$\mu_2(T) = \mu_1(T) + RT \ln \frac{p_2}{p_1}$$

$$\mu(T) = \mu^o(T) + RT \ln \frac{p}{p^o}$$

$$\mu(T) = \mu^o(T) + RT \ln p$$

$\mu^o$  = standard chemical potential, the chemical potential of the pure gas at 1 bar at temp  $T$ .

$p$  expressed in bar.

# Chemical Potential of Pure Real Gas

$$\mu(T) = \mu^\circ(T) + RT \ln f$$

$f$  = fugacity, an effective pressure in bar =  $\phi p$

$$= \mu^\circ(T) + RT \ln \phi p$$

$\phi$  = fugacity coefficient

$$= \mu^{\text{ideal}}(T) + RT \ln \phi$$

$$\ln \phi = \int_0^p \frac{Z-1}{p} dp \quad Z = \text{Compressibility factor}$$

At low pressure,

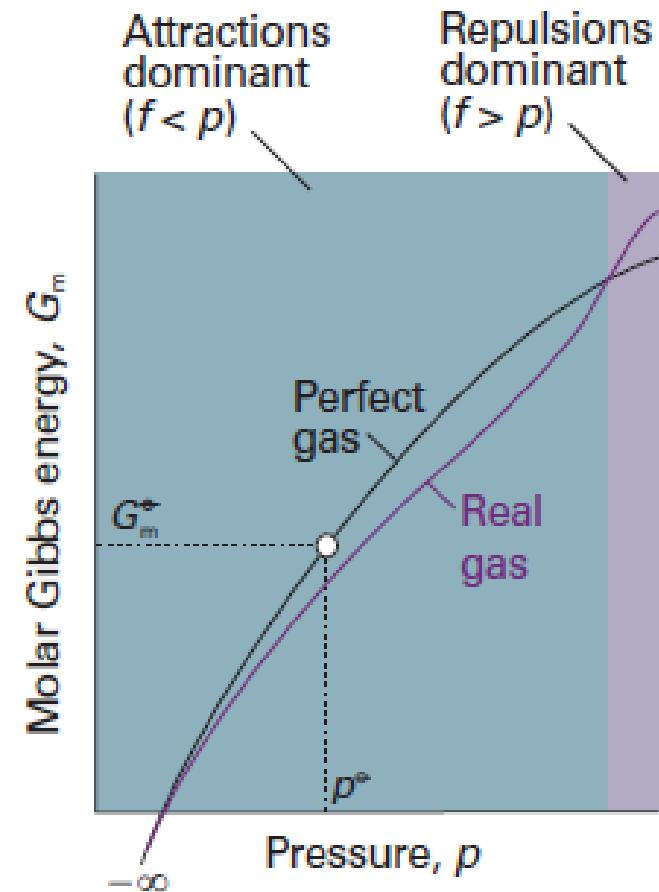
$$Z < 1 \Rightarrow \ln \phi < 0 \Rightarrow \boxed{\mu^{\text{real}} < \mu^{\text{ideal}}}$$

$$\phi < 1 \Rightarrow f < p$$

At high pressure,

$$Z > 1 \Rightarrow \ln \phi > 0 \Rightarrow \boxed{\mu^{\text{real}} > \mu^{\text{ideal}}}$$

$$\phi > 1 \Rightarrow f > p$$

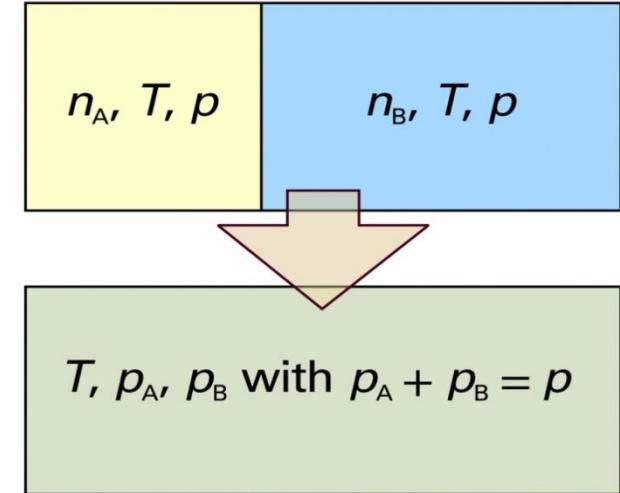


# The Gibbs Energy of Mixing of Ideal Gases

$$\mu_i(T) = \mu_i^o(T) + RT \ln p_i \quad p_i = \text{partial pressure of } i^{\text{th}} \text{ gas in bar.}$$

Before mixing:

$$G_{\text{before mixing}} = \sum_i n_i (\mu_i^o(T) + RT \ln p_i)$$



After mixing:

$$\begin{aligned} G_{\text{mixture}} &= \sum_i n_i \mu_i = \sum_i n_i (\mu_i^o(T) + RT \ln p_i) \\ &= \sum_i n_i (\mu_i^o(T) + RT \ln \chi_i p) \end{aligned}$$

Dalton's law of partial pressure,  $p_i = \chi_i p$

$$\Delta G_{\text{mix}} = nRT \sum_i \chi_i \ln \chi_i$$

Gibbs free energy of mixing of ideal gases is always negative, and hence spontaneous

# The Enthalpy of Mixing of Ideal Gases

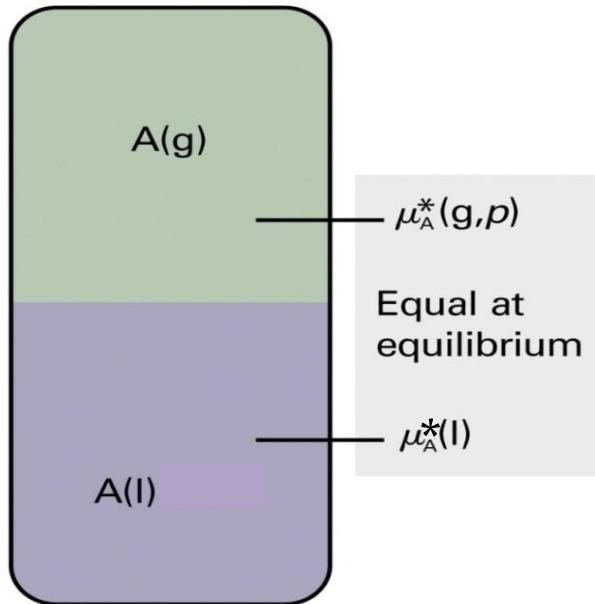
$$\Delta G_{mix} = nRT \sum_i \chi_i \ln \chi_i$$

$$\Delta S_{mix} = -\left( \frac{\partial(\Delta G_{mix})}{\partial T} \right)_{p,n} = -nR \sum_i \chi_i \ln \chi_i$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0$$

Ideal gases show no  
intermolecular interactions and  
hence change in enthalpy is zero

# Chemical Potential of Liquids: Ideal Solutions



\* means pure

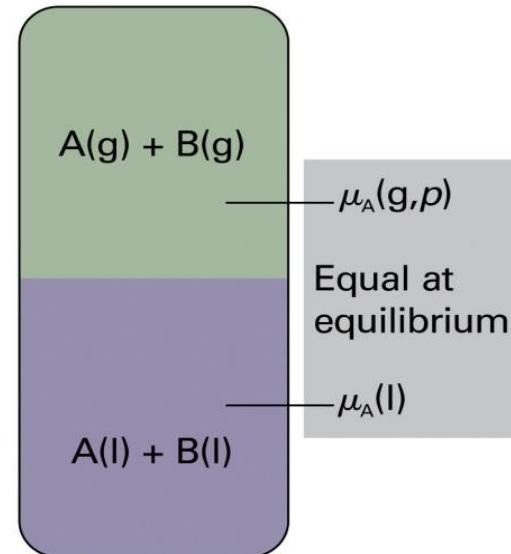


Figure 5-10  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

$$\mu_{A,l}^* = \mu_{A,g}^* = \mu_{A,g}^0 + RT \ln p_A^*$$

$$\mu_{A,g}^0 = \mu_{A,l}^* - RT \ln p_A^*$$

$$\mu_{A,l} = \mu_{A,g} = \mu_{A,g}^0 + RT \ln p_A$$

$$\mu_{A,l} = \mu_{A,l}^* - RT \ln p_A^* + RT \ln p_A$$

$$\mu_{A,l} = \mu_{A,l}^* + RT \ln \frac{p_A}{p_A^*}$$

$$\mu_{A,l} = \mu_{A,l}^* + RT \ln \frac{p_A}{p_A^*}$$

$p_A^*$  vapour pressure of pure A(l)  
 $p_A$  vapour pressure of A(l) in a mixture

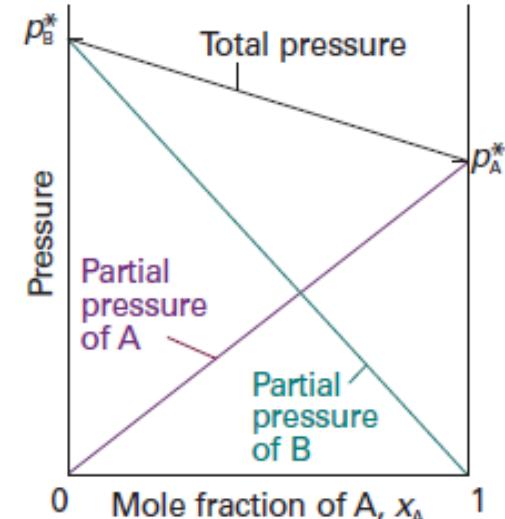
*Relationship between ratio of vapor pressures and composition of liquid.*

# Raoult's Law

$$\frac{p_A}{p_A^*} = \chi_A$$

$$p_A = \chi_A p_A^*$$

The ratio of partial vapor pressure of each component to its vapor pressure as a pure liquid is equal to the mole fraction A in the liquid mixture ( $\chi_A$ ).



Ideal solutions obey Raoult's law for the entire range of mole fraction, from pure A to pure B

$$\mu_{A,l} = \mu_{A,l}^* + RT \ln \chi_A$$

$$\mu_{B,l} = \mu_{B,l}^* + RT \ln \chi_B$$

For ideal solution - *solvent* & *solute* both obey Raoult's law

$$p_A < p_A^*$$

$$\mu_{A,l} < \mu_{A,l}^*$$

The vapor pressure (and chemical potential) of the solvent in the solution is lower than that of the pure solvent

Fig. 5.11 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

# Ideal-Dilute Solutions

**Henry's Law:** In dilute solution, **for solute**, B

$$p_B \propto \chi_B \quad \text{but} \quad p_B \neq \chi_B p_B^*$$

$$p_B = \chi_B K_B$$

For practical applications

$$p_B = b_B K_B \quad b_B = \text{molality of } B$$

$K_B$  = Empirical constant (dimension of  $p$ )  
called Henry's law constant

Solutions in which solvent obeys Raoult's law and  
solute obeys Henry's law is an **Ideal-Dilute** solution

$$\begin{aligned}\mu_B &= \mu_B^* + RT \ln(p_B / p_B^*) \\ &= \mu_B^* + RT \ln(\chi_B K_B / p_B^*) \\ &= \mu_B^* + RT \ln(K_B / p_B^*) + RT \ln \chi_B \\ &= \mu_B^0 + RT \ln \chi_B\end{aligned}$$

if  $p_B^* = K_B \Rightarrow \mu_B^0 = \mu_B^*$

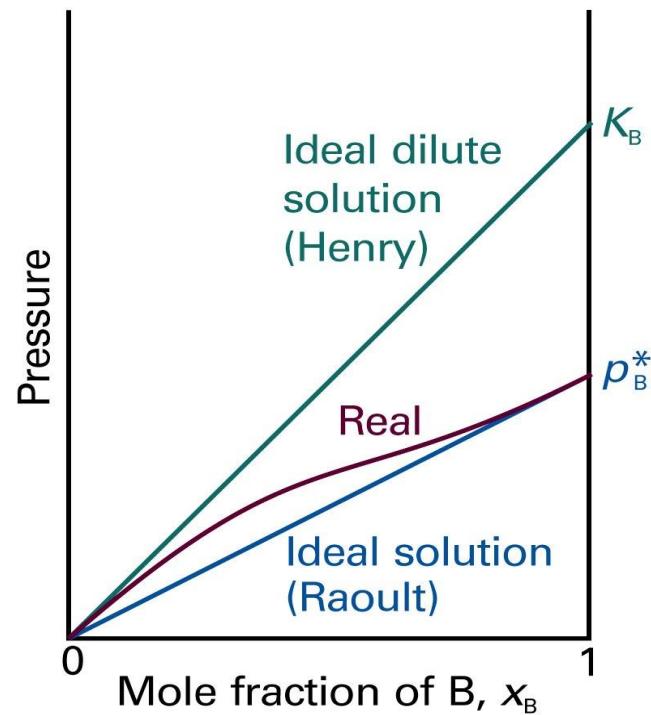


Figure 5-15  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

# Real Solutions: (Activity, the effective mole fraction)

## The Solvent Activity

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

For ideal solution (Raoult's law)

$$\mu_A = \mu_A^* + RT \ln \chi_A$$

For real solution

$$\mu_A = \mu_A^* + RT \ln a_A$$

$$a_A = \frac{p_A}{p_A^*}$$

$$a_A = \chi_A \quad \text{as } \chi_A \rightarrow 1$$

$$a_A = \gamma_A \chi_A ; \quad \gamma_A \rightarrow 1 \quad \text{as } \chi_A \rightarrow 1$$

$\gamma_A$  is activity coefficient

## The Solute Activity:

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*}$$

For Ideal Dilute Solution (Henry's law)

$$\mu_B = \mu_B^0 + RT \ln \chi_B$$

For real solutions,

$$\mu_B = \mu_B^0 + RT \ln a_B$$

$$a_B = \gamma_B \chi_B$$

$$a_B \rightarrow \chi_B \text{ and } \gamma_B \rightarrow 1 \text{ as } \chi_B \rightarrow 0$$

LECTURE  
**13**

CY11001  
Spring 2015-16

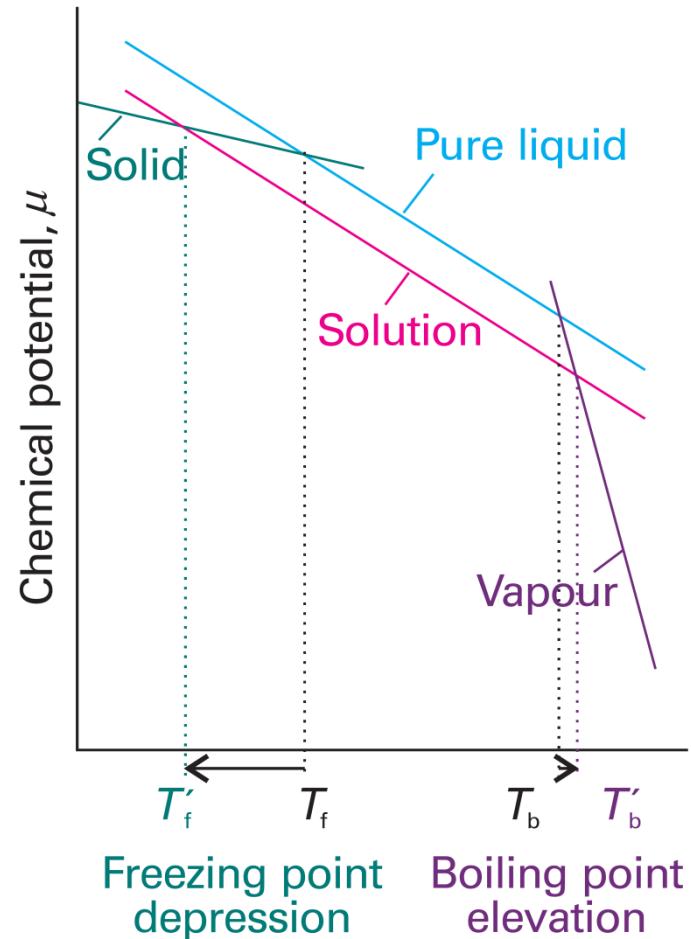


Department of Chemistry  
Indian Institute of Technology  
Kharagpur

# Effect of solute on boiling and melting points of solvent

$$\mu_A = \mu_A^* + RT \ln \chi_A$$

$$\mu_A = \mu_A^* + RT \ln a_A$$



# Thermodynamics of Simple Mixtures

## Partial Molar Volume

1 mol of water added to a huge volume of water increases the volume by 18 cm<sup>3</sup>.

$$V_m = 18 \text{ cm}^3/\text{mol}$$

1 mol of water added to a huge volume of *ethanol* increases the volume by 14 cm<sup>3</sup>.

$$V_m = 14 \text{ cm}^3/\text{mol}$$

$$V_i = \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n_{j \neq i}} \quad \text{Partial Molar Volume} \quad \text{Can be +ve, -ve, or 0!}$$

$$dV = \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n_B} dn_A + \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$$

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A n_A + V_B n_B$$

$$G_{p,T} = n_1 \mu_1 + n_2 \mu_2 + \dots = \sum_i n_i \mu_i$$

# Gibbs-Duhem Equation

$$G_{p,T} = n_1\mu_1 + n_2\mu_2 + \dots = \sum_i n_i \mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i$$

At thermal and mechanical equilibrium.

At constant  $p$  and  $T$

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

**Gibbs-Duhem Equation**

For a binary mixture,  $n_1 d\mu_1 + n_2 d\mu_2 = 0$

Hence,  $d\mu_1 = - (n_2/n_1) d\mu_2$

If  $n_2 > n_1$ , a small change in  $\mu_2$  causes a large change in  $\mu_1$

Chemical potential of one component of a mixture can not change independently of the chemical potentials of other components.

## Mixing of Ideal Solutions

$$G_i = n_A \mu_A^* + n_B \mu_B^*$$

$$G_f = n_A (\mu_A^* + RT \ln \chi_A) + n_B (\mu_B^* + RT \ln \chi_B)$$

$$\Delta G_{mix} = nRT \sum_i \chi_i \ln \chi_i$$

$$\Delta S_{mix} = -nR \sum_i \chi_i \ln \chi_i$$

$$\Delta H_{mix} = 0$$

$$\Delta V_{mix} = \left( \frac{\partial \Delta G_{mix}}{\partial p} \right)_T = 0$$

## Mixing of Real Solutions (excess functions)

$$S^E = \Delta S_{mix} - \Delta S_{mix}(ideal)$$

Excess entropy

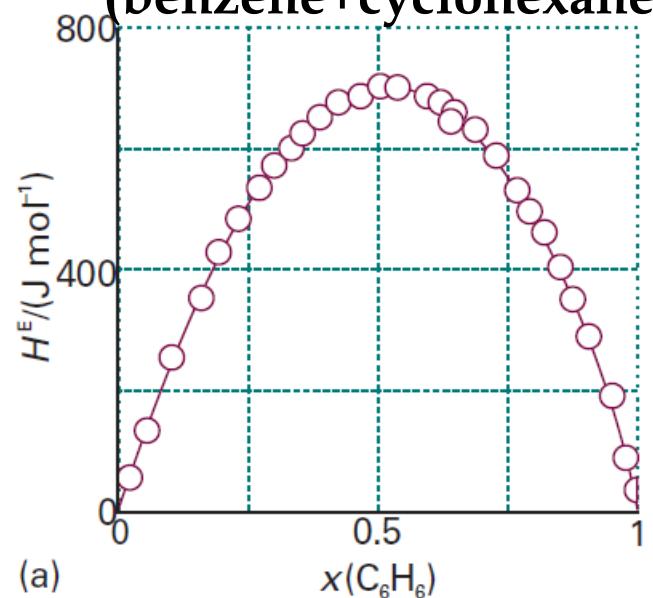
Interaction<sub>AB</sub> < Interaction<sub>AA</sub>  
Interaction<sub>AB</sub> < Interaction<sub>BB</sub>

Ideal solution - Raoult's law

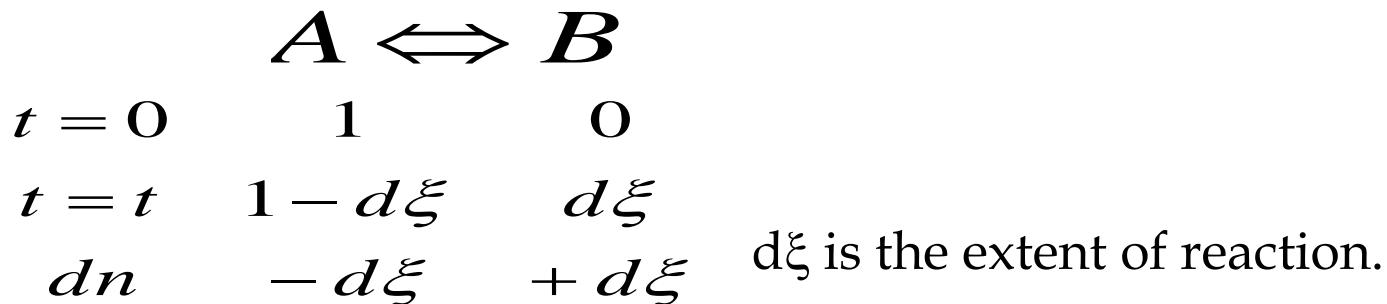
Leading to ideal solution, similar to mixing of ideal gases.

Interaction<sub>AB</sub> = Interaction<sub>AA</sub> = Interaction<sub>BB</sub>

**Excess enthalpy  
(benzene+cyclohexane)**



# Reaction Gibbs Energy ( $\Delta_r G$ )



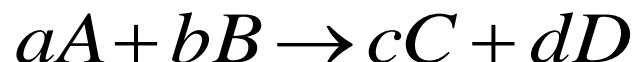
$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

$$\left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_B - \mu_A$$

$$\boxed{\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_B - \mu_A}$$

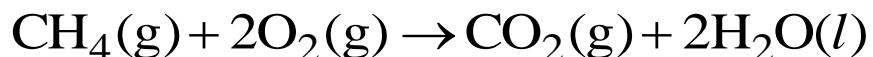
The reaction Gibbs energy is the difference between the chemical potential of product and reactant at the *composition of the reaction mixture*.

# Reaction Gibbs Energy ( $\Delta_r G$ )



$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p,T} = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$$

$$\boxed{\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_i \nu_i \mu_i}$$



$$\Delta_r G = (2\mu_{\text{H}_2\text{O}(l)} + \mu_{\text{CO}_2(g)}) - (\mu_{\text{CH}_4(g)} + 2\mu_{\text{O}_2(g)})$$

At equilibrium,

$$\boxed{\sum_i \mu_i \nu_i = 0}$$

Condition for chemical reaction equilibrium.

At the reaction equilibrium, the chemical potentials of the product balance those of the reactants

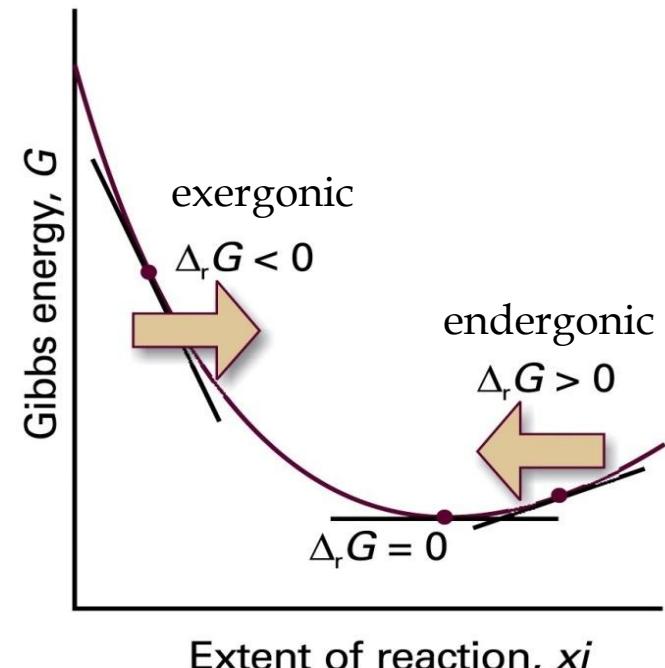


Figure 7-1  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

# Reaction Equilibrium

$$\begin{aligned}\Delta_r G &= \sum_i v_i \mu_i = \sum_i v_i [\mu_i^0(T) + RT \ln a_i] \\ &= \sum_i v_i \mu_i^0(T) + \sum_i RT \ln a_i^{v_i}\end{aligned}$$

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln \prod_i a_i^{v_i} = \Delta_r G^0(T) + RT \ln Q$$

$$Q = \prod_i a_i^{v_i}$$

The reaction Quotient  
(at any extent of the reaction)

At equilibrium,

$$K = \left[ \prod_i a_i^{v_i} \right]_{\text{at equilibrium}}$$

Thermodynamic  
equilibrium constant

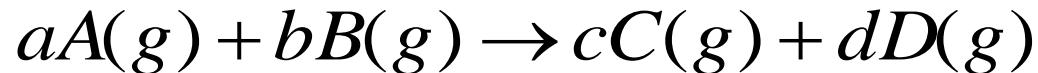
$$\Delta_r G(T) = 0 = \Delta_r G^0(T) + RT \ln K$$

Practically  $a_i$  approximated by numerical values of molalities /  
by molar concentration / numerical values of partial pressures

$$\Delta_r G^0 = -RT \ln K$$

Can be used to calculate  
equilibrium constant for any  
reaction from tables of  
thermodynamic data.

# Reaction Equilibrium in ideal gas reaction



$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln Q$$

$$Q = \prod_i a_i^{v_i} = \prod_i \left( \frac{p_i}{p^0} \right)^{v_i}$$

The reaction Quotient in terms of partial pressure (at any extent of reaction)  
 $p^0 = 1 \text{ bar}$

At equilibrium,

$$K_p = \prod_i \left( \frac{p_i}{p^0} \right)^{v_i} \text{ (at equilibrium)}$$

$$\Delta_r G(T) = 0 = \Delta_r G^0(T) + RT \ln K_p$$

$$\Delta_r G^0 = -RT \ln K_p$$

# Different types of equilibrium constants

$$K = \left[ \prod_i a_i^{\nu_i} \right]_{equilibrium}$$

Thermodynamic equilibrium constant in terms of activity coefficients ( $a_i$ )

$$K_p = \left[ \prod_i p_i^{\nu_i} \right]_{equilibrium}$$

Standard equilibrium constant for gaseous reaction  
 $p_i$  **(in bar units)**

$$K_c = \left[ \prod_i c_i^{\nu_i} \right]_{equilibrium}$$

Standard concentration equilibrium constant.  
 $c_i$  **in mol/L**

$$K_\chi = \left[ \prod_i \chi_i^{\nu_i} \right]_{equilibrium}$$

Mole-fraction equilibrium constant

# Response of equilibria to pressure change



$t = 0$	1	0
at eqlbr	$1 - \alpha$	$2\alpha$

$\alpha$  is the degree of dissociation

$$\begin{aligned} \chi_i & \frac{1 - \alpha}{1 + \alpha} & \frac{2\alpha}{1 + \alpha} \\ p_i & \frac{1 - \alpha}{1 + \alpha} p & \frac{2\alpha}{1 + \alpha} p \end{aligned}$$

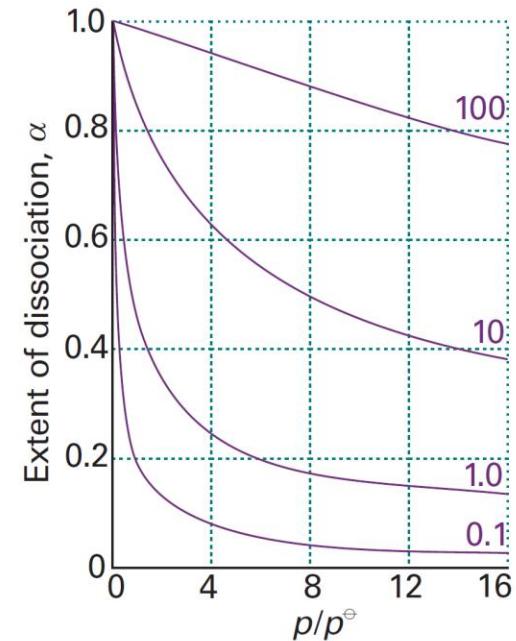
$p$  is in bar

$$K_p = \prod_i \left( \frac{p_i}{p^0} \right)^{\nu_i} = \frac{4\alpha^2}{1 - \alpha^2} p$$

$$\text{But we know, } \left( \frac{\partial K_p}{\partial p} \right)_T = 0$$

$$\alpha = \left( \frac{1}{1 + \frac{4p}{K_p}} \right)^{1/2}$$

Le-Chatelier principle



**Fig. 7.7** The pressure dependence of the degree of dissociation,  $\alpha$ , at equilibrium for an  $A(g) \rightleftharpoons 2 B(g)$  reaction for different values of the equilibrium constant  $K$ . The value  $\alpha = 0$  corresponds to pure A;  $\alpha = 1$  corresponds to pure B.

# Temperature dependence of equilibrium constant

$$\Delta_r G^0 = -RT \ln K$$

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^0 / T)}{dT}$$

$$\frac{d(\Delta_r G^0 / T)}{dT} = -\frac{\Delta_r H^0}{T^2} \text{ (GibbsHelmholtzEquation)}$$

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2}} \quad \text{van't Hoff equation}$$

For exothermic reactions,  $K$  decreases with increasing  $T$

$$\boxed{\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$