

Why Thermodynamics

Natural processes

Modeling in Sciences

**geometry** (shapes and behaviour of particles/system)  $\iff$  **Linear Algebra**

**change** (evolution with time other relevant parameters)  $\iff$  **calculus**

**Chance**  $\iff$  **Probability**

## Macroscopic and microscopic processes

relevant questions :

- ▶ Why do things happen unidirectionally,
  - ▶ e.g. aging, falling of a leaf from a tree, etc.
- ▶ Is there a **quantitative** way of characterising **spontaneity**?

Microscopic Disorder  $\Leftarrow$

dynamical laws:

classical : Newton/Lagrange/Hamilton( $\dot{p}, \dot{q}$ )

stochastic (random forces) : Langevin

QM : Langevin, Schrödinger

The law of large numbers(Central Limit Theorem)

Grand journey from bi(multi)-nomial to Gaussian

Thermodynamics  $\implies$  Entropy, Free energy



Criteria for stability and equilibrium- Criteria for spontaneity

Construct a system appropriately  $\leftarrow \leftarrow \begin{cases} \text{physically meaningful B.C.} \\ \text{inter-particle interactions} \end{cases}$



molecular dynamics : monte carlo simulations



equilibrium properties

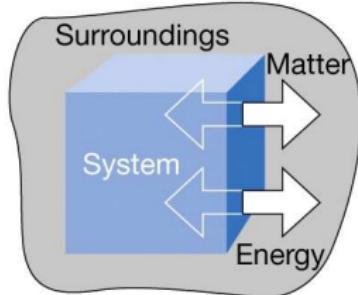
## Thermodynamic space

Thermodynamic state : A point in the thermodynamic space is a description of a system in terms of macroscopic variables -  $n, p V T, \dots$

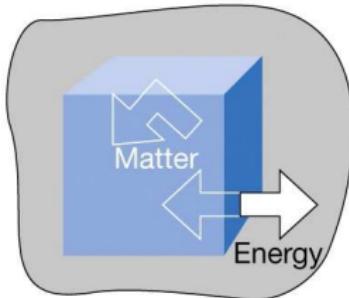
physical state of a sample of a substance, its physical condition  
is defined by its physical properties

Two samples of same substance with same physical properties  
are in the same **state**

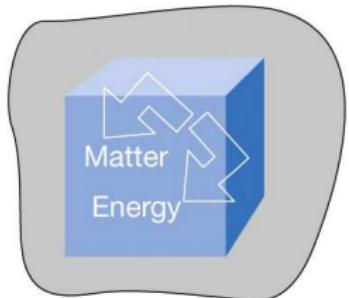
## Thermodynamic systems :



(a) Open



(b) Closed



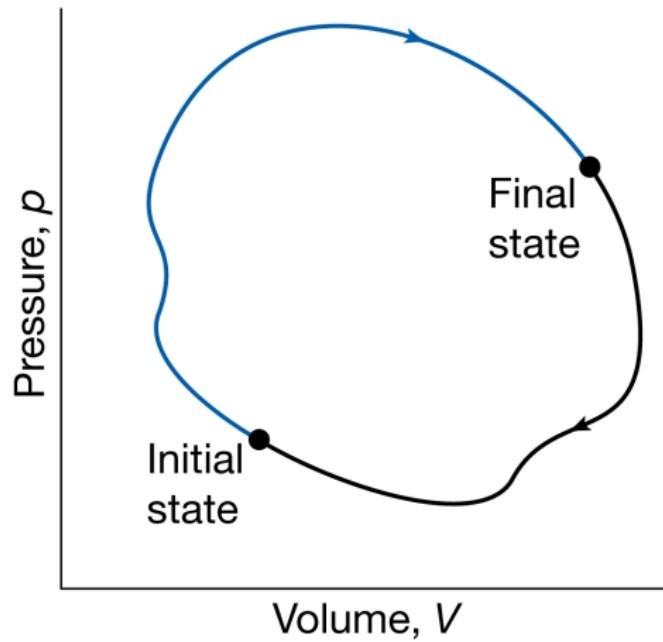
(c) Isolated

Variables, functions, processes, paths,

**state** functions

**path** functions

cyclic process :  $\oint dX = 0$  , if  $X$  is a state function



Wall : Whatever separates

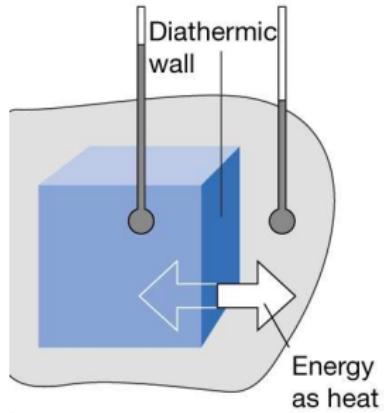
a system from its surroundings

or one system from another

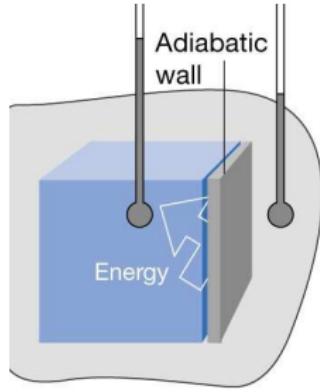
or a system from its subsystems

## Heat : flow of energy

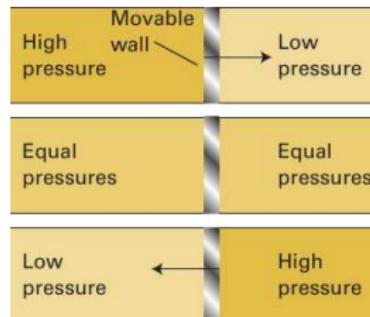
Diathermal wall  
allows heat flow both ways



adiabatic wall does not  
allow heat flow



## Mechanical motion - **Movable** and **rigid** walls

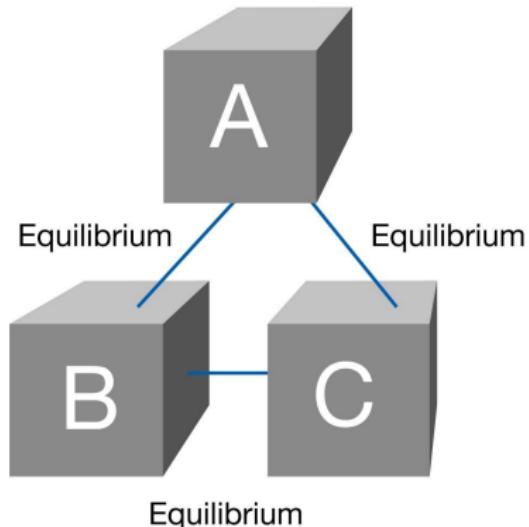


## Mass flow : **Permeable** and **impermeable** walls

What equilibrium thermodynamics **does not** deal with :

- ▶ time
- ▶ and rate at which processes occur

## Zeroth Law of thermodynamics



If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C then systems A and C are in thermal equilibrium with each other

The qualitative observation is quantified by associating a parameter with each system, which is a real number, called Temperature

$$\forall x_i \in \mathcal{R}, \text{ if } x_A = x_B \text{ and } x_B = x_C \implies x_A = x_C$$

Bulk matter

States of matter : solid, liquid, gas

Properties of bulk matter : **mass**, **volume**, **composition**

**extensive** property : depends on amount of substance present in the sample

**intensive** property : independent of amount of substance present

Modeling a gas :

Perfect gas:  $pV = nRT$

What is perfect or ideal about it?

$\therefore$  it is perfect

$\therefore$  it does not exist

A good example of **Reductionism** in modern science

SATP : 298.15 K and 1 bar (exactly  $10^5$  Pa);  $V_m = \frac{RT}{p} = 24.789 \text{ dm}^3 \text{ mol}^{-1}$

STP : 0°C and 1 atm; molar volume of a perfect gas,  $V_m = 22.414 \text{ dm}^3 \text{ mol}^{-1}$

All gases obey perfect gas equation ever more closely as  $p \rightarrow 0$

Perfect gas law is a limiting law

normal atmospheric pressure at sea level ( $\approx 1$  atm) is already low enough for most gases to behave almost perfectly

**molecular explanation** of Boyle's law :

if a sample of gas is compressed to half its volume, then twice as many molecules strike the walls in a given period of time than before it was compressed

⇒ average force exerted on the walls is doubled

∴ when the volume is halved, pressure is doubled, and  $pV$  is a constant

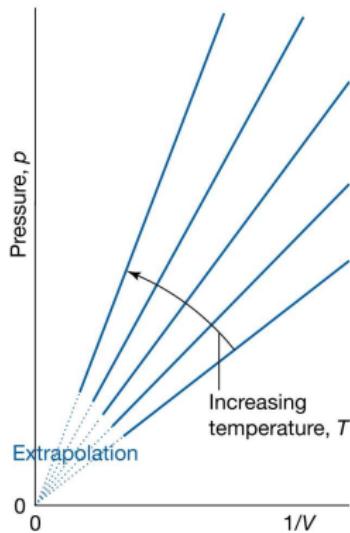
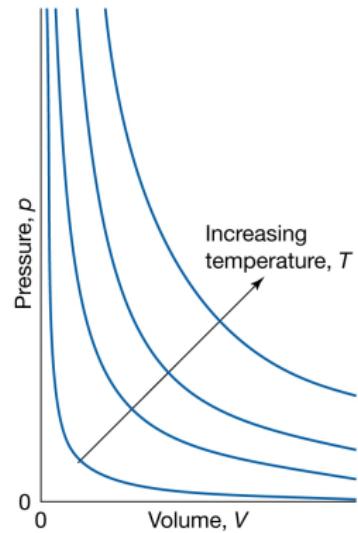
Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently

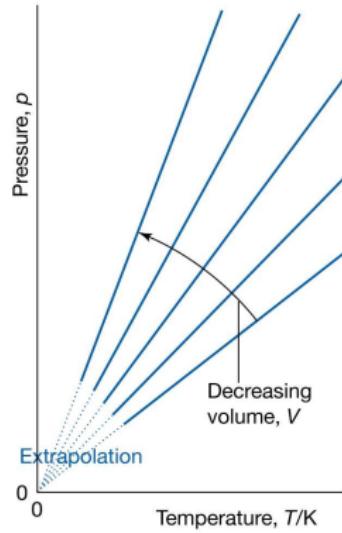
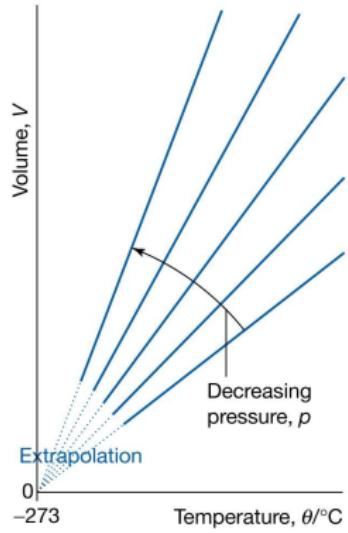
**molecular explanation** of Charles's law :

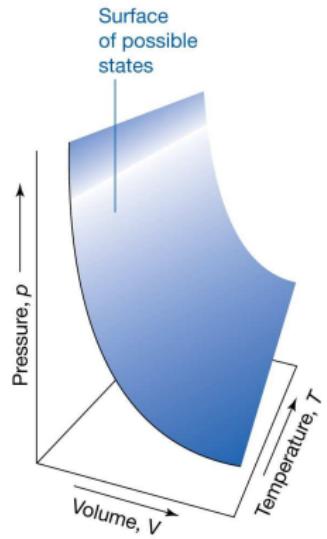
raising temperature of a gas increases average speed of molecules

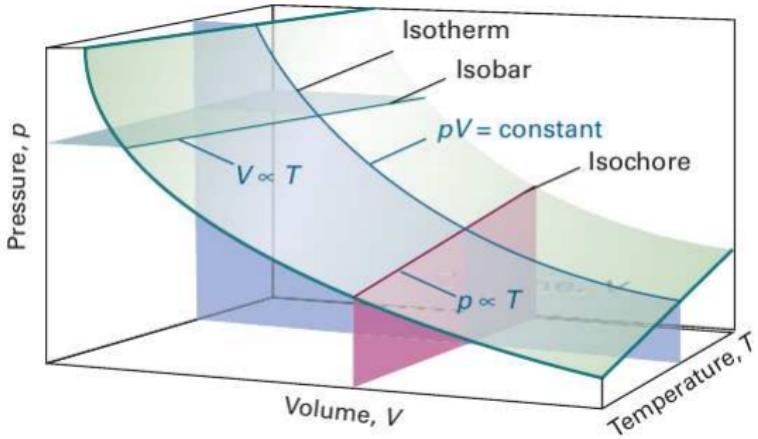
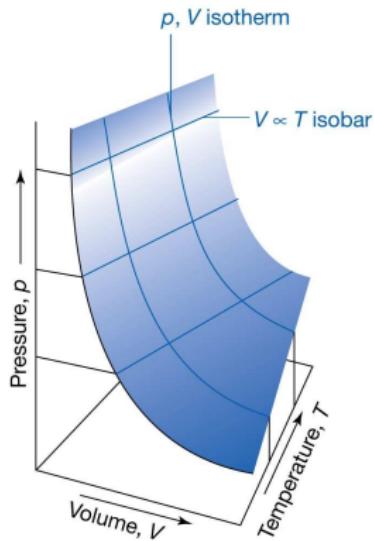
molecules collide with the walls more frequently and with greater impact  
⇒ exert greater pressure on the walls of the container

p-V-T plots : Boyle's/Charles' law and perfect gases:

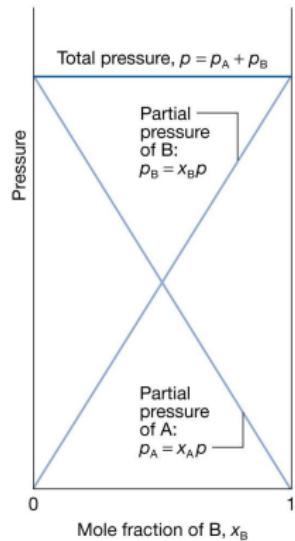




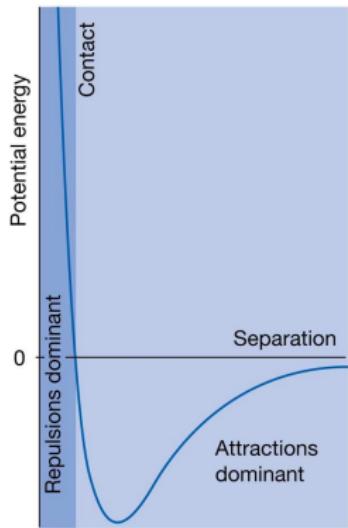




## mixtures - partial pressures :



real gases :



$$\text{van der Waals equation : } p = \frac{nRT}{V-nb} - a \left( \frac{n}{V} \right)^2 \equiv \frac{RT}{V_m-b} - \frac{a}{V_m^2}$$

- ▶ repulsive interactions cause molecules to behave as small but impenetrable spheres
- ▶ non-zero volume of molecules implies restriction to smaller volume  $V - nb$   
where  $nb \approx$  total volume taken up by molecules

$\Rightarrow$  gas law should be replaced by  $p = \frac{nRT}{V-nb}$  for significant repulsions

- ▶ closest distance of two hard-sphere molecules of radius  $r$ , is  $2r$ 
  - ▶ volume excluded =  $\frac{4}{3}\pi (2r)^3 = 8V_{\text{molecule}}$
- ▶ volume excluded per molecule =  $4V_{\text{molecule}}$        $\therefore b = 4V_{\text{molecule}} \cdot N_A$
- ▶ pressure depends on
  - ▶ frequency of collisions with walls
  - ▶ and force of each collision

Both reduced by attractive forces of strength  $\propto$  molar concentration,  $\frac{n}{V}$

- ▶  $\therefore$  pressure is reduced in proportion to square of concentration
- ▶ reduction of pressure =  $-a \left( \frac{n}{V} \right)^2 \Rightarrow p = \frac{nRT}{V-nb} - a \left( \frac{n}{V} \right)^2 \equiv \frac{RT}{V_m-b} - \frac{a}{V_m^2}$

$$\text{van der Waals equation : } p = \frac{nRT}{V-nb} - a \left( \frac{n}{V} \right)^2 \equiv \frac{RT}{V_m-b} - \frac{a}{V_m^2}$$

solved problem : Estimate molar volume of  $\text{CO}_2$  at 500 K and 100 atm treating it as a van der Waals gas , given  $\begin{cases} a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2} \\ b = 4.257 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \end{cases}$

$$(V_m - b) V_m^2 p = RT V_m^2 - (V_m - b) a$$

$$\text{get cubic eqn. for } V_m : x^3 - \left( b + \frac{RT}{p} \right) x^2 + \left( \frac{a}{p} \right) x - \frac{ab}{p} = 0$$

$$\text{or, } x = 0.366 \text{ dm}^3 \text{ mol}^{-1} \text{ (perfect gas : } 0.41 \text{ dm}^3 \text{ mol}^{-1})$$

To what extent does the van der Waals equation predict behaviour of real gases?

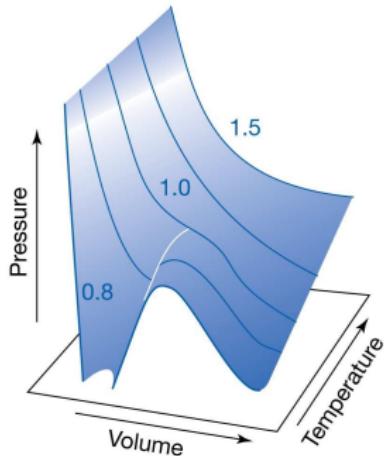
too optimistic to expect a single simple expression to be eqn. of state of all things

advantage :

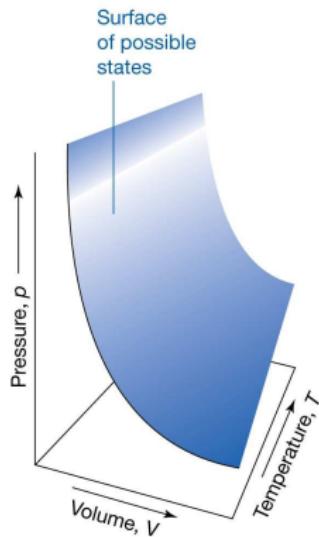
- ▶ analytical equation
- ▶ allows us to draw some general conclusions about real gases

Isotherms reflect consequences of interactions

van der Waals (label  $T/T_C$ )



perfect gas



low pressures - large volume : molecules far apart for most of the time and intermolecular forces play no significant role  
gas behaves virtually perfectly

#### moderate pressures :

average separation of molecules  
a few molecular diameters

**attractive forces dominate**

gas more compressible than perfect gas because the forces help to draw molecules together

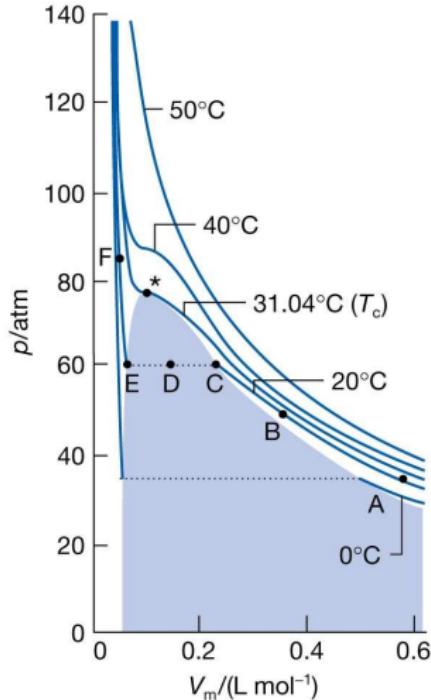
#### high pressures :

average separation of molecules small

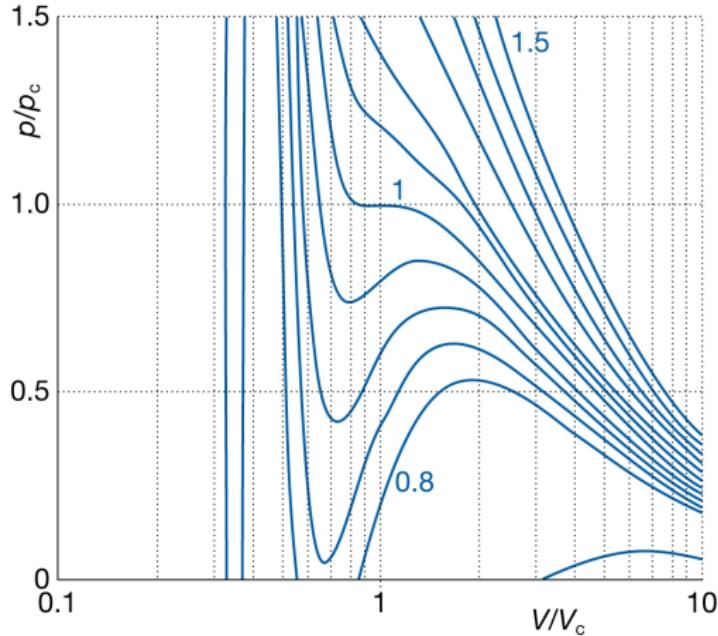
**repulsive forces dominate**

gas less compressible because the forces help to drive molecules apart

experimental data for CO<sub>2</sub>

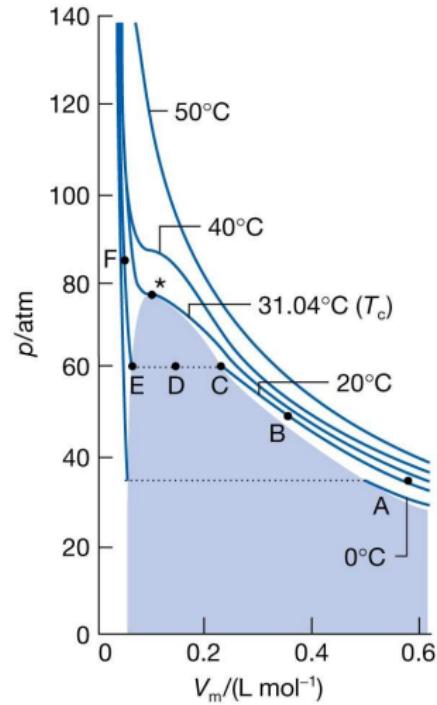


van der Waals isotherms at several values of  $\frac{T}{T_c}$

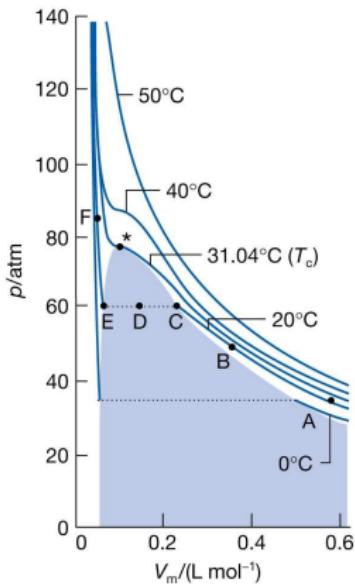


critical isotherm is for  $\frac{T}{T_c} = 1$

experimental data for CO<sub>2</sub>



compress gas initially n state A at constant  $T$  by pushing a piston



Near A, pressure rises  
≈ as in Boyle's law

► Increase pressure  
move along A-B-C

At C ( $\approx 60$  atm for  $\text{CO}_2$ ) :

all similarity to perfect behaviour is lost  
suddenly piston slides in

without any rise in pressure: **horizontal line CDE**

just to the left of C, liquid appears, and there are two phases separated by a sharply defined surface  
As volume is decreased from C through D to E, the amount of liquid increases

line CDE : both liquid and vapour are present in equilibrium- pressure is vapour pressure of liquid at experimental temperature

E : sample is entirely liquid and piston rests on surface  
further reduction of volume requires exertion of considerable pressure

At  $T \lesssim T_c$  :

at a certain pressure, a liquid condenses from the gas  
and is distinguishable from it by a visible surface

At  $T = T_c$

surface separating two phases does not appear and the volumes at each end of the horizontal part of the isotherm have merged to a single point  $\Rightarrow$  critical point

The temperature, pressure, and molar volume at the critical point are called critical constants :

critical temperature,  $T_c$

critical pressure,  $p_c$

critical molar volume,  $V_c$

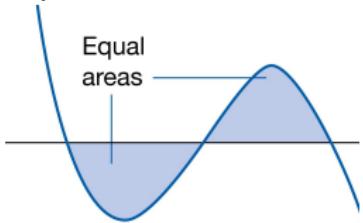
At  $T \geq T_c$ , sample is a single gas phase occupying entire volume

Liquid phase of a substance does not form above the critical temperature

single phase that fills entire volume when  $T \gtrsim T_c$  is denser than typical gas

: supercritical fluid

Apart from oscillations, van der Waals' loops, below critical temperature calculations resemble experimental isotherms well



loops are unrealistic because they suggest that under some conditions an increase of pressure results in increase of volume

Maxwell construction : loops replaced by horizontal lines drawn with equal areas

above and below  
van der Waals coefficients are found by fitting calculated curves to the experimental curves

$$a/\text{atm dm}^6 \text{ mol}^{-2} \quad b/10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$

Ar	1.337	3.20
CO <sub>2</sub>	3.61	4.29
He	0.0341	2.38
Xe	4.137	5.16

features of the van der Waals eqn

(1) Perfect gas isotherms obtained at high  $T$  and large  $V_m$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \xrightarrow[V_m \gg b]{\text{high } T} \quad \frac{RT}{V_m}$$

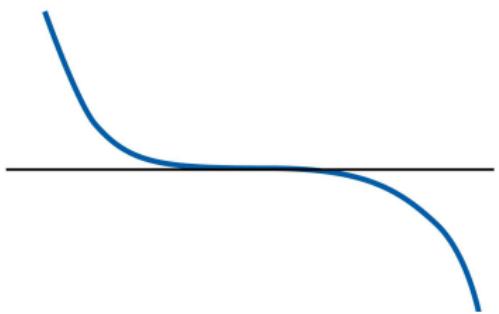
(2) Liquids and gases coexist when cohesive and dispersing effects are in balance  
van der Waals loops occur when both terms have similar magnitude

- ▶ first term : kinetic energy of molecules and repulsive interactions
- ▶ second term : attractive interactions

(3) critical constants related to van der Waals coefficients

- ▶  $T < T_C$  : calculated isotherms oscillate, and each one passes through a minimum followed by a maximum
- ▶ These extrema converge as  $T \rightarrow T_C$
- ▶ and coincide at  $T = T_C$  at the critical point the curve has a flat inflexion
- ▶ inflexion occurs when both the first and second derivatives are zero
- ▶ class ex. : find critical constants

near critical point behaviour :



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

obtain :  $V_c = 3b$ ;  $p_c = \frac{a}{27b^2}$

$$T_C = \frac{8a}{27Rb}$$

critical compression factor,

$$Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8}$$

An important general technique:  
for comparing properties of objects,  
choose a related fundamental property of the same kind  
and set up a relative scale

critical constants are characteristic properties of gases  
it may be that a scale can be set up by using them as yardsticks

∴ define : dimensionless reduced variables  
- divide actual variable by corresponding critical constant:

$$V_r = \frac{V}{V_c}; p_r = \frac{p}{p_c}; T_r = \frac{T}{T_c}$$

$$p = p_r p_c; V = V_r V_c; T = T_r T_c$$

van der Waals hoped that gases confined to same reduced volume,  $V_r$

at same reduced temperature,  $T_r$

would exert the same reduced pressure,  $p_r$

### **The principle of corresponding states :**

real gases at the same reduced volume and reduced temperature exert the same reduced pressure

The principle is only an approximation

works best for gases composed of spherical molecules

fails when molecules are non-spherical or polar

Express van der Waals eqn in terms of reduced variables and obtain :

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

coefficients a and b, which differ from gas to gas, have disappeared

⇒ if isotherms are plotted in terms of the reduced variables

then same curves are obtained whatever the gas

⇐ principle of corresponding states

van der Waals eqn is compatible with it

## The principle of corresponding states :

			Critical constants		
	Equation	Reduced form*	$p_c$	$V_c$	$T_c$
Perfect gas	$p = \frac{nRT}{V}$				
van der Waals	$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$	$p_r = \frac{8T_r}{3V_r-1} - \frac{3}{V_r^2}$	$\frac{a}{27b^2}$	$3b$	$\frac{8a}{27bR}$
Berthelot	$p = \frac{nRT}{V-nb} - \frac{n^2a}{TV^2}$	$p_r = \frac{8T_r}{3V_r-1} - \frac{3}{T_r V_r^2}$	$\frac{1}{12} \left( \frac{2aR}{3b^3} \right)^{1/2}$	$3b$	$\frac{2}{3} \left( \frac{2a}{3bR} \right)^{1/2}$
Dieterici	$p = \frac{nRT e^{-aRTV/n}}{V-nb}$	$p_r = \frac{T_r e^{2(1-1/T_r V_r)}}{2V_r-1}$	$\frac{a}{4e^2 b^2}$	$2b$	$\frac{a}{4bR}$
Virial	$p = \frac{nRT}{V} \left\{ 1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2} + \dots \right\}$				

critical constants : typical values

gas	p <sub>c</sub> atm	V <sub>c</sub> cm <sup>3</sup>	T <sub>c</sub> K	Z <sub>c</sub> = $\frac{\rho V_m}{RT}$	T <sub>B</sub> K
Ar	48.0	75.3	150.7	0.292	411.5
CO <sub>2</sub>	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O <sub>2</sub>	50.14	78.0	154.8	0.308	405.9

$$\text{compression factor : } Z = \frac{V_m}{V_m^\circ}$$

where  $V_m^\circ$  = molar volume of a perfect gas at same  $T$  and  $p$

$$Z = \frac{pV_m}{RT}; \quad \text{for a perfect gas, } Z = 1$$

$\therefore$  deviation of  $Z$  from 1 is a measure of departure from perfect behaviour

low pressures : for all gases  $Z \approx 1$

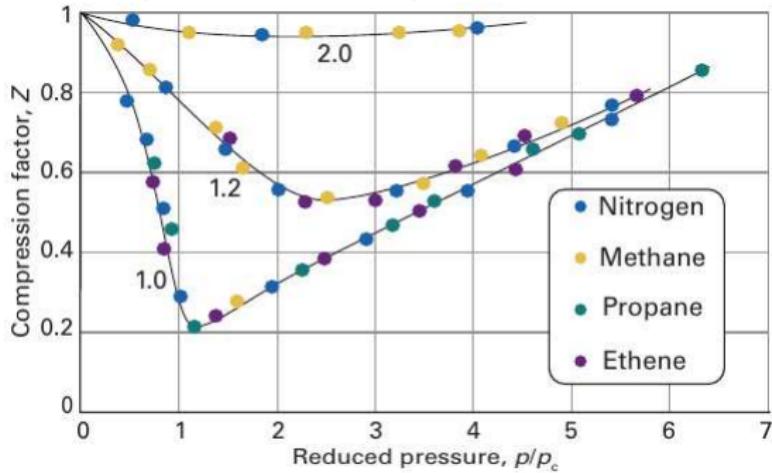
high pressures : for all gases  $Z > 1$

$\Rightarrow$  larger molar volume than perfect gas; Repulsive forces dominant

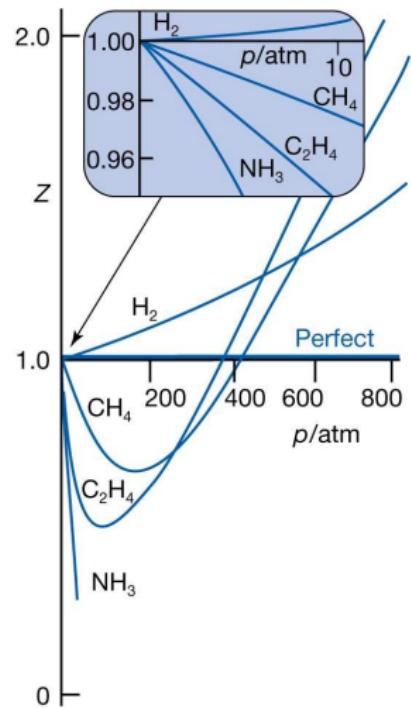
intermediate pressures, for most gases  $Z < 1$

$\Rightarrow$  attractive forces are reducing molar volume relative to that of perfect gas

compression factor for real gases :  
 $Z$  vs.  $p_r$ (reduced pressure)



experimental data  
 compression factor :



Virial coefficients and eqn. of state :  $pV_m = RT (1 + B'_2 p + B'_3 p^2 + \dots)$

or,  $pV_m = RT \left(1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \dots\right); \quad B_2 = \text{second Virial coeff.}$

$$\frac{dZ}{dp} = B'_2 + 2B'_3 p + \dots \rightarrow B'_2 \text{ as } p \rightarrow 0$$

$$\text{or, } \frac{dZ}{d\left(\frac{1}{V_m}\right)} \rightarrow B_2 \text{ as } V_m \rightarrow \infty$$

Because virial coefficients depend on temperature  
there may be a temperature at which  $Z \rightarrow 1$  with zero slope at low pressure or  
high molar volume

this is called Boyle temperature,  $T_B$

at  $T = T_B$ ,

properties of real gas coincide with those of  
perfect gas as  $p \rightarrow 0$

$$\therefore \frac{dZ}{d\left(\frac{1}{V_m}\right)} \longrightarrow B_2$$

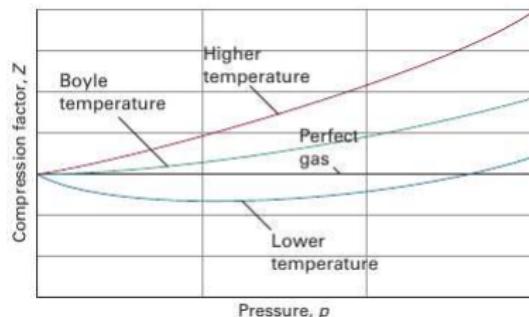
zero slope if  $B_2 = 0$

$$\therefore \text{at } T = T_B, B_2 = 0$$

and  $pV_m = RT_B$  for extended range of  
pressures than at other temperatures  
because in virial equation

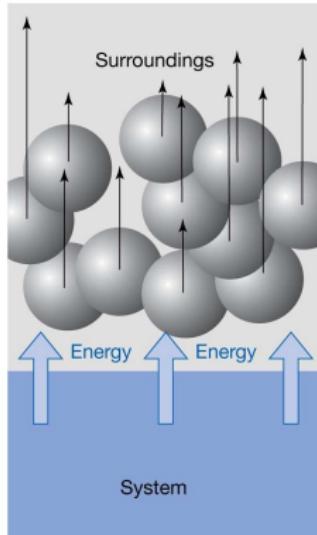
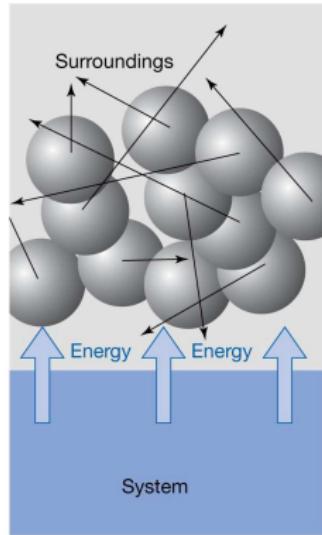
$$\text{first term after 1, } \frac{B_2}{V_m} = 0$$

and higher terms are negligibly small

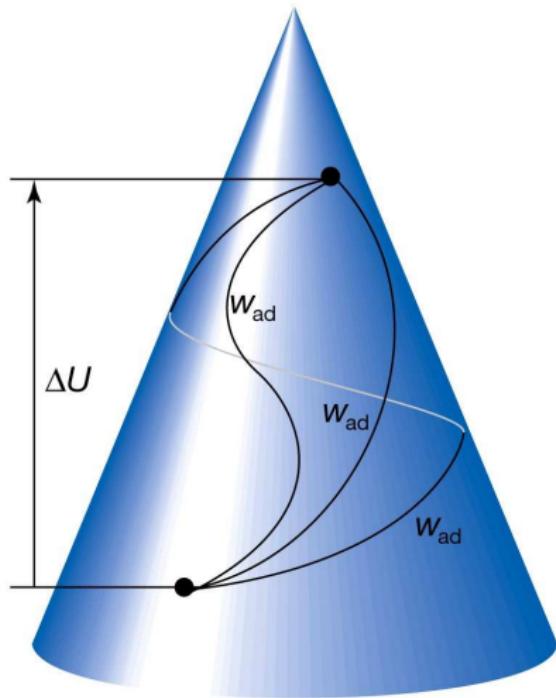


For He  $T_B = 22.64$  K  
for air  $T_B = 346.8$  K

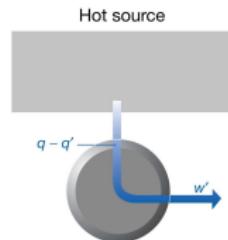
## Heat and work :



path functions: work  $\Delta U = w_{\text{ad}}$



Thermodynamic engine : Any device that converts heat into work



Nature has efficient engines, can we make them ourselves?



Type of work	$dw$	Comments	Units <sup>†</sup>
Expansion	$-p_{\text{ex}}dV$	$p_{\text{ex}}$ is the external pressure $dV$ is the change in volume	Pa m <sup>3</sup>
Surface expansion	$\gamma d\sigma$	$\gamma$ is the surface tension $d\sigma$ is the change in area	N m <sup>-1</sup> m <sup>2</sup>
Extension	$f dl$	$f$ is the tension $dl$ is the change in length	N m
Electrical	$\phi dQ$	$\phi$ is the electric potential $dQ$ is the change in charge	V C
	$Q d\phi$	$d\phi$ is the potential difference Q is the charge transferred	V C

Reversible change : can be reversed by an infinitesimal modification of a variable

example : thermal equilibrium of two systems with same temperature

transfer of energy as heat between the two is reversible because  
if temperature of either system is lowered infinitesimally  
then energy flows into the system with the lower temperature

If temperature of either system at thermal equilibrium is raised infinitesimally  
then energy flows out of the hotter system

There is a very close relationship between reversibility and equilibrium:

systems at equilibrium are poised to undergo reversible change

Say, a gas is confined by a piston and external pressure,  $p_{\text{ex}}$  is set equal to the pressure,  $p$ , of the confined gas

Such a system is in **mechanical equilibrium** with its surroundings

because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions

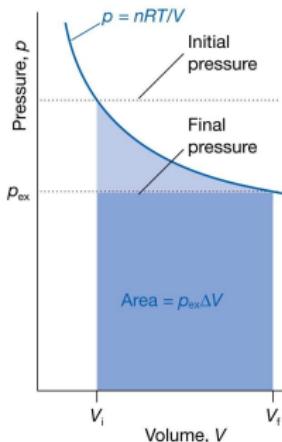
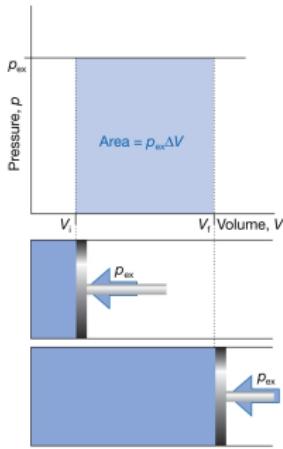
If external pressure is **reduced** infinitesimally, the gas **expands** slightly  
**increased** infinitesimally, the gas **contracts** slightly

In either case change is reversible in the thermodynamic sense

If, external pressure differs measurably from internal pressure  
then changing  $p_{\text{ex}}$  infinitesimally will not decrease it below the pressure of the gas  
so will not change the direction of the process

Such a system is **not** in mechanical equilibrium

## Calculating work :

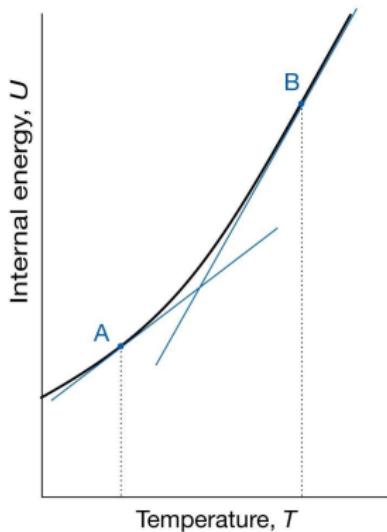


For a perfect gas, reversible work of isothermal expansion =

$$\begin{aligned} - \int_{V_i}^{V_f} p_{\text{ext}} dV &= - \int_{V_i}^{V_f} pdV \\ &= -nRT \ln \frac{V_f}{V_i} \end{aligned}$$

for spontaneous expansion :  
work =  $-p_{\text{ext}} (V_f - V_i)$

Internal energy ( $U$ ) as a function of temperature :  $U(V, T)$

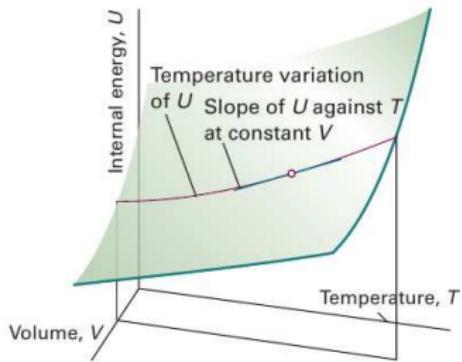


internal energy of a system  
increases as temperature is raised  
slope of tangent at any  
temperature =heat capacity,  $C$

in the Fig.,

$$C \text{ at A} < C \text{ at B}$$

$$U(V, T)$$



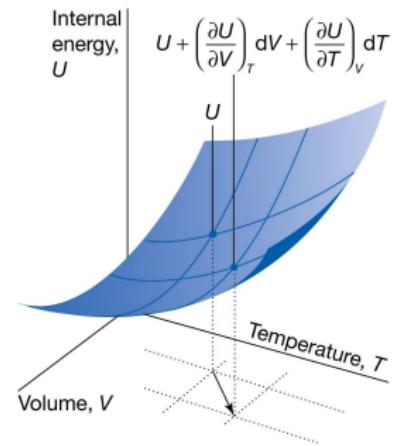
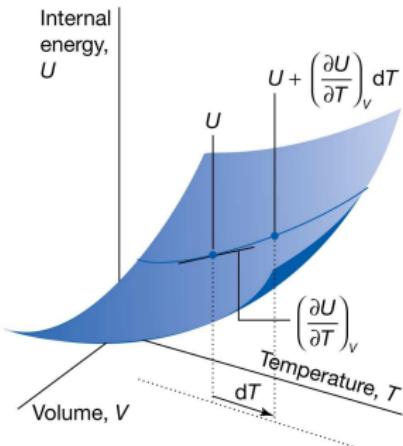
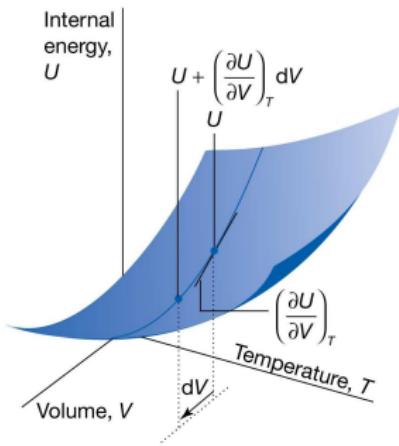
$$C_V = \left( \frac{dq}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$
$$\implies dU = C_V dT$$

If heat capacity is independent of temperature over range of temperatures of interest

$$\text{then } \Delta U = C_V \Delta T$$

for  $f \equiv f(x, y)$

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



- ▶ large heat capacity  $\Rightarrow$  for given quantity of energy transferred as heat, a small increase in temperature
- ▶ phase transition : heat capacity of a sample is infinite

mean energy of a molecule due to its translational motion =  $\frac{3}{2}k_B T$

$$\therefore \text{contribution to molar energy} = \frac{3}{2}RT$$

$\Rightarrow$  considering only translational contribution to internal energy

$$U_m(T) = U_m(0) + \frac{3}{2}RT$$

For polyatomics, rotational and vibrational contributions must be added :

$$\text{e.g., for CO}_2, U_m(T) = U_m(0) + \frac{3}{2}RT + RT + \dots$$

no intermolecular interactions in a perfect gas

Thermodynamic definition of a perfect gas :  $(\frac{\partial U}{\partial V})_T = 0$

∴ distance between molecules has no effect on energy

⇒ internal energy of a perfect gas is independent of the volume it occupies

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

↑      ↑ ↗      ↑      ↑  
upper case   lower case   expansion extra

$$dU = dq_V$$

Heat and work are ways of changing a system's internal energy

A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy

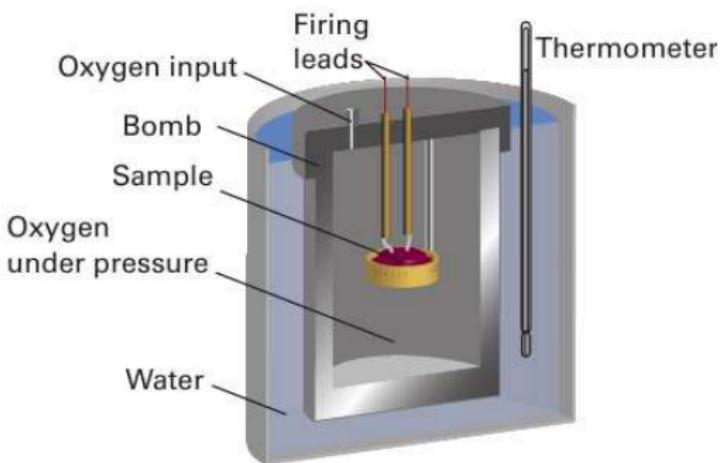
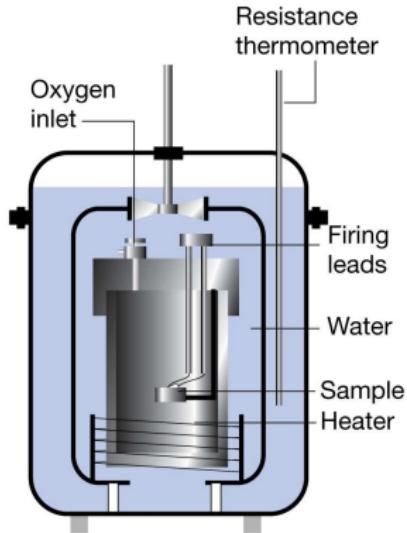
First Law : internal energy of an isolated system is constant

$$\boxed{\Delta U = q + w}$$

$$dU = dq + dw$$

## Calorimetry

- Constant volume bomb calorimeter : measurement of  $q_V$



'bomb' : central vessel, strong enough to withstand high pressures

To ensure adiabaticity, calorimeter is immersed in a water bath with temperature continuously readjusted to that of calorimeter at each stage of combustion

change in calorimeter temperature,  $\Delta T \propto$  energy released or absorbed in reaction  
measuring  $\Delta T \implies q_V$  and hence  $\Delta U$

Calibration : use a process of known energy output and determine calorimeter constant

$$q = C\Delta T$$

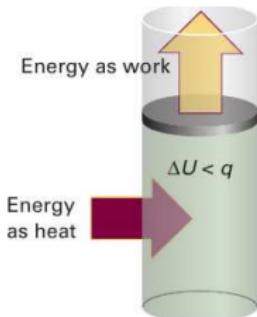
Or, a current,  $I$ , is passed  
from a source of known potential difference,  $\Delta\varphi$   
through a heater for a known period of time,  $t$

$$\text{then } q = It\Delta\varphi = C\Delta T$$

## Enthalpy

$\Delta$ energy  $\neq$  energy transferred as heat  
when system is free to change its volume

Under these circumstances  
some of the energy supplied as heat to  
system is returned to surroundings as  
expansion work, so  $dU < dq$



def.  $H = U + pV$ , a state function

$$dH = d(U + pV) = dU + pdV + Vdp = dq + Vdp \implies dq_p = dH$$

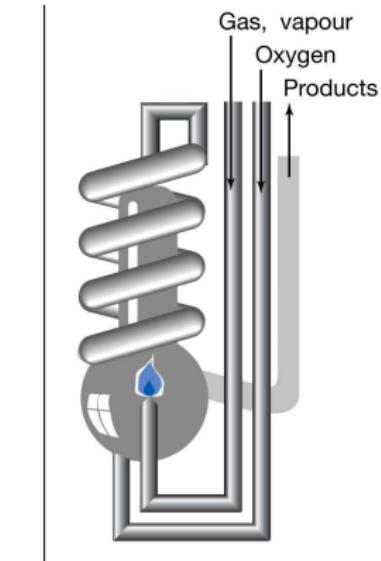
$$\text{def. } c_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \implies dH = C_p dT$$

$$\underbrace{H_f - H_i}_f \int_i^f dH = \underbrace{q_p}_f \int_i^f dq_p$$

Part of a **constant-pressure** adiabatic flame calorimeter

it is immersed in a stirred waterbath

Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.



Alternately : measure  $\Delta U$  by using bomb calorimeter and convert  $\Delta U$  to  $\Delta H$

solids/liquids have small molar volumes, for them  $pV_m$  is so small that molar enthalpy and molar internal energy are almost identical ( $H_m = U_m + pV_m \approx U_m$ )

$\Rightarrow$  if a process involves only solids or liquids,  $\Delta H \approx \Delta U$

such processes are accompanied by a very small change in volume

System does negligible work on the surroundings when the process occurs  
so energy supplied as heat stays entirely within system

Ex. : when 1.0 mol  $\text{CaCO}_3$  as calcite converts to aragonite,  $\Delta U = 0.21 \text{ kJ}$

Calculate  $\Delta H - \Delta U$  when  $p=1 \text{ bar}$  given densities of solids :  $2.71 \text{ g cm}^{-3}$   
and  $2.93 \text{ g cm}^{-3}$  respectively

- ▶ 
$$\Delta[H(\text{aragonite}) - H(\text{calcite})] = [U + pV](\text{a}) - [U + pV](\text{c}) = \Delta U + p[V(\text{a}) - V(\text{c})] = \Delta U + p\Delta V$$
- ▶  $V_m$  for  $\text{CaCO}_3$  (100 g) =  $\frac{34(\text{a})}{37(\text{c})} \text{ cm}^3$
- ▶  $\therefore p\Delta V = 10^5 \text{ Pa} \times (34 - 37) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J}$
- ▶  $\therefore \Delta H - \Delta U = -0.3 \text{ J}$  ( $\approx 0.15\%$  of  $\Delta U$ )

usually justifiable to ignore  $\Delta H - \Delta U$  for condensed phases

except at very high pressures, when  $pV$  is not negligible

Ex. Calculate  $\Delta H - \Delta U$  when 1.0 mol Sn(s, grey) of density 5.75 g cm<sup>-3</sup> changes to Sn(s, white) of density 7.31 g cm<sup>-3</sup> at 10.0 bar. At 298 K,  $\Delta H = 2.1$  kJ

- ▶ 
$$\begin{aligned}\Delta[H(\text{w}) - H(\text{g})] &= [U + pV](\text{w}) - [U + pV](\text{g}) \\ &= \Delta U + p[V(\text{w}) - V(\text{g})] = \Delta U + p\Delta V\end{aligned}$$
- ▶  $V_m$  for Sn (118.71 g) =  $\frac{20.65(\text{g})}{16.24(\text{w})}$  cm<sup>3</sup>
- ▶  $\therefore p\Delta V = 10 \times 10^5 \text{ Pa} \times (16.24 - 20.65) \times 10^{-6} \text{ m}^3 = -4.4 \text{ J}$
- ▶  $\therefore \Delta H - \Delta U = -0.44 \text{ J}$  ( $\approx 0.2\%$  of  $\Delta U$ )

enthalpy of a perfect gas:

$$H = U + pV = U + nRT \implies \Delta H = \Delta U + \Delta nRT$$

ex. : Water is heated to boiling under  $p = 1.0$  atm

Electric current of 0.50 A from a 12 V supply is passed for 300 s

through a resistance in thermal contact with it,

0.798 g of water is vaporized. Calculate  $\Delta U_m$ ,  $\Delta H_m$  at the boiling point, 373.15 K

$$\Delta H = q_p = 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s}$$

$$\Delta H_m = q_p = \frac{0.50 \times 12 \times 300}{\frac{0.798}{18}} = 41 \text{ kJ mol}^{-1}$$

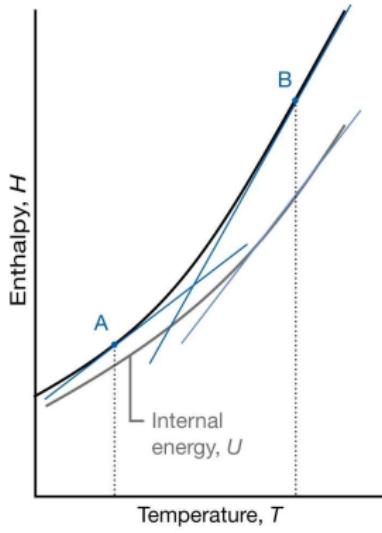
$$\Delta U_m = \Delta H_m - RT = 38 \text{ kJ mol}^{-1} [\because p(V_g - V_l) \approx pV_g = RT]$$

Notice  $\Delta U_m < \Delta H_m$

because energy has been used to drive back surrounding atmosphere

to make room for vapour

Enthalpy ( $H$ ) as a function of temperature :



internal energy and enthalpy of system increase as temperature is raised

at constant pressure

slope of tangent at any temperature  
= heat capacity,  $C_p$

For gases, at a given temperature the slope is steeper than that of internal energy versus temperature

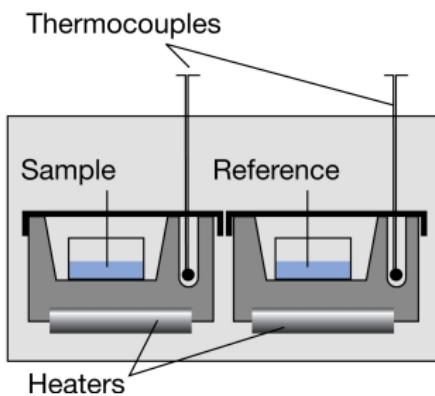
$$C_{p,m} > C_{V,m}$$

Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physico-chemical change

'differential'  $\Rightarrow$  behaviour of sample is compared to a reference material which does not undergo a physico-chemical change during analysis

'scanning' : temperatures are increased, or scanned, during the analysis

DSC : two small, separate but identical compartments heated electrically at constant rate



output : difference in power  
needed to maintain heat  
sinks at equal temperatures

$$T(t) = T_0 + \alpha t, \text{ where } T_0 = \text{initial temperature}$$

$\alpha = \text{temperature scan rate (in } K s^{-1} \text{)}$

A computer controls electrical power to maintain same temperature in both compartments  
sample temperature changes significantly relative to reference material if transfer of energy occurs in the sample during scan

To maintain same temperature in both compartments, excess energy is transferred as heat to or from sample during the process

an endothermic process lowers sample temperature relative to that of reference

. $\therefore$  sample must be heated more than reference to maintain equal temperatures  
if transfer of energy as heat occurs in the sample during the scan

If no physical or chemical change occurs in sample at temperature T

heat transferred to sample,  $q_p = C_p \Delta T$

if transfer of energy as heat occurs in the sample during the scan

the process requires the transfer of  $q_p + q_{p, ex}$

where  $q_{p, ex}$ =excess energy transferred to attain same change in temp. of sample

$C_{p, ex}$ =apparent change in heat capacity at constant pressure,  $C_p$  during temp. scan

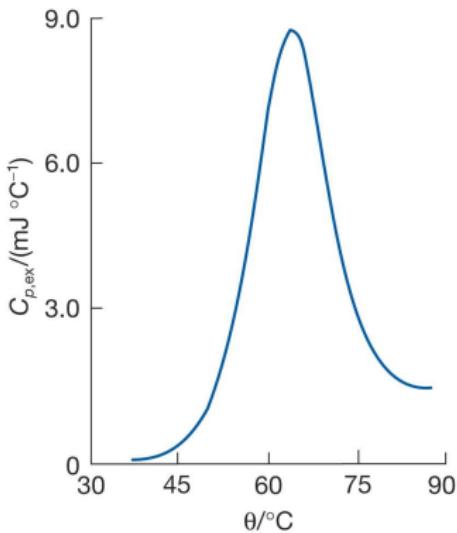
heat capacity =  $C_p + C_{p, ex}$  and  $q_p + q_{p, ex} = (C_p + C_{p, ex}) \Delta T$

. $\therefore C_{p, ex} = \frac{q_{p, ex}}{\Delta T} = \frac{q_{p, ex}}{\alpha t} = \frac{P_{ex}}{\alpha}$ ;  $P_{ex}$  = excess electrical power necessary to  
equalize the temperature of sample and reference compartments

DSC trace - a thermogram : plot of  $P_{ex}$  or  $C$  against  $T$

thermogram for protein ubiquitin at pH = 2.45

native structure up to  $\approx 45^\circ\text{C}$   
and then endothermic  
conformational change

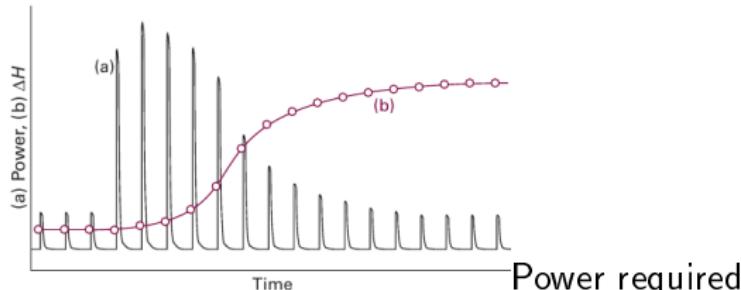
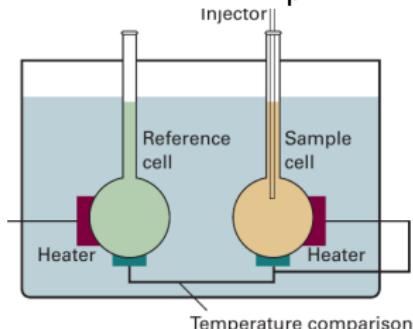


Broad peaks in thermogram indicate processes requiring transfer of energy as heat

$$\Delta H = \int_{T_1}^{T_2} C_{p, ex} dT$$

Reveals formation of new intermolecular interactions in denatured form  
Increase in  $C_p$  for native  $\rightarrow$  denatured transition reflects change from a more compact native conformation to one in which more exposed amino acid side chains in the denatured form have more extensive interactions with the surrounding water molecules

Isothermal titration calorimetry : 'differential' technique in which thermal behaviour of a sample is compared with that of a reference



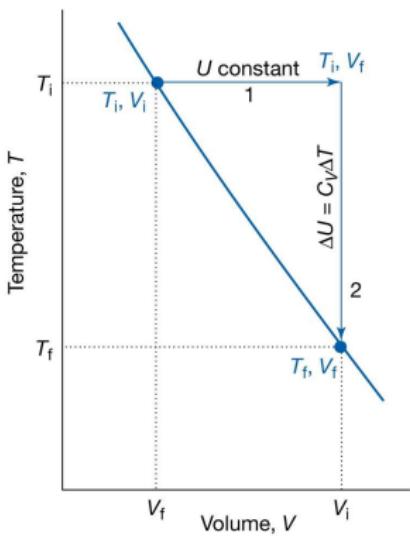
One thermally conducting vessels, has reference (few ml), e.g.  $\text{H}_2\text{O}$  and a heater rated at a few mW second vessel contains a reagent, e.g., soln. of macromolecule with binding sites and a heater Both heaters activated, and precisely determined amounts ( $\sim \mu\text{l}$ ) of second reagent added to reaction cell

sum of all such quantities =  $\Delta_r H$

to maintain same temperature differential with reference cell,  $P_i$  if length of time for injection  $i$  is  $\delta t$ , then heat  $\delta q_i = P_i \delta t$  volume of solution =  $V$  change in molar concentration of unreacted reagent at  $i$ th injection =  $\delta c_i$  and heat generated (or absorbed) =  $V \Delta_r H \cdot \delta c_i = \delta q_i$

exo(endo)thermic : less(more) power needed

Adiabatic expansion :  $T_i, V_i \rightarrow T_f, V_f$



when a perfect gas expands adiabatically work is done but no heat enters the system internal energy falls - kinetic energy of molecules falls, average speed decreases ∴ temperature falls

$\Delta U$  for temperature change from  $T_i$  to  $T_f$  and the volume change from  $V_i$  to  $V_f$  can be seen as the sum of two steps

1st step : only volume changes and temperature is constant

$U$  for perfect gas is independent of volume of molecules, the overall  $\Delta U$  arises solely from second step, the change in temperature at constant volume

$$\Delta U = C_v (T_f - T_i) = w_{ad}$$

## Adiabatic processes

$$w_{ad} = C_v \Delta T$$

reversible adiabatic expansion :

$$C_v dT = -pdV$$

For perfect gas,  $C_v \frac{dT}{T} = -\frac{nRdV}{V}$

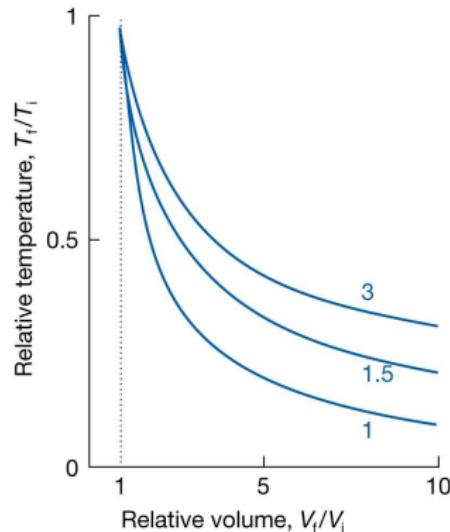
$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{nRdV}{V}$$

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

$$\text{or, } \ln \left( \frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \ln \left( \frac{V_1}{V_2} \right) \text{ or, } \left( \frac{T_2}{T_1} \right)^{\frac{C_v}{nR}} = \frac{V_1}{V_2}$$

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\frac{nR}{C_v}} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \text{ or, } TV^{\gamma-1} = \text{const.}$$

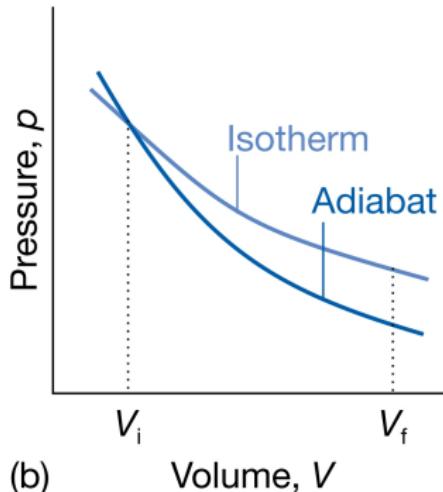
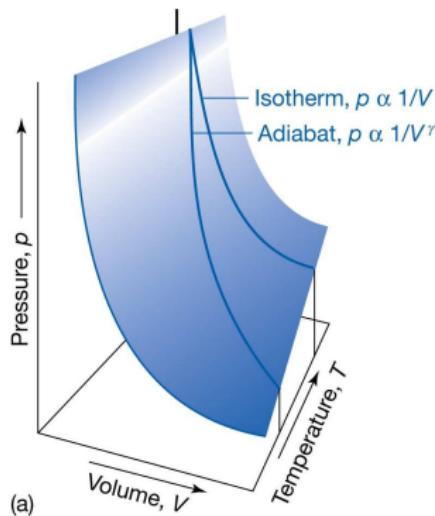
show:  $pV^\gamma = \text{const}$



label :  $\frac{C_v}{R}$

p-V-T plots : isotherms and adiabats

pressure declines more steeply for an adiabat than for an isotherm



in isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, pressure does not fall as much as in adiabatic expansion

ex. :

adiabatic, reversible expansion of 0.020 mol Ar  
initially at 25°C, from 0.50 dm<sup>3</sup> to 1.00 dm<sup>3</sup>

$$C_V \text{ of argon} = 12.48 \text{ JK}^{-1} \text{ mol}^{-1}, \gamma = \frac{12.48+8.314}{12.48} = \frac{20.794}{12.48} = 1.666$$

$$\text{Using } T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$\text{we have } T_f = 298 \times \left(\frac{0.50}{1}\right)^{0.666} = 188 \text{ K}$$

$$\Delta T = 188 - 298 = -110 \text{ K} \text{ and } w_{ad} = n C_v \Delta T = -0.020 \times 12.48 \times 110 = -27 \text{ J}$$

Note :  $\Delta T$  is independent of the amount of gas but the work is not  
where  $q_{p, ex}$ =excess energy transferred as heat, to attain same change in temp.  
of sample

$C_{p, ex}$  = apparent change in heat capacity at constant pressure,  $C_p$  during  
temperature scan

## Thermochemistry

a reaction vessel and its contents form a system, and chemical reactions result in exchange of energy between system and surroundings

use calorimetry to measure energy supplied or discarded as heat by a reaction

identify  $q_V = \Delta U$  or  $q_p = \Delta H$

Conversely, if we know  $\Delta U$  or  $\Delta H$  for a reaction, predict the energy (transferred as heat) the reaction produces

exothermic process at constant pressure :  $\Delta H < 0$

endothermic process at constant pressure :  $\Delta H > 0$

Standard state :

standard state of a substance **at a specified temperature** is its pure form at 1 bar

ex. liquid ethanol at 298 K : pure liquid ethanol at 298 K and 1 bar

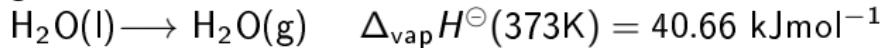
solid iron at 500 K is pure iron at 500 K and 1 bar

Standard enthalpy change,  $\Delta H^\ominus =$

enthalpy of products<sub>standard states</sub> — enthalpy of reactants<sub>standard states</sub>

standard enthalpy of vaporization :

$\Delta_{\text{vap}}H^\ominus$  = enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar



standard enthalpy of fusion :

$\Delta_{\text{fus}}H^\ominus$  = enthalpy change per mole when a pure liquid at 1 bar condenses to solid at 1 bar



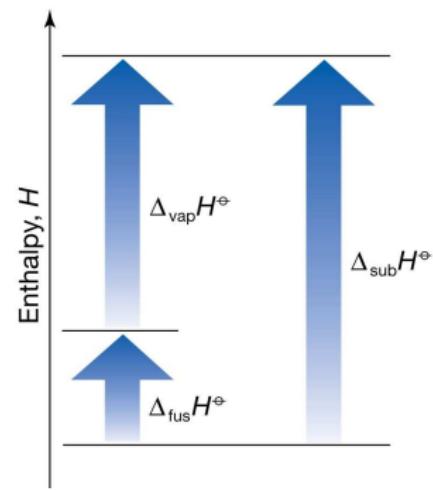
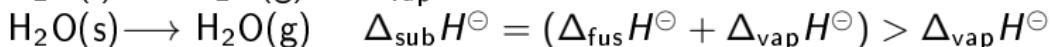
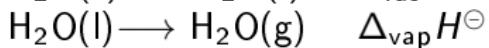
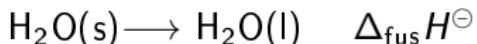
**standard enthalpies may be reported for any temperature**

enthalpy is a state function

$\Delta H$  is independent of path between the two states

same  $\Delta H^\ominus$  for change brought about between same initial and final states

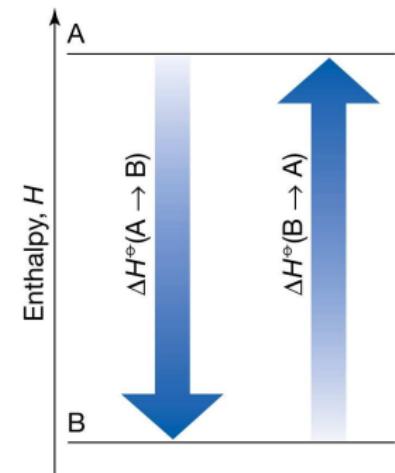
e.g., conversion of a solid to a vapour either as occurring by sublimation



$\Delta H^\ominus$  for a forward process and its reverse differ in sign

e.g., conversion of a solid to a vapour either as occurring by sublimation

$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A)$$



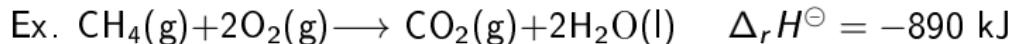
Transition	Process	Symbol
Transition	Phase $\alpha \rightarrow$ phase $\beta$	$\Delta_{trs}H$
Fusion	$s \rightarrow l$	$\Delta_{fus}H$
Vaporization	$l \rightarrow g$	$\Delta_{vap}H$
Sublimation	$s \rightarrow g$	$\Delta_{sub}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{mix}H$
Solution	Solute $\rightarrow$ 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	$\Delta^\ddagger H$

Standard reaction enthalpy :

change in enthalpy for

Pure, separate reactants in standard states →

pure, separate products in standard states



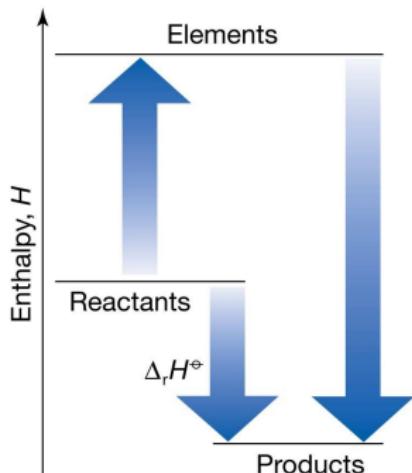
For the reaction  $2\text{A} + \text{B} \rightarrow 3\text{C} + \text{D}$

$$\Delta_r H^\ominus = \{3H_m^\ominus(\text{C}) + H_m^\ominus(\text{D})\} - \{2H_m^\ominus(\text{A}) + H_m^\ominus(\text{B})\}$$

$$\text{generally, } \Delta_r H^\ominus = \sum_{\text{products}} \nu H_m^\ominus - \sum_{\text{reactants}} \nu H_m^\ominus$$

standard enthalpy of combustion,  $\Delta_C H^\ominus$  = standard reaction enthalpy for the complete oxidation of an organic compound to  $\text{CO}_2$  gas and liquid water if the compound contains C, H, and O, and to  $\text{N}_2$  gas if N is also present

## reaction enthalpy in terms of enthalpies of formation

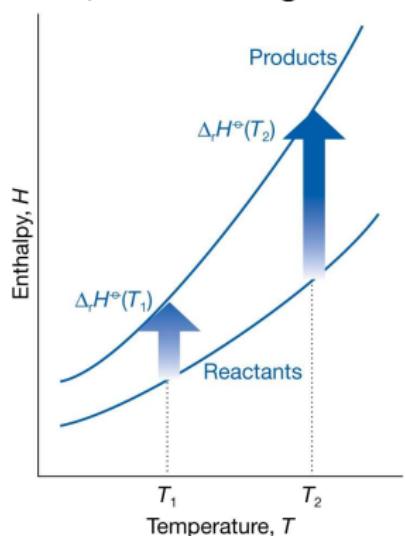


$$\Delta_r H^\ominus = \sum_{\text{products}} \nu \Delta_f H^\ominus - \sum_{\text{reactants}} \nu \Delta_f H^\ominus$$

Can we construct  $\Delta_f H^\ominus$  from a knowledge of chemical constitution of the species?  
no thermodynamically exact way of expressing enthalpies of formation in terms of contributions from individual atoms and bonds

$$dH = C_p dT \implies H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

assuming no phase transition in temperature range of interest



Kirchhoff's law :

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

$$\text{where } \Delta_r C_p^\ominus = \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus$$

solved prob.:  $\Delta_f H^\ominus(\text{H}_2\text{O}(g); 298 \text{ K}) = -241.82 \text{ kJ mol}^{-1}$

Estimate  $\Delta_f H^\ominus$  at 100°C

given  $C_{p,m}(\text{H}_2\text{O}, g) = 33.58 \text{ J K}^{-1}\text{mol}^{-1}$ ;  $C_{p,m}(\text{H}_2, g) = 28.84 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  
 $C_{p,m}(\text{O}_2, g) = 29.37 \text{ JK}^{-1} \text{ mol}^{-1}$

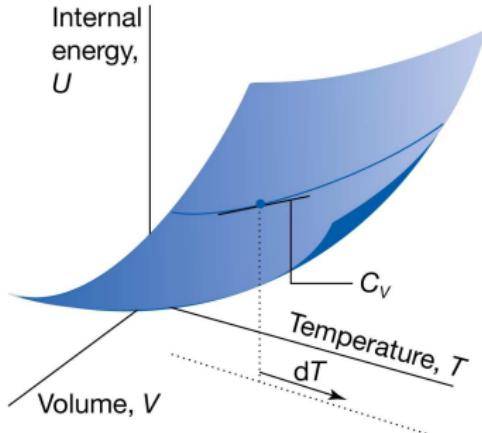
$$\Delta_r C_p^\ominus = C_{p,m}(\text{H}_2\text{O}, g) - \{C_{p,m}(\text{H}_2, g) + \frac{1}{2}C_{p,m}(\text{O}_2, g)\} = -9.94 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}\therefore \Delta_r H^\ominus(T_2) &= \Delta_r H^\ominus(T_1) + (T_2 - T_1) \Delta_r C_p^\ominus \\ &= -241.82 - 75 \times 9.94 \times 10^{-3} = -242.6 \text{ kJ mol}^{-1}\end{aligned}$$

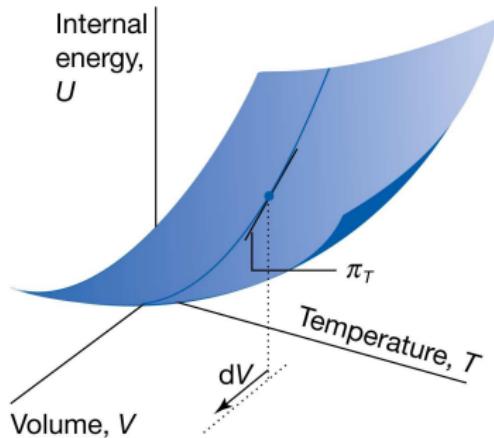
Real systems :

heat capacity at constant volume

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

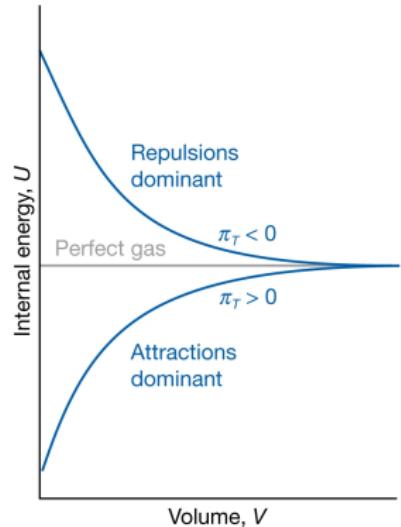


internal pressure :  $\Pi_T = \left( \frac{\partial U}{\partial V} \right)_T$



If  $\Delta U > 0$  as  $\Delta V > 0$  isothermally  
with attractive forces between the particles

then plot of  $U$  against  $V$  slopes upwards and  $\pi_T > 0$



Joule-experiment : could we measure  $\pi_T$  by observing  $\Delta T$  for a gas  
when it is allowed to expand into a vacuum?

He used two metal vessels immersed in a water bath

One filled with air at about 22 atm and other  
evacuated

measured  $\Delta T$  of water when a stopcock was  
opened and air expanded into a vacuum  
observed  $\Delta T = 0$

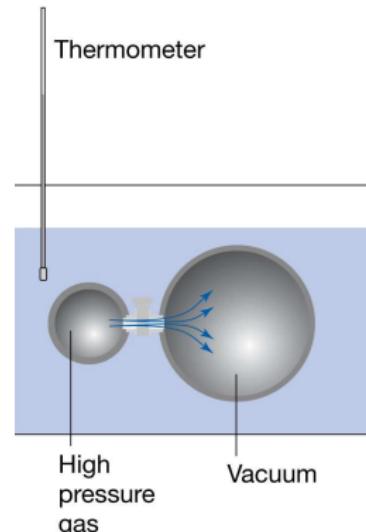
experimental limitations

No work done  $w = 0$

No energy entered or left the system as heat  
because the temperature of the bath did not  
change, so  $q = 0$

within experimental accuracy,  $\Delta U = 0$

$\therefore \pi_T = 0$  (incorrect result)



some important relations :

$$U \equiv U(V, T)$$

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

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

def. : expansion coefficient,  $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ , then,  $\left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$

show :  $\alpha = \frac{1}{T}$  for perfect gas

Also, for a perfect gas,  $\pi_T = 0$ ,  $\therefore \left(\frac{\partial U}{\partial T}\right)_p = C_V$

$$\begin{aligned}C_p - C_V &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial [U+pV]}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \\&= (\alpha\pi_T V + C_V) + p \left(\frac{\partial V}{\partial T}\right)_p - C_V = \alpha\pi_T V + p \left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

For perfect gas,  $C_p - C_V = p \left(\frac{\partial V}{\partial T}\right)_p = nR$

Generally,  $p \left(\frac{\partial V}{\partial T}\right)_p = \alpha pV$  and  $C_p - C_V = \alpha(p + \pi_T)V$

$$z = f(x, y)$$

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

$$\text{for constant } z, dz = 0, \implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = - \left(\frac{\partial z}{\partial y}\right)_x dy_z$$

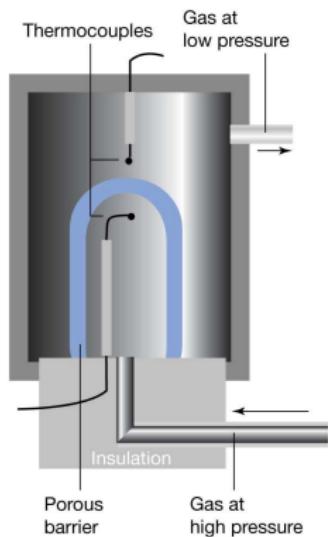
$$\text{or, } \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial z}{\partial y}\right)_x, \implies \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

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

$$-\underbrace{\frac{1}{\left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p}}_{\substack{\text{J} \\ \uparrow \\ \text{T coefficient}}} = -\underbrace{\left(\frac{\partial T}{\partial p}\right)_H}_{\mu} \left(\frac{\partial H}{\partial T}\right)_p = -\mu C_p$$

$$\therefore dH = -\mu C_p dp + C_p dT$$

## Joule-Thomson coefficient - apparatus



let a gas expand through a porous barrier from one constant pressure to another

monitor the difference of temperature that arises from expansion

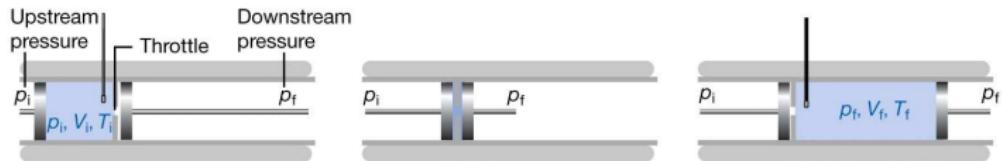
whole apparatus is insulated : adiabatic

$$q=0 \implies \Delta U=w$$

observed lower temperature on low pressure side,  $\Delta T \propto$  pressure difference

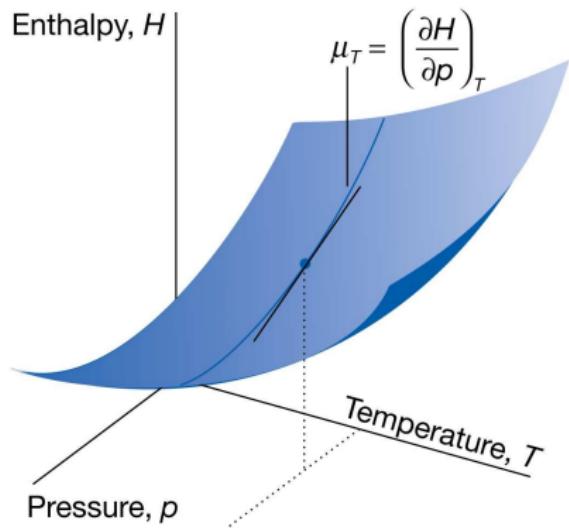
Joule-Thomson effect : cooling by isenthalpic expansion

## Joule-Thomson coefficient - thermodynamic basis



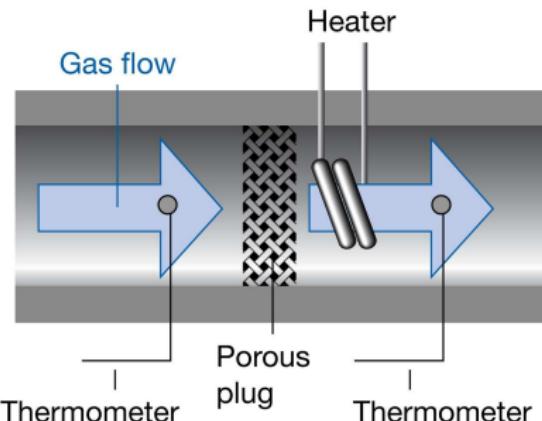
$$\Delta U = U_f - U_i = w = w_1 + w_2 = -p_i (0 - V_i) - p_f (V_f - 0) = p_i V_i - p_f V_f$$
$$\therefore U_f + p_f V_f = U_i + p_i V_i = \text{const } H$$

isothermal Joule-Thomson coefficient,  $\mu_T = \left( \frac{\partial H}{\partial p} \right)_T = -C_p \mu$



## Isothermal Joule-Thomson coefficient - measurement

gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)



then through a porous plug inside a thermally insulated container

steep pressure drop is measured, and cooling effect is exactly offset by an electric heater placed immediately after the plug

energy provided by the heater is monitored  
energy transferred as heat =  $\Delta H_p$

find  $\mu_T = \lim_{p \rightarrow 0} \frac{\Delta H}{\Delta p}$  and convert to  $\mu$

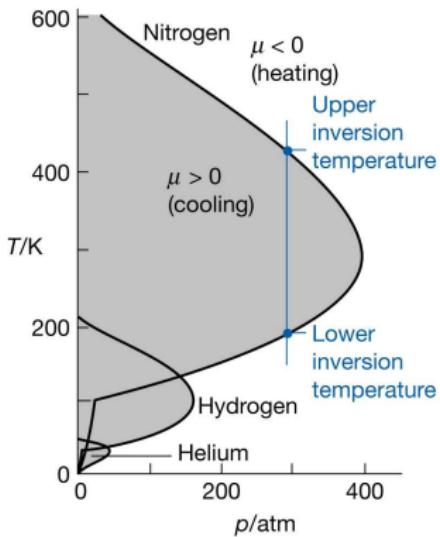
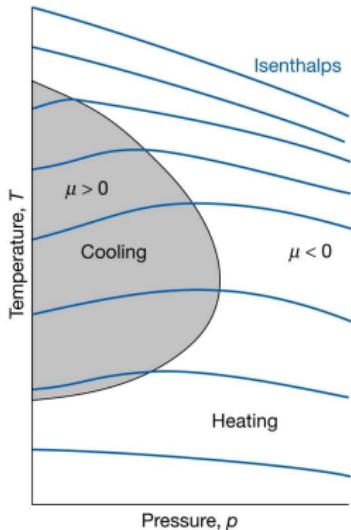
- ▶ Real gases have nonzero  $J_T$  coefficients
- ▶ speed of molecules  $\propto T$ 
  - ▶ reducing average speed is equivalent to cooling
- ▶ If speed is reduced to a point that neighbours capture each other by intermolecular attractions, then it condenses to a liquid
- ▶ Sign of  $\mu$  depends on the gas,  $p$ , relative magnitudes of attractive and repulsive forces and  $T$
- ▶ if molecules are moved away from each other, then they should slow
  - ▶ Allow gas to expand increasing average separation
- ▶ To cool a gas, allow expansion without any energy entering from outside

molecular interpretation :

- ▶ expansion : molecules move apart to fill available volume, working against attraction of neighbours
- ▶ some kinetic energy is converted into potential energy to reach greater separations, molecules travel more slowly as separation increases
- ▶ This sequence explains the J T effect: **cooling** of a real gas by adiabatic expansion.

$\mu > 0 \implies dT < 0$  when  $dp < 0 \implies$  gas cools on expansion, attractive interactions dominant - molecules work against attractive force to travel slower

- ▶ when repulsions dominant,  $Z > 1$  : heating effect
- ▶ inversion temperature : Where shift in behaviour occurs - **cooling** to **heating** on **lowering** pressure
- ▶ typically  $\exists$  two inversion temperatures, one at high temperature and other at low :  $\mu < 0$  at one temperature
  - ▶ cooling effect  $\mu > 0$  when  $T <$  upper inversion temperature

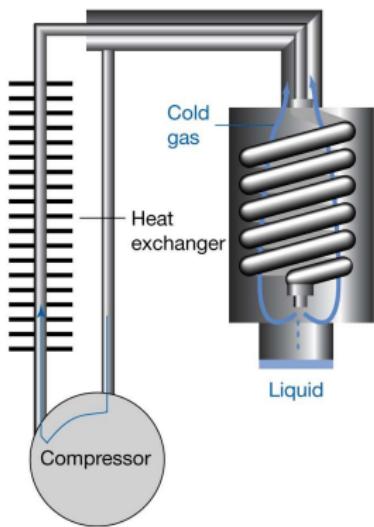


Inversion temperature : boundary at a given pressure

For a given pressure, temperature must be below a certain value for cooling but, if it becomes too low, boundary is crossed again and heating occurs  
 Reduction of pressure under adiabatic conditions moves system along one of the isenthalps, or curves of constant enthalpy

inversion temperature curve runs through points of isenthalps where slope changes from negative to positive

## Linde Refrigerator for liquefying gases



gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas

That gas is cooled, and its subsequent expansion cools it still further

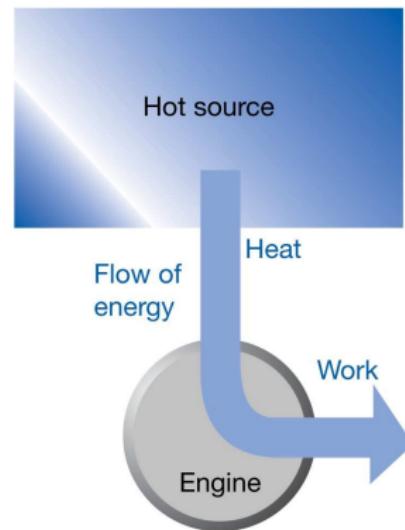
There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

- ▶ For a perfect gas,  $\mu = 0$
- ▶  $\therefore$  temperature of perfect gas is unchanged by J T expansion
- ▶ However,  $\mu$  for a real gas does not necessarily approach zero as  $p$  is reduced even though equation of state approaches that of a perfect gas
- ▶ The coefficient depends on derivatives and not on  $p$ ,  $V$  and  $T$  themselves

## Second law :

- ▶ Kelvin : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work
- ▶ Kelvin-Planck : It is impossible to construct an engine that, operating in a cycle, will produce no effect other than extraction of heat from a reservoir and the performance of an equivalent amount of work
- ▶ Clausius : It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher temperature sink
- ▶ Carnot : No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. The efficiency of an engine can never be 100%
- ▶ Entropy principle : Entropy of universe (System+surroundings) always increases in a natural (spontaneous) process
- ▶ Clausius inequality :  $\Delta S \geq \int \frac{dq}{T}$  neighbourhood
- ▶ Caratheodory axiom : In the neighbourhood of any arbitrary initial state of a physical system,  $P_0$ , there exist neighbouring states that are not accessible from  $P_0$  along reversible adiabatic paths

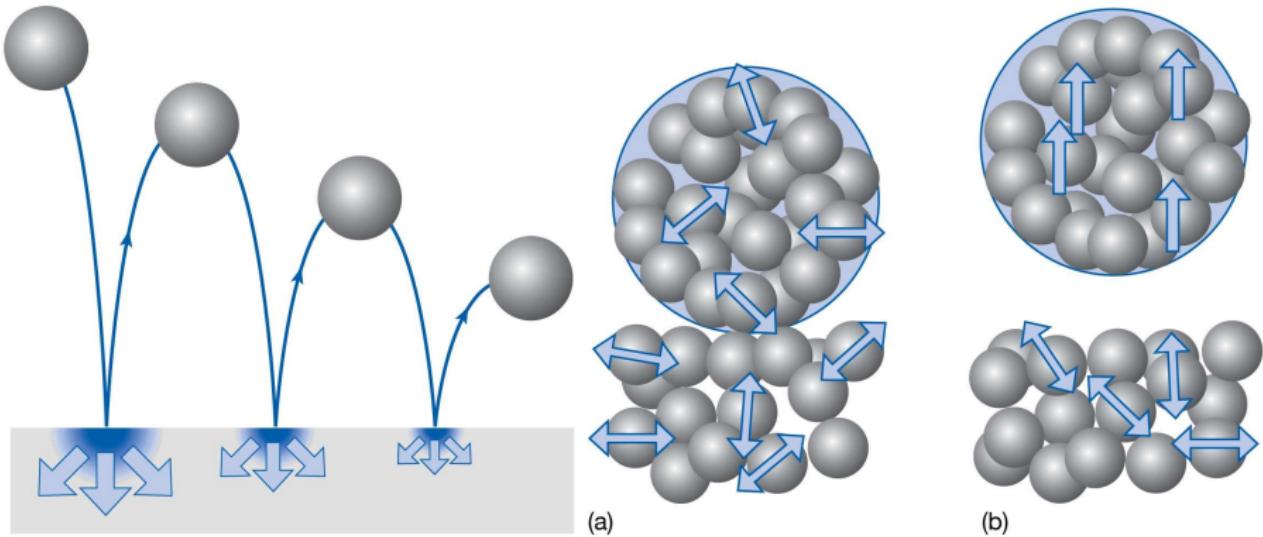
Thermodynamic engine : device that allows a system to draw heat from a source, convert part of it into work and dump unused heat to a sink



Second law : complete conversion  
of heat into work impossible

NOT POSSIBLE

## Heat and work : molecular understanding



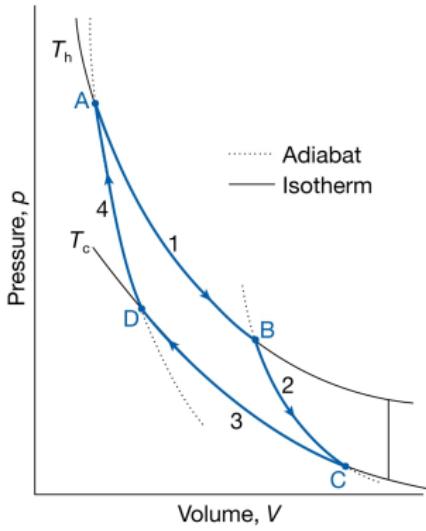
spontaneous change: direction of change leading to dispersal of total energy of isolated systems

Entropy :  $dS = \frac{dq_{\text{rev}}}{T}$  and  $\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$

isothermal expansion :  $\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = -\frac{w_{\text{rev}}}{T} = nR \ln \frac{V_f}{V_i}$

adiabatic process :  $\Delta S = 0$

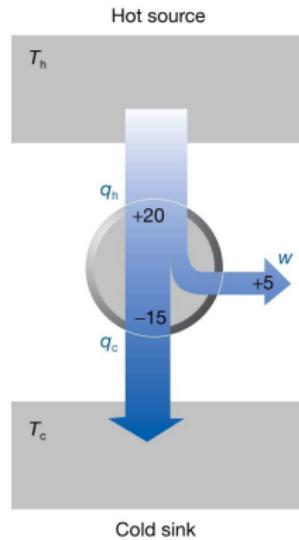
Carnot cycle : a model - perfect gas as fuel for an engine



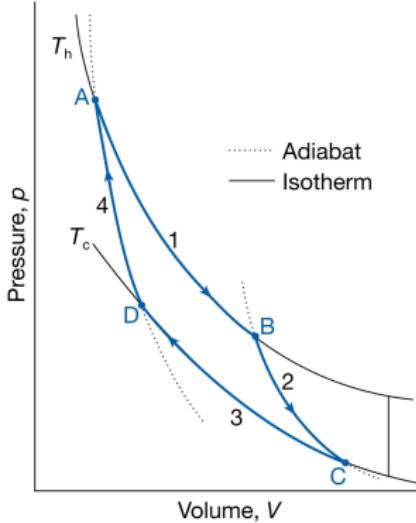
1. Reversible isothermal expansion from A to B at  $T_h$ ;  $\Delta S = \frac{q_h}{T_h}$ ;  
where  $q_h$  = energy supplied from hot source  $> 0$
2. Reversible adiabatic expansion from B to C  
 $\Delta S = 0$ ;  $\Delta T = -(T_h - T_c)$
3. Reversible isothermal compression from C to D at  $T_c$ ;  $\Delta S = \frac{q_c}{T_c}$   
Energy released as heat to the cold sink  $< 0$
4. Reversible adiabatic compression from D to A  
 $\Delta S = 0$ ;  $\Delta T = T_h - T_c$

$$\text{Total } \Delta S = \oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

## Example of a Carnot engine



$$q_h = nRT_h \ln \frac{V_B}{V_A}; \quad q_c = nRT_c \ln \frac{V_D}{V_C}$$



adiabats:  $V_A T_h^c = V_D T_c^c$  (exponent  $c = \frac{C_V}{nR}$ )  
and  $V_C T_c^c = V_B T_h^c$

obtain :  $V_A V_C T_h^c T_c^c = V_D V_B T_h^c T_c^c$   
and  $\therefore \frac{V_A}{V_B} = \frac{V_D}{V_C} \implies q_c = -nRT_c \ln \frac{V_B}{V_A}$

$$\therefore \frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

$$\text{efficiency, } \eta = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h} \\ = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h}$$

$$\Delta S = \frac{q_h}{T_h} + 0 + \frac{q_c}{T_c} + 0 = 0$$

2nd Law : all reversible engines have same efficiency regardless of their construction  
Proof by contradiction

Let  $\eta_A > \eta_B$

engine A takes heat  $q_h$  from hot source and dumps  $q_c$  in cold reservoir

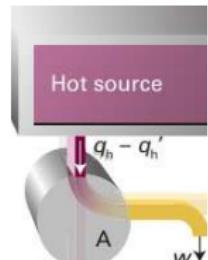
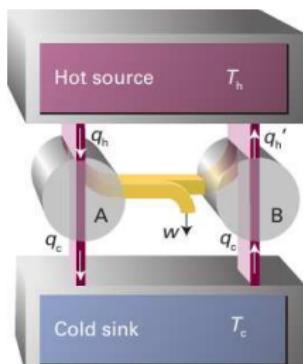
Reverse engine B

engine B acquires energy heat  $q_c$  from cold reservoir and releases  $q'_h < q_h$  to the hot end

Form composite engine C : A+B

C takes heat  $q_h - q'_h$  from hot source and converts it completely into work

$\implies$  violation of Kelvin-Planck statement

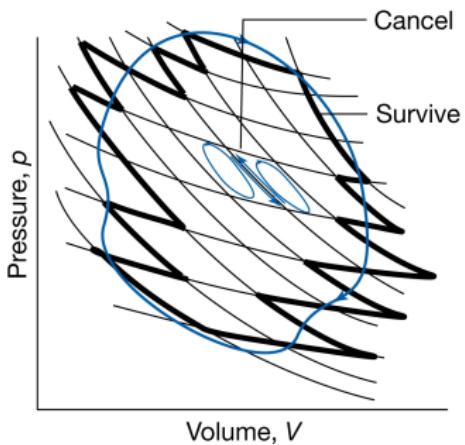


universality of 2nd law :

any reversible cycle  $\approx$   
collection of Carnot cycles

$\oint$ (arbitrary path)

$$= \sum \oint (\text{each cycle})$$



$\Delta S$  along an individual path inside is  
cancelled by  $\Delta S$  along the path it shares with  
neighbouring cycle

The approxmn. becomes exact as individual  
cycles become infinitesimal

$$\oint(\text{arbitrary path}) = \sum \oint (\text{each cycle}) = 0$$

$\therefore$  all entropy changes cancel except for those  
along perimeter of the overall cycle

$$\sum_{\text{all}} \frac{q_{\text{rev}}}{T} = \sum_{\text{perimeter}} \frac{q_{\text{rev}}}{T} = 0$$

In the limit of infinitesimal cycles, the  
non-cancelling edges of Carnot cycles match  
the overall cycle exactly, and the sum  
becomes an integral

$\implies dS$  is exact differential and  $S$  is state function

## Clausius inequality

more work is done when a change is reversible than when it is irreversible,

$$\text{i.e., } |dw_{\text{rev}}| \geq |dw|$$

$\therefore dw_{\text{rev}}$  and  $dw$  are negative when energy leaves the system as work

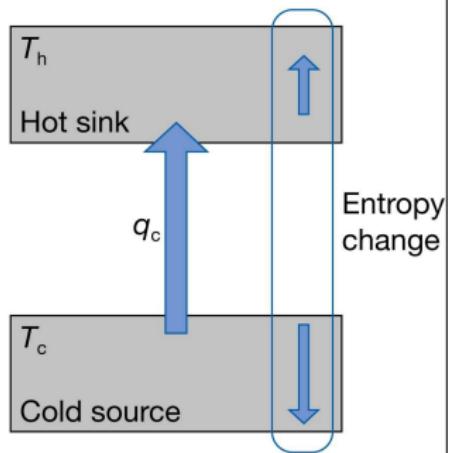
$$\therefore -dw_{\text{rev}} \geq -dw \text{ or, } dw \geq dw_{\text{rev}}$$

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

$$dq_{\text{rev}} \geq dq, \therefore \Delta S = \int \frac{dq_{\text{rev}}}{T} \geq \int \frac{dq}{T}$$

Consider transfer of energy as heat from one system - cold source-at  $T_c$  to another system - hot sink- at  $T_h$

**thermodynamic refrigerator**



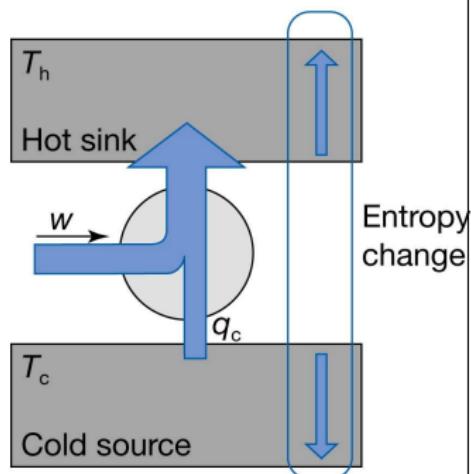
energy removed from cool source at temp.  $T_c$   
 $= \frac{|q_c|}{T_c}$

and deposited in warmer sink at temp.  $T_h$

$$\Delta S = -\frac{|q_c|}{T_c} + \frac{|q_c|}{T_h} < 0 \implies \text{not spontaneous}$$

to generate more entropy, energy must be added to the stream that enters the warm sink.  
task: find minimum energy to be supplied

## Thermodynamic refrigerator



Entropy  
change

coefficient of performance,

$$c = \frac{\text{energy transferred as heat}}{\text{energy transferred as work}} = \frac{|q_c|}{|w|}$$

The less the work required to achieve a given transfer, greater is  $c$

and more efficient the refrigerator.

$$\frac{1}{c} = \frac{|q_h| - |q_c|}{|q_c|} = \frac{|q_h|}{|q_c|} - 1$$

using  $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$ , we get,  $c = \frac{T_c}{T_h - T_c}$

work to maintain a low temperature is relevant to design of refrigerators

No thermal insulation is perfect

there is always a flow of energy as heat into the sample at a rate  $\propto \Delta T$

If rate at which energy leaks =  $A(T_h - T_c)$

where A depends on sample size and insulation

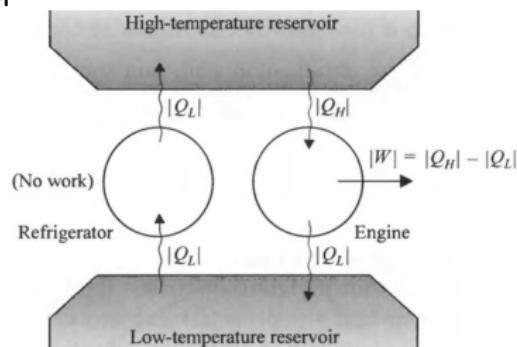
then minimum power,  $P$ , required to maintain original  $\Delta T$  by pumping out energy by heating surroundings

$$P = \frac{1}{c} \cdot A (T_h - T_c) = \frac{A(T_h - T_c)^2}{T_c} \propto (\Delta T)^2$$

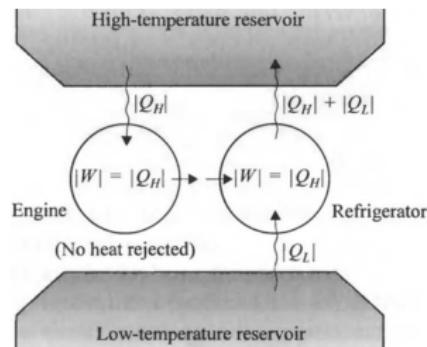
power increases as  $(\Delta T)^2$

$\therefore$  air-conditioners more expensive to run on hot days than on mild days

## Equivalence of Kelvin-Planck and Clausius statements

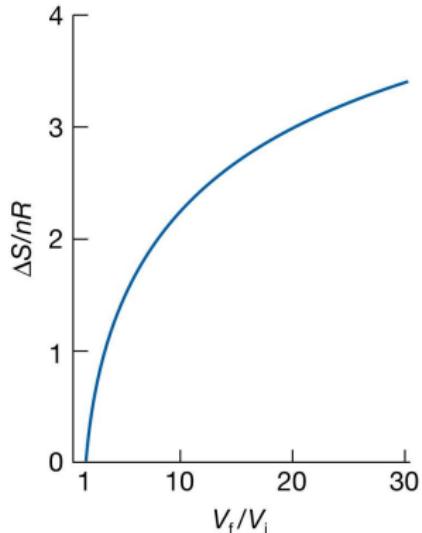


$$-C \subset -K$$



$$-K \subset -C$$

entropy change in isothermal expansion :



$$\Delta S_{\text{sys}} = nR \ln \frac{V_f}{V_i}$$

$$\Delta S_{\text{surr (rev)}} = -\Delta S_{\text{sys}}$$

$\Delta U = 0$ ;  $\therefore$  If isothermal expansion occurs freely,  $w = 0$  and irreversibly, then  $q = 0$

$$\therefore \Delta S_{\text{surr (irrev)}} = 0$$

$$\Delta S_{\text{total (rev)}} = 0 \text{ rev}$$
$$> 0 \text{ irrev}$$

$$\text{Phase transition : } \Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

Trotton's rule :

wide range of liquids have approx. same  $\Delta_{\text{vap}} S$  ( $\approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$ )

Ex. liq.  $\text{Br}_2$ :

- no complexity like hydrogen bonding in liquid  $\text{Br}_2$
- there is no unusual behaviour in the gas phase
- safe to use Trotton's rule

$$\begin{aligned}\text{- boils at } 59.2^\circ\text{C, } \Delta_{\text{vap}} H^\ominus &= T_b \times 85 \text{ J mol}^{-1} \\ &= 332.4 \times 85 = 28 \text{ kJ mol}^{-1}\end{aligned}$$

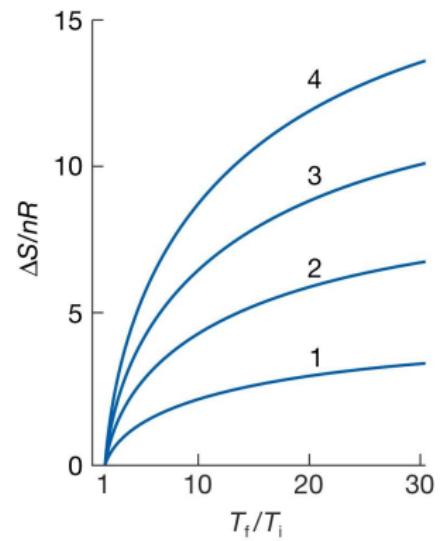
experimental value :  $29.45 \text{ kJ mol}^{-1}$

entropy change as a function of temperature (varying heat capacity) :

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{\text{rev}}}{T}$$

const.  $p(V)$  :  $S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_{p(V)} dT}{T}$

$$= S(T_i) + C_{p(V)} \ln \frac{T_f}{T_i}$$

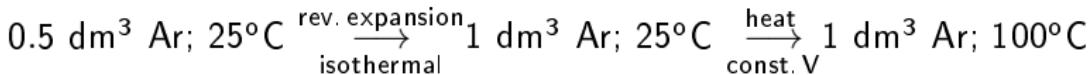


label : heat capacity

solved problem : Calculate  $\Delta S$  when 0.500 dm<sup>3</sup> of Ar at 25°C and 1.00 bar expands to 1.000 dm<sup>3</sup> and is simultaneously heated to 100°C

$S$  is a state function

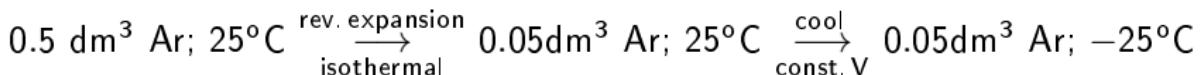
∴ choose a convenient path from initial state



$$\Delta S_I = nR \ln \frac{V_f}{V_i} = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i}; \quad \Delta S_{II} = C_V \ln \frac{T_f}{T_i}$$

$$\begin{aligned}\Delta S &= \Delta S_I + \Delta S_{II} = nR \left( \ln \frac{V_f}{V_i} + \frac{3}{2} \ln \frac{T_f}{T_i} \right) = \frac{p_i V_i}{T_i} \ln \left( \frac{V_f}{V_i} \left[ \frac{T_f}{T_i} \right]^{\frac{3}{2}} \right) \\ &= \frac{10^5 \text{ Pa} \times 0.5 \times 10^{-3} \text{ m}^3}{298} \ln \left( \frac{1}{0.5} \left[ \frac{373}{298} \right]^{\frac{3}{2}} \right) \\ &= \frac{10^5 \text{ Pa} \times 0.5 \times 10^{-3} \text{ m}^3}{298} \ln \left( \frac{1}{0.5} \left[ \frac{373}{298} \right]^{\frac{3}{2}} \right) = 0.173 \text{ JK}^{-1}\end{aligned}$$

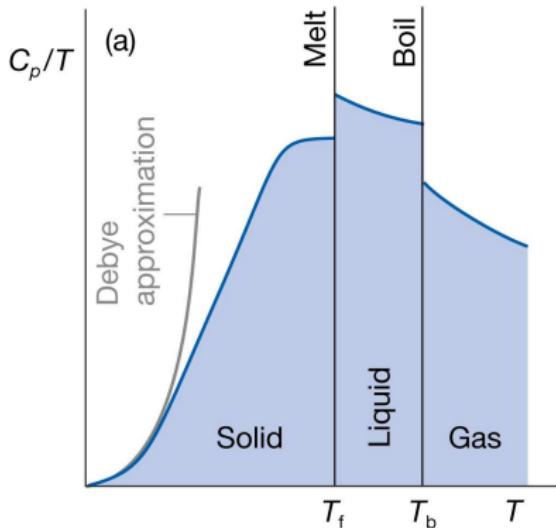
solved problem : Calculate  $\Delta S$  when 0.5 dm<sup>3</sup> of Ar at 25°C and 1.00 bar is compressed to 0.05 dm<sup>3</sup> and is simultaneously cooled to -25°C



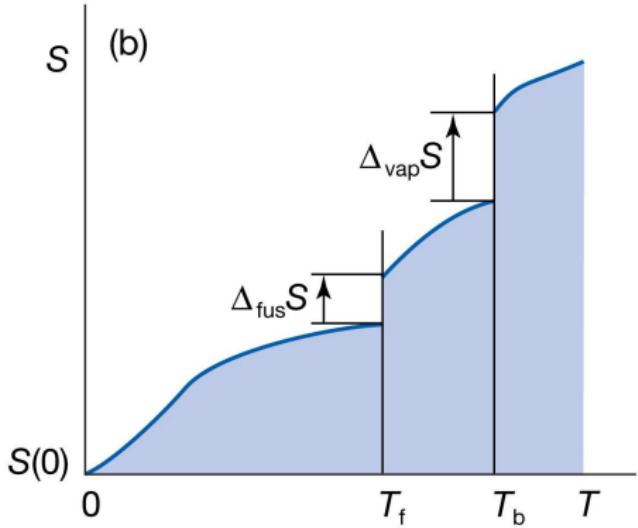
$$\Delta S_I = nR \ln \frac{V_f}{V_i} = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i}; \quad \Delta S_{II} = C_V \ln \frac{T_f}{T_i}$$

$$\begin{aligned}\Delta S &= \Delta S_I + \Delta S_{II} = nR \left( \ln \frac{V_f}{V_i} + \frac{3}{2} \ln \frac{T_f}{T_i} \right) = \frac{p_i V_i}{T_i} \ln \left( \frac{V_f}{V_i} \left[ \frac{T_f}{T_i} \right]^{\frac{3}{2}} \right) \\ &= \frac{10^5 \text{ Pa} \times 0.5 \times 10^{-3} \text{ m}^3}{298} \ln \left( \frac{0.05}{0.5} \left[ \frac{248}{298} \right]^{\frac{3}{2}} \right) = \\ &\qquad\qquad\qquad = -0.44 \text{ JK}^{-1}\end{aligned}$$

Heat capacity vs. temp.



entropy vs.  $T$



$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)dT}{T} + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} + \int_{T_1}^{T_b} \frac{C_p(l)dT}{T} + \frac{\Delta_{\text{vap}} H}{T_{\text{vap}}} + \int_{T_b}^T \frac{C_p(g)dT}{T}$$

All terms except  $S(0)$  can be measured calorimetrically

integrals can be evaluated either graphically or by fitting a polynomial to the data and integrating analytically

$\therefore \frac{dT}{T} = \ln T$ , one can evaluate area under a plot of  $C_p$  against  $\ln T$

Debye extrapolation :  $\lim_{T \rightarrow 0} C_p \longrightarrow aT^3$

Ex.  $S_m^\ominus$  for  $\text{N}_2(\text{g})$  at  $25^\circ\text{C}$  calculated from following data :

	$S_m^\ominus / \text{J K}^{-1}\text{mol}^{-1}$
Debye extrapolation	1.92
$\int_{10}^{35.61}$	25.25
Phase transition : $35.61\text{K}$	6.43
$\int_{35.61}^{63.14}$	23.38
Fusion : $63.14\text{K}$	11.42
$\int_{63.14}^{77.32}$	11.41
Vaporization : $77.32\text{K}$	72.13
$\int_{77.32}^{298.15}$	39.20
Correction for gas imperfection	0.92
Total	192.06

$$S_m(298.15\text{K}) = S_m(0) + 192.06 \text{ J K}^{-1}\text{mol}^{-1}$$

Nernst heat theorem :  $\lim_{T \rightarrow 0} \Delta S \longrightarrow 0$  for any transformation provided all substances involved are perfectly crystalline

3rd law (?) :

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

Boltzmann formula :  $S = k_B \ln \Omega$

$\Omega$  = #ways the molecules can be arranged in a crystalline form

In most cases,  $\lim_{T \rightarrow 0} \Omega = 1$ ,  $\therefore \lim_{T \rightarrow 0} S = 0$

when  $\Omega \neq 0$ , then  $S = S(0)$ , residual entropy

$\text{Ice-I}_h$  :

each H atom can lie either close to or far from its 'parent' O atom

total # of arrangements in sample of  $N$

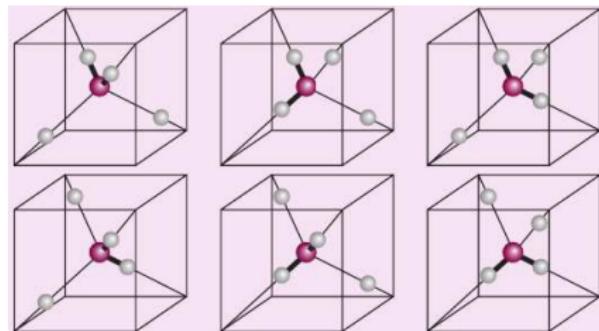
$\text{H}_2\text{O}$  molecules with  $2N$  H atoms =  $2^{2N}$

consider a single central O atom.

total number of arrangements of locations of H atoms around central O atom of one  $\text{H}_2\text{O}$  molecule is  $2^4 = 16$

Of these , only 6 correspond to two short and two long bonds

only  $\frac{6}{16} = \frac{3}{8}$  of all arrangements are possible, and for  $N$  molecules only  $(3/8)^N$  of all arrangements are possible



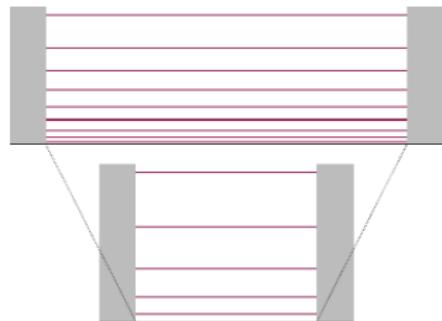
$$\begin{aligned}\therefore \text{for } N \text{ water molecules} \\ \# \text{ of possible configurations} \\ = 2^{2N} (3/8)^N = \left(\frac{3}{2}\right)^N\end{aligned}$$

$$S(0) = Nk_B \ln \left(\frac{3}{2}\right) = 3.37 \text{ J mol}^{-1}\text{K}^{-1}$$

molecular interpretation : Consider the increase in entropy with volume

As the system size increases  
energy levels move closer together and more  
become accessible to the molecules

# ways of achieving same energy,  $\Omega$  increases



## **Maxwell's demon** : a thought experiment

A gas initially in one chamber, connected via a closed tap to a second chamber containing only vacuum

Open the tap and gas in first chamber expands to fill both chambers

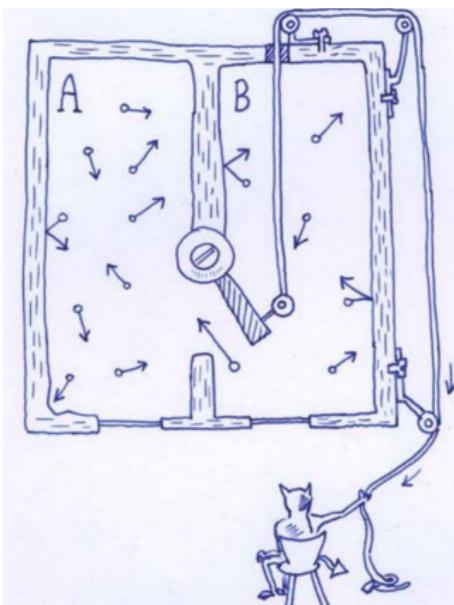
Equilibrium established and pressure in each

chamber is now half of what it was in the first chamber at the start

expansion is irreversible as there is no way to get the gas back into the initial chamber without doing work.

Maxwell imagined that the tap was operated by a microscopic intelligent creature. If it sees a molecule heading from the second chamber back into the first, it opens the tap and then shuts it, just letting the molecule through. If it sees a molecule heading from the first chamber back into the second chamber, it keeps the tap closed

Demon does no work and yet it makes molecules in second chamber all go back into the first chamber



Thus it creates a pressure difference between the two chambers where none existed before the demon started its mischief

as if the demon could therefore cause entropy to decrease in a system with no consequent increase in entropy anywhere else

- ▶ Conventional explanation : All observations and measurements require energy consumption : demon is no exception
- ▶ Modern explanation : demon needs to have a memory to operate, this act of storing information (actually erasing information) is associated with an increase of entropy, and this increase cancels out any decrease in entropy that the demon might be able to effect
- ▶ Demon is a computational device that processes and stores information
- ▶ It is possible to design a computational process that proceeds entirely reversibly, and therefore has no increase in entropy associated with it
- ▶ However, erasing information
  - ▶ is irreversible
  - ▶ has associated increase in entropy
- ▶ Maxwell's demon can operate reversibly therefore, but only if it has large enough hard disk that it doesn't ever need to clear space

**The Landauer principle** : “information is physical” - it has an energy equivalent  
- quantifies the thermodynamic cost of recording/erasure one bit of information

- ▶ Erasure of one bit of information requires minimum energy  $k_B T \ln 2 \approx 0.018 \text{ eV}$   
where  $T$  = temperature of thermal reservoir used
  - ▶ Information theory is usually supplied in a form that is independent of any physical embodiment
  - ▶ Landauer argued that information is physical and it has an energy equivalent
  - ▶ It may be stored in physical systems such as books and memory chips and transmitted by physical devices exploiting electrical or optical signals
  - ▶ it must obey laws of physics : first and foremost, laws of thermodynamics
- 
- a logically irreversible process must result in an entropy increase in non-information-bearing degrees of freedom of system and environment
  - a logically reversible process can be implemented thermodynamically reversibly
  - an amount of energy  $k_B T \ln 2$  ( $k_B T$  = thermal noise per unit bandwidth) is needed to transmit a bit of information, and more if quantized channels are used with photon energies  $h\nu > k_B T$

scale for  $S_m^\ominus$  of ions in solution:  $S_m^\ominus \text{ H}^+$  ions in water = 0  $\forall T$

$\Rightarrow S_m^\ominus$  of ions in water are values relative to  $\text{H}^+$

$> 0 \quad \Rightarrow \text{ion has higher molar entropy than H}^+ \text{ in water}$   
 $< 0 \quad \Rightarrow \text{ion has lower molar entropy than H}^+ \text{ in water}$

Ex.  $S_m^\ominus \text{ Cl}^-$ (aq) is  $57 \text{ J K}^{-1} \text{ mol}^{-1}$  and that of  $\text{Mg}^{+2}$ (aq) is  $-128 \text{ J K}^{-1} \text{ mol}^{-1}$

Ion entropies vary as expected : they are related to the degree to which ions order the water molecules around them in solution

Small, highly charged ions induce local structure in the surrounding water disorder of solution is decreased more than for large, singly charged ions

Absolute standard molar entropy of the proton in water can be estimated by proposing a model of the structure it induces, and there is some agreement on the value  $-21 \text{ J K}^{-1} \text{ mol}^{-1}$

negative value indicates that proton induces order in solvent

Standard reaction entropy :  $\Delta_r S^\ominus = \sum_{\text{products}} \nu S_m^\ominus - \sum_{\text{reactants}} \nu S_m^\ominus$

$\Delta_r S^\ominus$  is likely to be  $> 0$  if there is a net formation of gas in a reaction, and  
 $< 0$  if there is a net consumption of gas

Can we use  $\Delta U$  or  $\Delta H$  or  $\Delta S$  as a criterion for spontaneity?

General observation : Systems tend to evolve s. t. energy decreases in the process, but total energy of universe remains constant

$\Delta S$  for the universe tells us about the arrow of time

We can only measure details for the system, not the surroundings  
so we need better criteria for spontaneity that depend only on the system

starting from Clausius inequality,  $dq \leq TdS$

and ignoring extra non-mechanical work

$dq + dw = \boxed{dU \leq TdS - pdV}$  The variables  $S, V$  are natural variables for  $U$

$$U \equiv U(S, V); \quad dU_{S,V} \leq 0$$

similarly,  $dH \leq TdS + Vdp$ ; The variables  $S, p$  are natural variables for  $H$

$$H \equiv H(S, p); \quad dH_{S,p} \leq 0$$

Legendre transform : changing the natural variables :

$$y(x) = mx + c; \quad c(m) = -xm + y; \quad m = \frac{dy}{dx}$$

Information from  $(x, y) \equiv$  Information from  $(m, c)$

Try with  $U \equiv U(S, V); \quad (\frac{\partial U}{\partial S})_V = T, \quad \therefore$  Legendre transform,

$$\nearrow f = -S(\frac{\partial U}{\partial S})_V + U = U - TS$$

call it  $A$

Helmholtz free energy,  $A \equiv A(T, V)$ ;  $dA \leq -SdT - pdV$

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

Gibbs' free energy,  $G \equiv G(T, p)$

$$dG \leq Vdp - SdT$$

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

Maximum work :

$$dU \leq TdS + dw ; dw \geq dU - TdS$$

the most negative value of  $dw$ , and therefore the max. energy that can be obtained from system as work, is

$$dw_{\max} = dU - TdS; \text{ equality } \implies \text{reversible process}$$

$$\text{At const. } T, \quad dw_{\max} = dA; \quad \Delta A = \Delta U - T\Delta S$$

if  $\Delta S < 0$ , then RHS is not as negative as  $\Delta U$ ,  $\therefore w_{\max} < \Delta U$

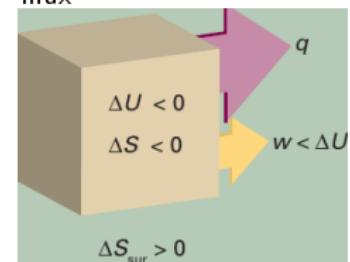
some energy must escape as heat to generate enough entropy in surroundings to overcome reduction in entropy in the system

For spontaneity,

Nature is taxing us as  $\Delta U$  is converted into work

$A = \text{part of } U \text{ that is free to use as work}; TS = \text{unavailable energy}$

$T \times S = \text{energy stored as thermal motion, unavailable part of } U \text{ for work}$



if  $\Delta S > 0$ , then RHS is more than  $\Delta U$ ;  $w_{\max} > \Delta U$

energy flows in as heat as work is done

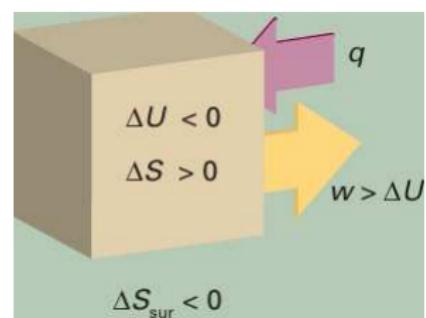
$S_{\text{system}}$  increases;  $S_{\text{surr}}$  decreases

$\Delta S_{\text{univ}} > 0 \implies$  spontaneous process

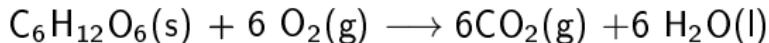
some energy (no more than the value of  $T\Delta S$ )

may leave the surroundings as heat and  
contribute to work

Nature is providing a tax refund



Ex. 1.0 mol C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> (glucose) is oxidized to CO<sub>2</sub> and water at 25°C



$$\Delta_r U^\ominus = -2808 \text{ kJ mol}^{-1} \text{ and } \Delta_r S^\ominus = 259.1 \text{ J K}^{-1}\text{mol}^{-1}$$

How much of this energy change can be extracted as  
(a) heat at constant pressure, (b) work?

$$\because \Delta\nu_g = 0, \quad \therefore \Delta_r H^\ominus = \Delta_r U^\ominus = -2808 \text{ kJ mol}^{-1}$$

$$\therefore q_p = \Delta_r H^\ominus = -2808 \text{ kJ mol}^{-1}$$

$$\Delta_r A^\ominus \stackrel{\text{const}}{=} \frac{\Delta_r U^\ominus - T\Delta_r S^\ominus}{T} = -2885 \text{ kJ mol}^{-1}$$

$$\text{max work} = 2885 \text{ kJ mol}^{-1} > |\Delta_r U^\ominus| \quad \therefore \Delta_r S^\ominus > 0$$

system can draw in energy from the surroundings (reducing their entropy) and make it available for work

Maximum non-expansion work :  $dG \leq Vdp - SdT + dw_{\text{add}}$

At constant  $T$  and  $p$ ,  $dw_{\text{add}} \geq dG$ ;  $w_{\text{add}} \geq \Delta G$

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

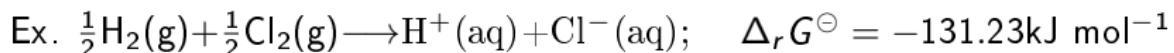
Ex. : energy available for sustaining muscular and nervous activity from combustion of 1.0 mol glucose under standard conditions at 37°C (blood temperature)?  $\Delta_r S^\ominus = 259.1 \text{ J mol}^{-1}$

$$\Delta_r G^\ominus \stackrel{T}{=} \Delta_r H^\ominus - T\Delta_r S^\ominus = -2808 - 310 \times 259.1 = -2885 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\ominus = \sum_{\text{products}} \nu \Delta_f G^\ominus - \sum_{\text{reactants}} \nu \Delta_f G^\ominus$$

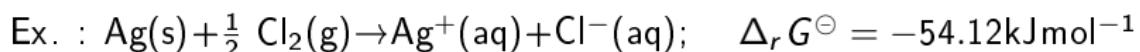
convenient defn.:  $\Delta_f G^\ominus(H^+, \text{aq}) = 0$  at all temps

$$\Delta_r G^\ominus(H^+, \text{aq}) = 0$$



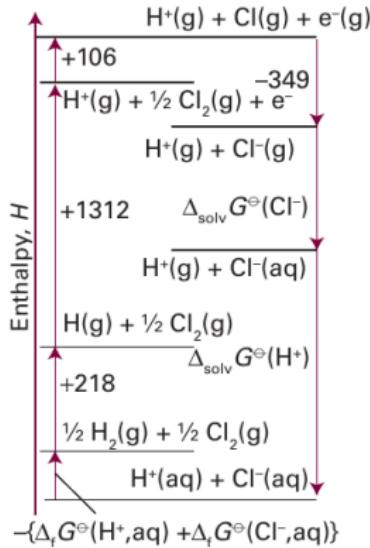
$$\therefore \Delta_f G^\ominus(Cl^-, \text{aq}) = -131.23 \text{ kJ mol}^{-1}$$

With  $\therefore \Delta_f G^\ominus(Cl^-, \text{aq})$  known, we can find  $\Delta_f G^\ominus$  for other ions

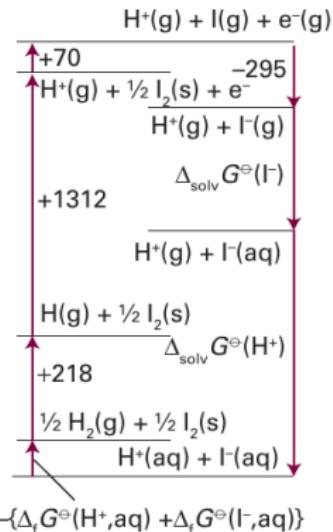


$$\Delta_f G^\ominus(Ag^+, \text{aq}) = -54.12 + 131.23 = 77.11 \text{ kJ mol}^{-1}$$

thermodynamic cycle:  
solvation of (a) chloride and (b) iodide ions:



$\Delta_f G^\ominus$  of an ion X is not determined by properties of X alone but includes contributions from dissociation, ionization, and hydration of hydrogen



Gibbs energy of solvation of individual ions

$$\Delta_f G^\ominus(\text{Cl}^-, \text{aq}) = 1287 \text{ kJ mol}^{-1} + \Delta_{\text{solv}} G^\ominus(\text{H}^+) + \Delta_{\text{solv}} G^\ominus(\text{Cl}^-)$$

Born equation :

$\Delta_{\text{solv}} G^\ominus$  = work of transferring an ion from a vacuum into solvent

model an ion as a sphere of radius  $r_i$ ; immersed in medium of permittivity  $\epsilon$

charge of the sphere =  $Q$

electric potential at surface is same as potential due to a point charge at its centre

$$\phi = \frac{Q}{4\pi\epsilon r_i}$$

work of bringing up a charge  $dQ$  to the sphere =  $\phi dQ$

total work of charging the sphere from 0 to  $z_i e$  =  $\frac{1}{4\pi\epsilon r_i} \int_0^{z_i e} Q dQ = \frac{z_i^2 e^2}{8\pi\epsilon r_i}$

In water,  $\Delta_{\text{solv}} G^\ominus = \Delta G^\ominus$  (charge in soln) -  $\Delta G^\ominus$  (charge in vacuum)

$$= -\frac{z_i^2 e^2}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right) = -\frac{z_i^2}{r_i (\text{pm})} \times (6.86 \times 10^4 \text{ kJ mol}^{-1})$$

Ex. :  $\Delta_{\text{solv}} G^\ominus (\text{Cl}^{-1}) - \Delta_{\text{solv}} G^\ominus (\text{I}^{-1})$

$$= -\left(\frac{1}{181} - \frac{1}{220}\right) \times (6.86 \times 10^4 \text{ kJ mol}^{-1}) = -67 \text{ kJ mol}^{-1}$$

Chemical potential :  $\mu = \left( \frac{\partial G}{\partial n_i} \right)_{p, T, n_j, j \neq i}$

For pure substance,  $\mu = \frac{G}{n}$

fundamental equation :  $dU = TdS - pdV + \mu dN$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$$

For irreversible processes,  $dS > \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$

analysis of one-component, two-phase isolated system :

definition of an isolated system : the following must be constant

1. internal energy,  $U$
2. total volume,  $V$
3. total mass of the one component,  $N$  (no. of moles)

1	2
---	---

Let superscripts (1) and (2) refer to the two phases

$$U = U^{(1)} + U^{(2)} = \text{const}, \text{ or, } dU = dU^{(1)} + dU^{(2)} = 0$$

$$V = V^{(1)} + V^{(2)} = \text{const}, \text{ or, } dV = dV^{(1)} + dV^{(2)} = 0$$

$$N = N^{(1)} + N^{(2)} = \text{const}, \text{ or, } dN = dN^{(1)} + dN^{(2)} = 0$$

and

$$dS = dS^{(1)} + dS^{(2)} = \frac{1}{T^{(1)}} dU^{(1)} + \frac{1}{T^{(2)}} dU^{(2)} + \frac{p^{(1)}}{T^{(1)}} dV^{(1)} + \frac{p^{(2)}}{T^{(2)}} dV^{(2)} - \frac{\mu^{(1)}}{T^{(1)}} dN^{(1)} - \frac{\mu^{(2)}}{T^{(2)}} dN^{(2)}$$

Let us consider three different cases for the wall between the phases :

1. impermeable, rigid, diathermal wall  $\Rightarrow dV^{(1)} = dV^{(2)} = 0$  and  $dN^{(1)} = dN^{(2)} = 0$
2. thermal equilibrium, flexible, impermeable, diathermal wall  $\Rightarrow T^{(1)} = T^{(2)}$  and  $dN^{(1)} = dN^{(2)} = 0$
3. thermal and mechanical equilibrium, flexible, permeable, diathermal wall  
 $\Rightarrow T^{(1)} = T^{(2)}$  and  $p^{(1)} = p^{(2)}$

To explore thermal equilibrium, consider only heat flow :

impermeable, rigid, diathermal wall  $\implies dV^{(1)} = dV^{(2)} = 0$   
 $dN^{(1)} = dN^{(2)} = 0$

$$\therefore dU^{(1)} + dU^{(2)} = 0 \implies dU^{(1)} = -dU^{(2)} = dU \text{ (say)}$$

$$\therefore dS = \frac{1}{T^{(1)}}dU - \frac{1}{T^{(2)}}dU = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)dU > 0$$

if  $dU > 0$  (flow of energy from phase 2 to phase 1),

then  $T^{(1)} < T^{(2)}$ , i.e. energy must flow from higher to lower temperature for thermal equilibrium to be reached

At  $T^{(1)} = T^{(2)}$  (thermal equilibrium),  $dS = 0$

Since there is no work involved, the energy here is heat

$\therefore$  heat must flow from higher to lower temperature

to explore condition for mechanical equilibrium, consider  
the phases to be in thermal equilibrium with

flexible, impermeable, diathermal wall  $\Rightarrow$   $T^{(1)} = T^{(2)} = T$   
 $dN^{(1)} = dN^{(2)} = 0$

$$\therefore dV^{(1)} + dV^{(2)} = 0 \quad \Rightarrow \quad dV^{(1)} = -dV^{(2)} = dV \text{ (say)}$$

$$\therefore dS = \frac{p^{(1)}}{T} dV - \frac{p^{(2)}}{T} dV = \frac{1}{T} (p^{(1)} - p^{(2)}) dV > 0$$

if  $dV > 0$  (wall moves away from phase 1 to phase 2),

then  $p^{(1)} < p^{(2)}$ , i.e. mechanical equilibrium requires movement of the wall from higher pressure to lower pressure region

When  $p^{(1)} = p^{(2)}$  (mechanical equilibrium),  $dS = 0$

to explore conditions for chemical equilibrium. consider the systems 1 and 2 at thermal and mechanical equilibrium, flexible, permeable, diathermal wall

$$\begin{aligned} T^{(1)} &= T^{(2)} \\ \implies p^{(1)} &= p^{(2)} \end{aligned}$$

$$\therefore dN^{(1)} + dN^{(2)} = 0 \implies dN^{(1)} = -dN^{(2)} = dN \text{ (say)}$$

$$\therefore dS = -\frac{\mu^{(1)}}{T} dN^{(1)} + \frac{\mu^{(2)}}{T} dN = \frac{1}{T} (\mu^{(2)} - \mu^{(1)}) dN > 0$$

if  $dN > 0$  (mass moves from phase 2 to phase 1),

then  $\mu^{(2)} > \mu^{(1)}$ , i.e., mass moves spontaneously from higher to lower chemical potentials

When  $\mu^{(1)} = \mu^{(2)}$  (chemical equilibrium),  $dS = 0$



A general property of exact differentials :

consider  $f(x, y)$  and  $df = gdx + hdy$ , where  $g \equiv g(x, y)$  and  $h \equiv h(x, y)$  e.g., for

$U(S, V)$ ,  $dU = TdS - pdV$  when  $df$  is an exact differential,

$$\left(\frac{\partial g}{\partial y}\right)_x = \underbrace{\frac{\partial^2 f}{\partial y \partial x}}_{\text{both } x \text{ and } y, \text{ vary}} = \frac{\partial^2 f}{\partial x \partial y} = \left(\frac{\partial h}{\partial x}\right)_y$$

Maxwell relations :

for reversible changes in systems with no non-mechanical work

$$dU = TdS - pdV$$

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

$$dH = TdS + Vdp$$

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

$$dA = -SdT - pdV$$

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

$$dG = Vdp - SdT$$

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

Another definition of temperature

$$dU = TdS - pdV \implies \boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V}$$

$$dH = TdS + Vdp \implies \frac{1}{T} = \left(\frac{\partial S}{\partial H}\right)_p$$

Thermodynamic equation of state :

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p \quad \text{or, } \pi_T = T \left(\frac{\partial S}{\partial V}\right)_T - p$$

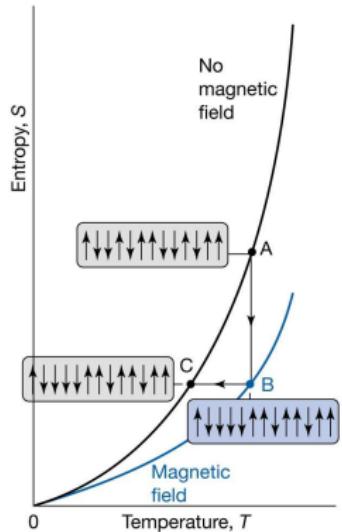
Using Maxwell relation  $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

$$\boxed{\pi_T = T \left(\frac{\partial p}{\partial T}\right)_V - p}$$

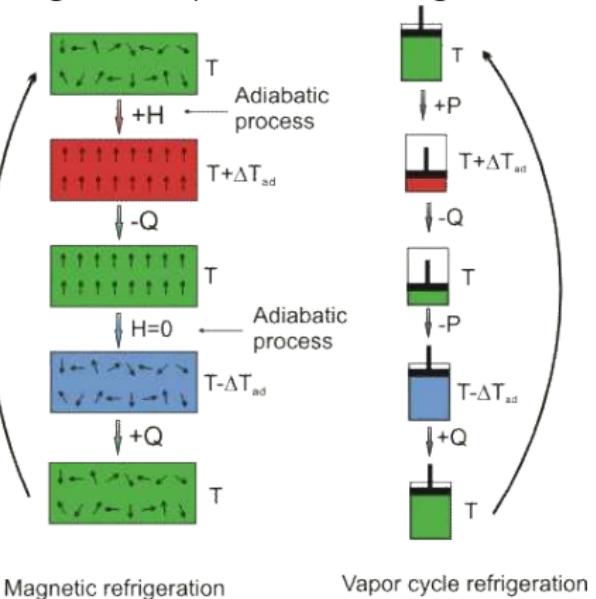
For perfect gas, show that this leads to  $\pi_T = 0 \int_{263}^{273}$

Find for van der Waals gas,  $\pi_T = a \frac{n^2}{V^2} > 0 \implies \left(\frac{\partial U}{\partial V}\right)_T > 0$

## Adiabatic demagnetisation - method of cooling below 0.3 K

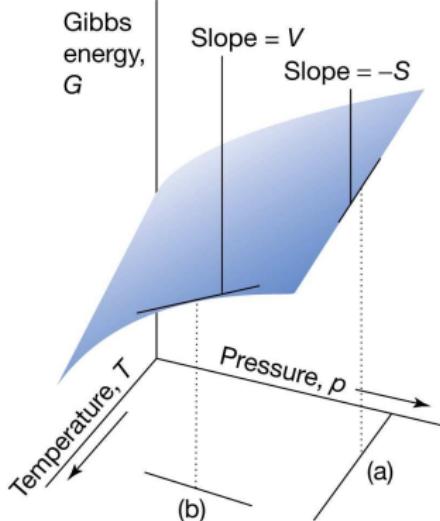


Analogy between magnetic refrigeration and vapor cycle or conventional refrigeration ( $H$  refers to magnetic field)

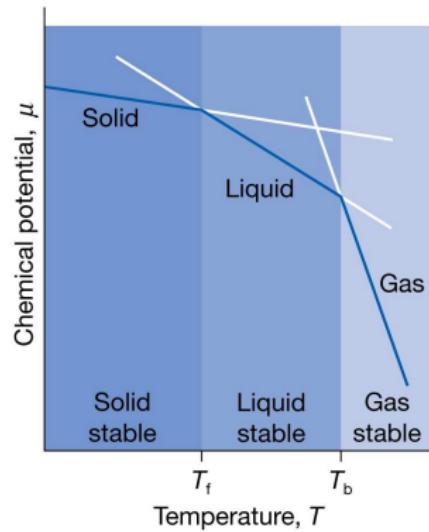


## Gibbs' Free energy and entropy

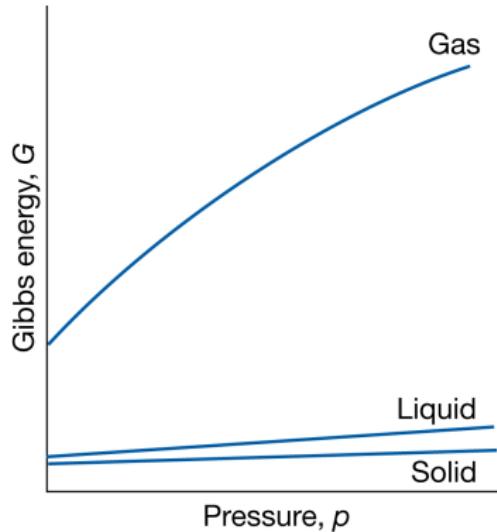
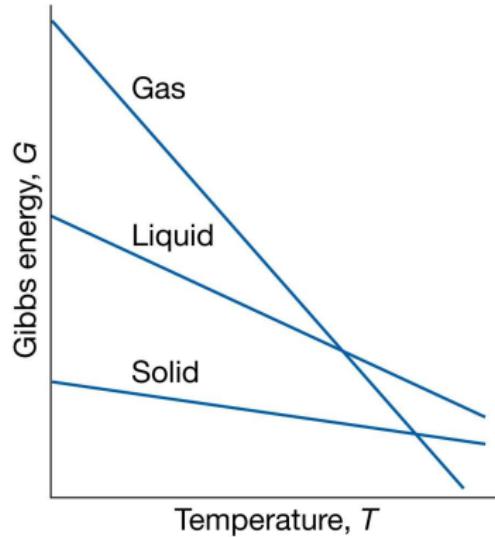
$$\left(\frac{\partial G}{\partial T}\right)_p = -S < 0$$
$$\left(\frac{\partial G}{\partial p}\right)_T = V > 0$$



chemical potential and phase equilibrium :  $\left(\frac{\partial\mu}{\partial T}\right)_p = -S_m$



sublimation before melting



Gibbs-Helmholtz equation :

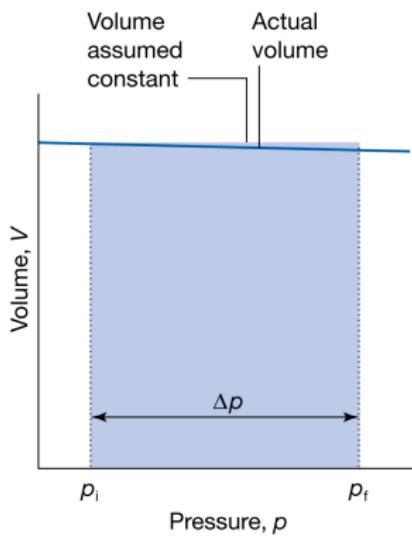
$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T}$$

Use this to show :  $\left(\frac{\partial \left[\frac{G}{T}\right]}{\partial T}\right)_p = -\frac{H}{T^2}$

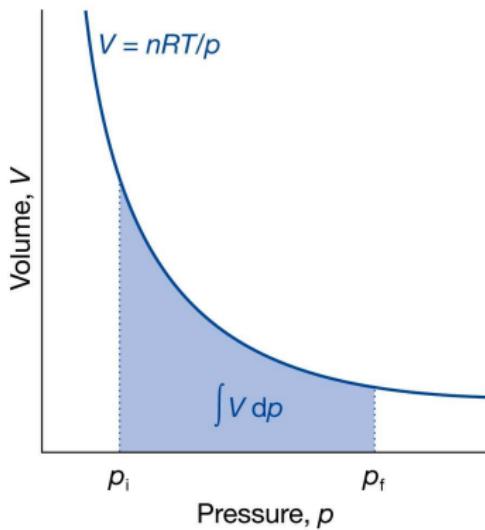
$$\boxed{\left(\frac{\partial \left[\frac{\Delta G}{T}\right]}{\partial T}\right)_p = -\frac{\Delta H}{T^2}}$$

Change in  $G$  with  $p$  :  $G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$

for condensed phases



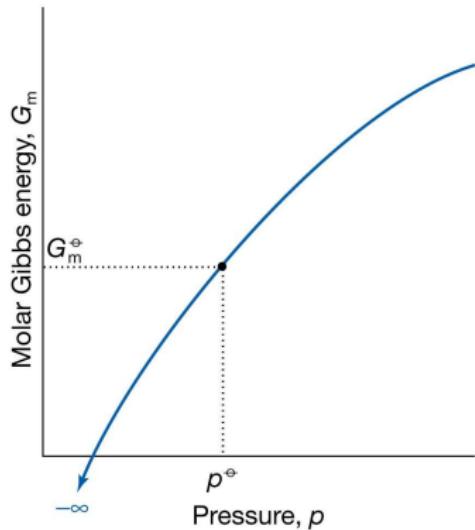
gases



$$G_m(p_f) = G_m(p_i) + V_m (p_f - p_i)$$

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

molar Gibbs energy vs p :  $G_m(p) = G_m^\ominus + RT \ln \frac{p}{p^\ominus}$



molar Gibbs energy vs p :  $G_m(p) = G_m^\ominus + RT \ln \frac{f}{p^\ominus}$ ;  $f$  (fugacity) =  $\underbrace{\phi}_{\text{fugacity coeff}}$  . p

$$\int_{p'}^p V_m dp = G_m(p) - G_m(p') = \left\{ G_m^\ominus + RT \ln \frac{f}{p^\ominus} \right\} - \left\{ G_m^\ominus + RT \ln \frac{f'}{p^\ominus} \right\}$$

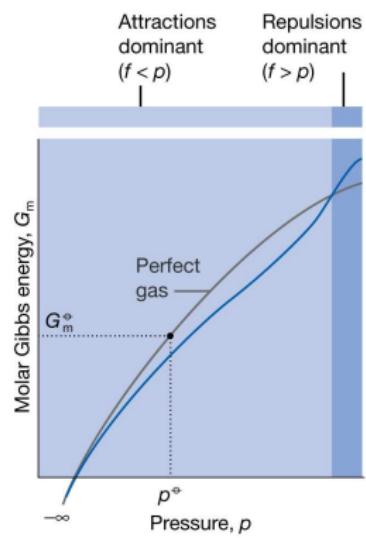
$$\int_{p'}^p V_{\text{perfect, } m} dp = RT \int_{p'}^p \frac{dp}{p} = RT \ln \frac{p}{p'}$$

$$\int_{p'}^p (V_m - V_{\text{perfect, } m}) dp = RT \left( \ln \frac{f}{f'} - \ln \frac{p}{p'} \right)$$

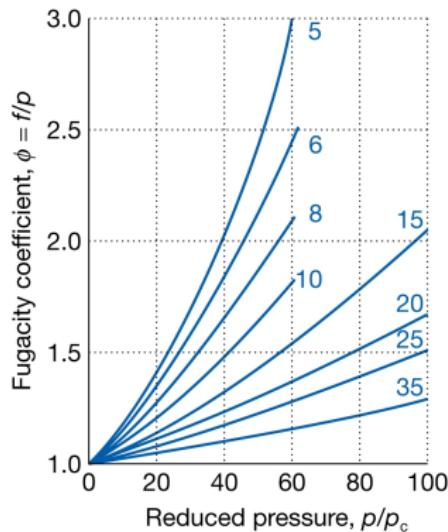
$$\text{or, } \ln \frac{f}{p} - \ln \frac{f'}{p'} = \frac{1}{RT} \int_{p'}^p (V_m - V_{\text{perfect, } m}) dp$$

$$\underset{p \rightarrow 0}{\mathcal{L} t} f \rightarrow p \implies \ln \frac{f}{p} = \frac{1}{RT} \int_0^p (V_m - V_{\text{perfect, } m}) dp$$

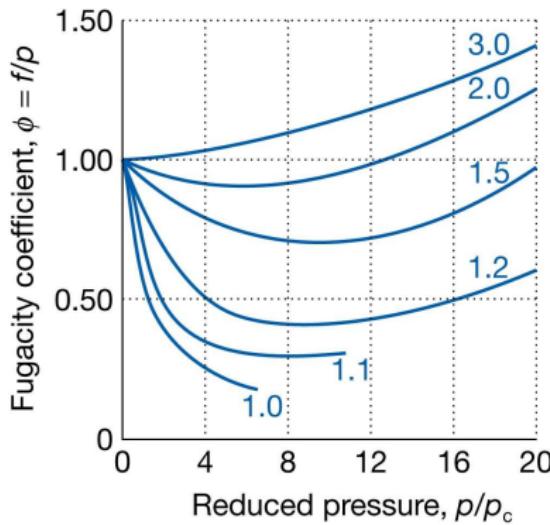
$$\text{or, } \ln \phi = \int_0^p \frac{V_m - V_{\text{perfect, } m}}{p} dp$$



fugacity coeff. of van der Waals gas as function of reduced pressure  
for various reduced temperatures



$$\text{label : } \frac{T}{T_c}$$

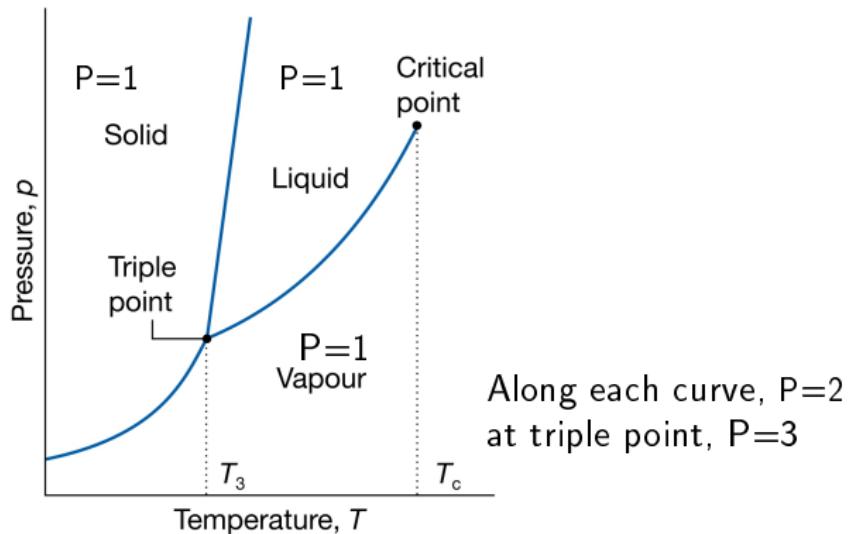




phase : form of matter that is uniform throughout in chemical composition and physical state

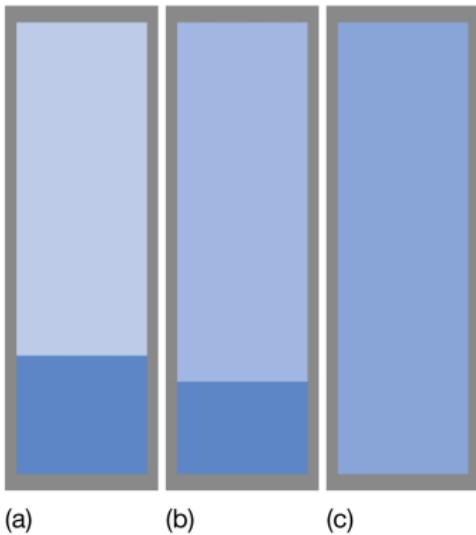
$P = \# \text{ phases in a system}$

Phase equilibria - triple point ( $T_3$ ) and critical point ( $T_c$ )



For water :  $T_3 = 273.16 \text{ K}$  and  $611 \text{ Pa}$  (6.11 mbar)

## Phase equilibria - coalescence at critical temp.



When a liquid is heated in a sealed container, density of vapour phase increases and that of the liquid decreases slightly a stage comes at which the two densities are equal and interface between the fluids disappears and a supercritical fluid fills the container

This occurs at the critical temperature

The container needs to be strong :

$T_C$  of water =  $374^\circ\text{C}$  and vapour pressure = 218atm

- ▶ Triple point marks the lowest pressure at which a liquid phase can exist
- ▶ If the slope of the solid–liquid phase boundary is positive
  - ▶ then triple point also marks the lowest temperature at which the liquid can exist
- ▶ the critical temperature is the upper limit

$$\text{Phase Rule : } F = C - P + 2$$

$F = \# \text{ degrees of freedom}$ ,  $C = \# \text{ components}$ ,  $P = \# \text{ phases}$

single-component, single-phase

$$F = 1 - 1 + 2 = 2$$

single-component, two-phases

$$F = 1 - 2 + 2 = 1$$

phases  $\alpha$  and  $\beta$  in equilibr. at given  $p$ ,  $T$

$$\mu_\alpha(p, T) = \mu_\beta(p, T)$$

eqn. relates  $p$  and  $T$ ,

so only one variable is independent

single-component

three-phases

$$F = 1 - 3 + 2 = 0$$

phases  $\alpha$ ,  $\beta$  and  $\gamma$  in equilibr. at given  $p$ ,  $T$ ,

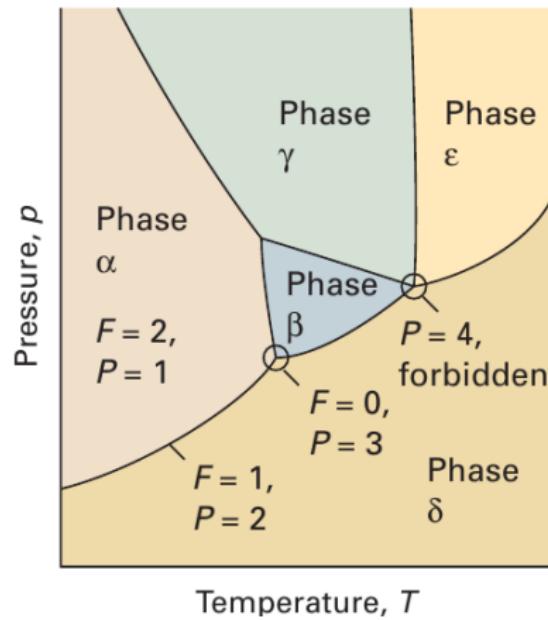
$$\begin{aligned} \mu(\alpha, p, T) &= \mu(\beta, p, T) \\ &= \mu(\gamma, p, T) \end{aligned}$$

two eqns. for two unknowns  $p$  and  $T$

fixed soln.

so no variation possible

## Typical phase diagram for a single component



Generally, total number of intensive variables ( $p, T$ ) = 2

We specify composition of a phase by giving mole fractions of  $C - 1$  components

$$\# \text{ composition variables} = P(C - 1)$$

$$\therefore \# \text{ intensive variables} = P(C - 1) + 2$$

For each component  $i$ , there are  $P - 1$  eqns. of the kind

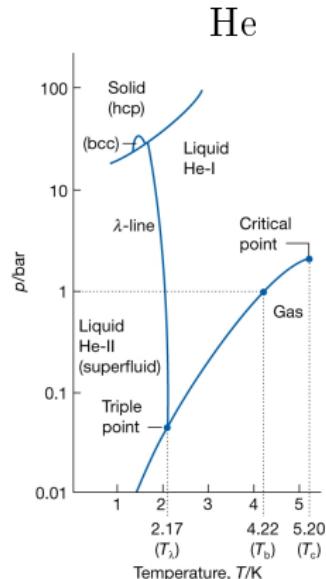
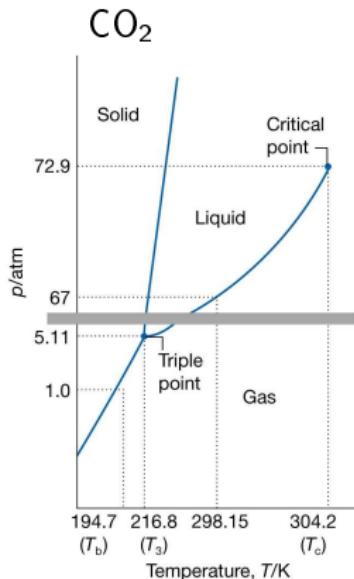
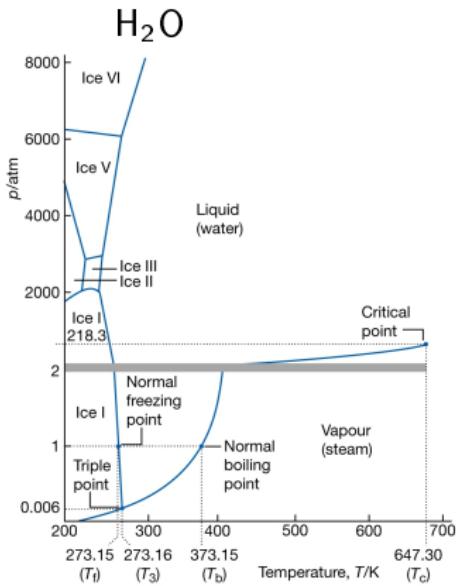
$$\mu_i(\alpha, p, T) = \mu_i(\beta, p, T) = \dots$$

Each eqn. is a constraint,

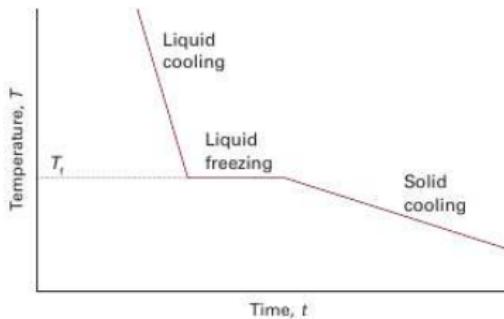
$$\# \text{ constraints} = C(P - 1)$$

$$\therefore \# \text{ degrees of freedom} = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

## Experimental phase diagrams



## Phase transition : Thermal analysis and Cooling curve

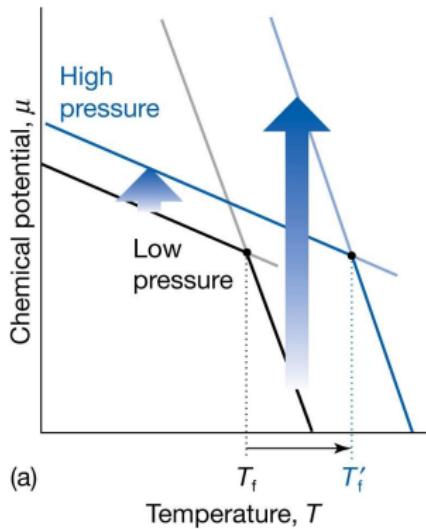


metastable phases : Kinetic barriers

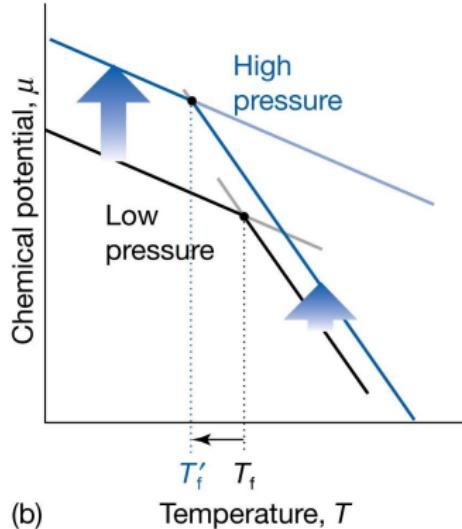
Response of melting to applied pressure

pressure-dependence of chemical potential :  $\left(\frac{\partial\mu}{\partial p}\right)_T = V_m$

usual liquids :  $V_m(l) > V_m(s)$



water :  $V_m(l) < V_m(s)$



$$\text{For perfect gas, } G_m(p) = G_m^\ominus + RT \ln \frac{p}{p^\ominus}$$

$$\implies \mu(p) = \mu^\ominus + RT \ln \frac{p}{p^\ominus} \stackrel{p^\ominus=1}{=} \mu^\ominus + RT \ln p$$

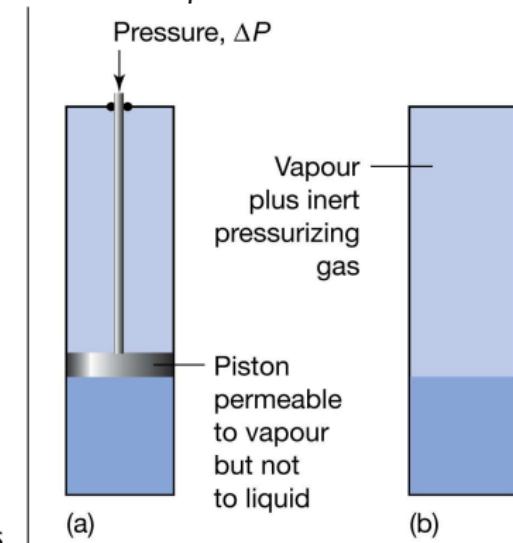
for pressure induced change in gas-liq equilibr.

$$d\mu(g) = d\mu(l) \text{ or, } \frac{RTdp}{p} = V_m(l)dp$$

integrating from an initial  $p_{\text{vap}} = p^*$  to  $p$ , we have,  $\ln \frac{p}{p^*} = \frac{V_m(l)}{RT} \Delta p_{\text{vap}}$

Pressure is applied to condensed phase either (a) by compressing directly or (b) by subjecting it to an inert pressurizing gas

When pressure is applied, the vapour pressure of the condensed phase increases

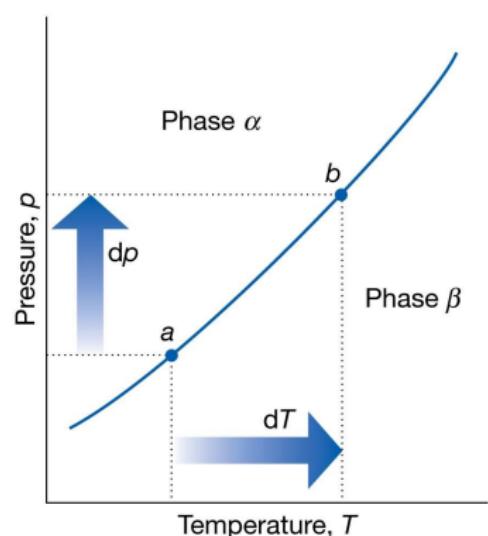


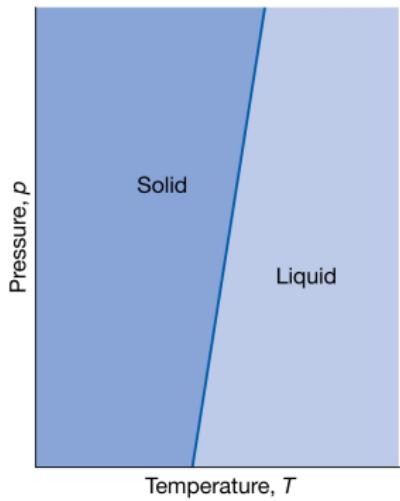
$$\text{location of phase boundaries : } \left( \frac{\partial p}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$

$$\text{solid/liq. : } \frac{dp}{dT} = \frac{\Delta_{fus} H}{T \Delta_{fus} V}$$

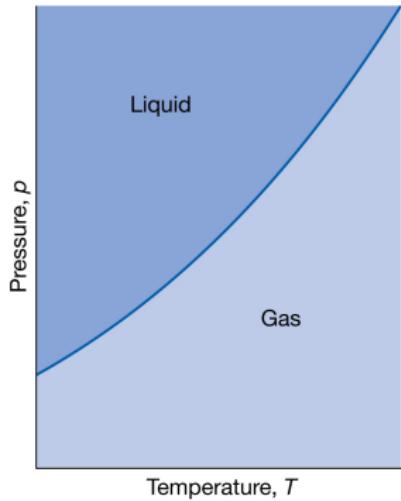
When pressure is applied to a system with two phases in equilibrium (at a), the equilibrium is disturbed  
It can be restored by changing  $T$ , moving state of system to b

relation between  $dp$  and  $dT$  ensures that system remains in equilibrium as either variable is changed

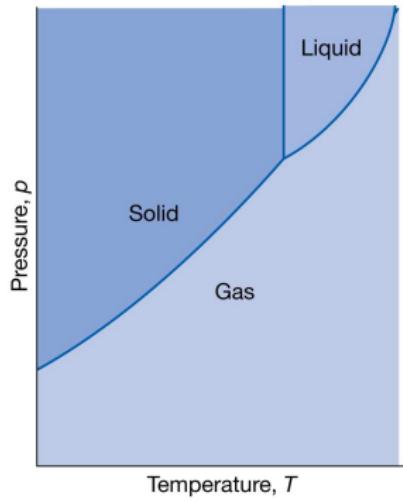




fairly linear



quite curved

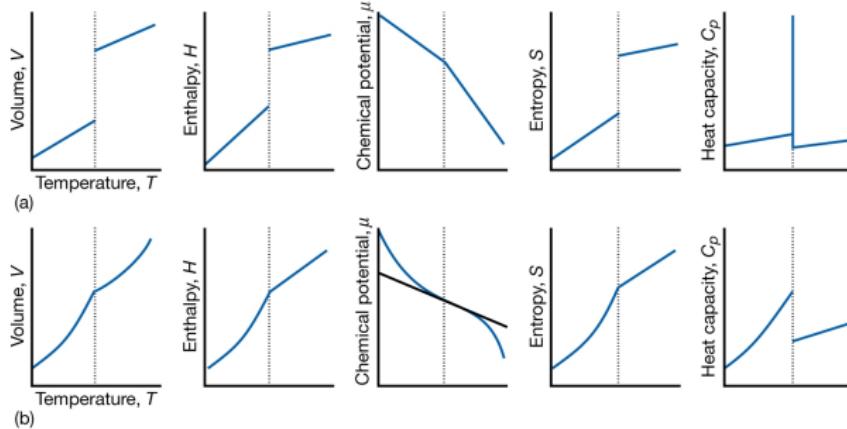


Temperature,  $T$

## Ehrenfest classification : 1st order and 2nd order phase transitions

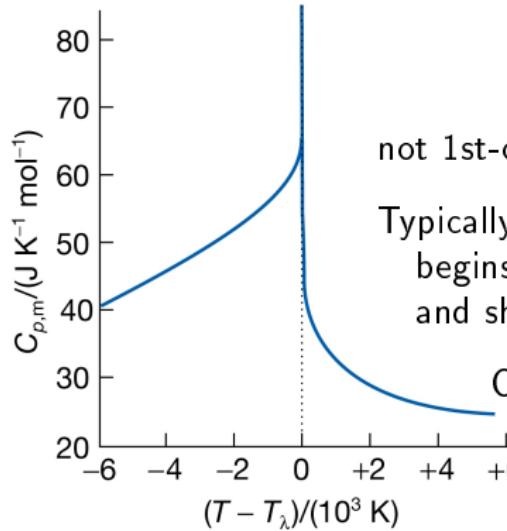
1st order : First derivative  $\frac{\partial \mu}{\partial T}$  discontinuous - typically involves relocation of atoms, molecules, or ions changing energies of interactions

2nd order : Second derivative  $\frac{\partial^2 \mu}{\partial T^2}$  discontinuous -  $V$  and  $S$  (and hence  $H$ ) do not change at transition  $C_p$  is discontinuous at transition but does not become infinite there



example of a 2nd-order transition : conducting–superconducting transition in metals at low  $T$

$\lambda$  curve for helium :



not 1st-order, yet  $C_p$  becomes  $\infty$  at transition temp.

Typically,  $C_p$  of a system that shows such a transition begins to increase well before transition and shape of  $C_p$  curve resembles letter  $\lambda$

Other examples :

order-disorder transitions in alloys

onset of ferromagnetism

and fluid–superfluid transition of liquid He

Molecular interpretation :

1st-order transitions typically involve relocation of atoms, molecules, or ions with consequent change in the energies of their interactions

vaporization eliminates attractions between molecules

and 1st-order phase transition from one ionic polymorph to another

e.g., calcite to aragonite, involves adjustment of relative positions of ions

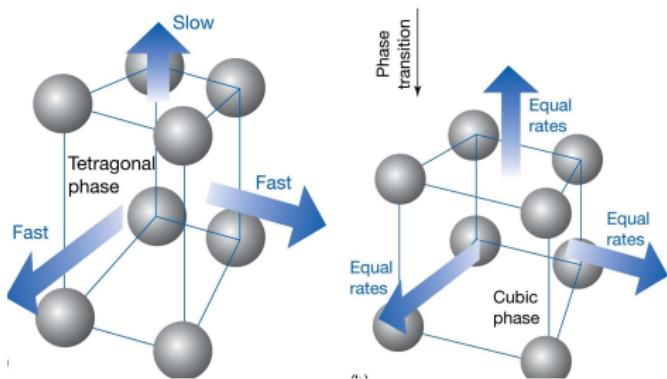
One type of 2nd-order transition : change in symmetry of crystal structure

if arrangement of atoms in a solid is s. t. one dimension (of the unit cell) is longer than the other two, which are equal  $\Rightarrow$  tetragonal

suppose the shorter dimensions increase more than long dimension when  $T$  is raised - at some stage three dimensions become equal

then crystal has cubic symmetry

at higher  $T$  it will expand equally in all three directions



tetragonal  $\rightarrow$  cubic transition  
with no discontinuity in  
interaction energy between atoms  
or the volume they  
occupy, transition not 1st-order

order-disorder transition in  $\beta$ -brass ( $\text{CuZn}$ ) is  $\lambda$ -transition

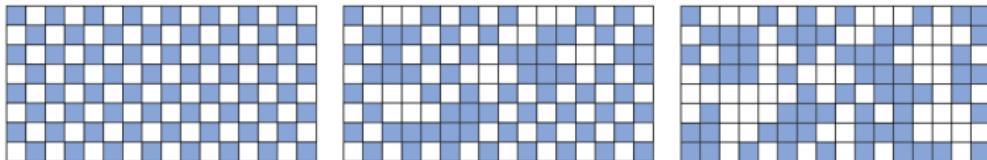
low- $T$  phase : orderly array of alternating Cu/Zn atoms

high- $T$  phase : random array of atoms

At  $T = 0$  perfect order, but islands of disorder appear as  $T$  raised  
islands form because transition is cooperative : once two atoms have exchanged  
locations, it is easier for neighbours to exchange their locations

islands grow in extent and merge throughout the crystal at  $T_{\text{transn.}} = 742 \text{ K}$

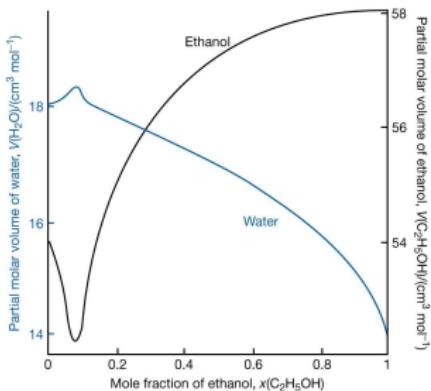
$C_p$  increases as  $T_{\text{transn.}}$  approaches because cooperative nature makes it  
increasingly easy for heat supplied to drive phase transition rather than be stored  
as thermal motion



## Partial molar volume :

add 1 mol  $\text{H}_2\text{O}$  to a huge volume of pure ethanol,  $\Delta V = +14 \text{ cm}^3$

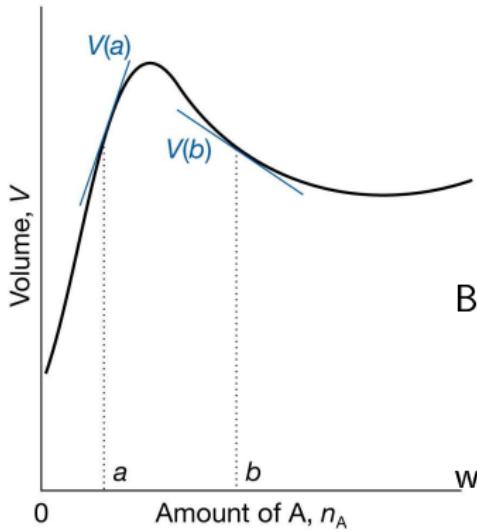
reason : volume occupied by water molecules depends on identity of molecules that surround them



there is so much ethanol present that each  $\text{H}_2\text{O}$  molecule is surrounded by ethanol molecules. network of H-bonds that normally hold  $\text{H}_2\text{O}$  molecules at certain distances from each other in pure water does not form packing of molecules results in  $\text{H}_2\text{O}$  molecules increasing the volume by only  $14 \text{ cm}^3$  = partial molar volume of water in pure ethanol

In general, partial molar volume of a substance A in a mixture  
 $= \Delta V$  per mole of A added to large volume of mixture

$$V_J = \left( \frac{\partial V}{\partial n_J} \right)_{p, T, n'}$$



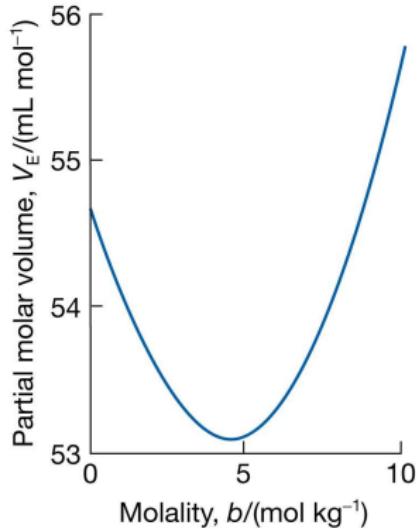
Binary mixture :

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

with relative composition held constant :

$$V = V_A n_A + V_B n_B$$

solved ex. :



polynomial fit to measurements of total volume (cm<sup>3</sup>) of a water/ethanol mixture at 25°C containing 1.0 kg of water :

$$V = 1002.93 + 54.6664x - 0.36394x^2 + 0.028256x^3$$

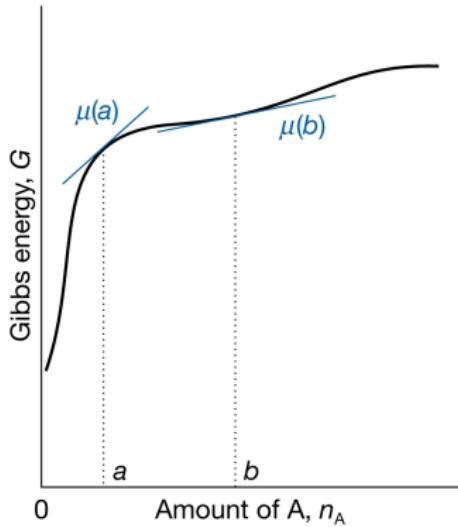
where  $x$  = mole fraction of ethanol (E)

$$\begin{aligned}\therefore V_E &= \left(\frac{\partial V}{\partial x}\right)_{p,T,nw} \\ &= 54.6664 - 2 \times 0.36394x + 3 \times 0.028256x^2 \\ &= 54.6664 - 0.72788x + 0.084768x^2\end{aligned}$$

partial molar quantities can be negative

$$V_{\text{MgSO}_4} \text{ in water} = -1.4 \text{ cm}^3/\text{mol}$$

Partial molar Gibbs energies  $\equiv$  chemical potential



In a binary mixture,  $G = n_A\mu_A + n_B\mu_B$

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

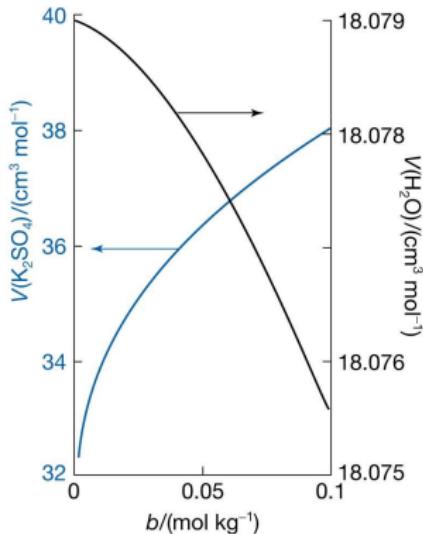
But  $dG = Vdp - SdT + \sum_i \mu_i dn_i$ ; or,  $dG_{p,T} = \mu_A dn_A + \mu_B dn_B$

$\therefore n_A d\mu_A + n_B d\mu_B = 0$

or, generally, 
$$\boxed{\sum_i n_i d\mu_i = 0}$$
 : Gibbs–Duhem equation

- ▶ chemical potential of one component of a mixture cannot change independently of chemical potentials of the other components
- ▶ In a binary mixture, if one partial molar quantity increases, then the other must decrease, with the two changes related by  $d\mu_B = -\frac{n_A}{n_B} d\mu_A$
- ▶ The same applies to all partial molar quantities
- ▶ small change in  $V_A$  corresponds to a large change in the  $V_B$  if  $\frac{n_A}{n_B}$  is large
- ▶ the opposite is true when this ratio is small
- ▶ Gibbs–Duhem equation is used to determine the  $V_J$  of one component of a binary mixture from measurements of the  $V_J$  of the second component

solved ex. : At 298 K experimental values of  $V_{K_2SO_4(aq)} = 32.280 + 18.216\sqrt{x}$  in  $\text{cm}^3/\text{mol}$  and  $x = \text{molality of } K_2SO_4$ . What is  $V_{m,H_2O}$  in the soln.?  $V_m$  of pure water at 298 K =  $18.079 \text{ cm}^3 \text{ mol}^{-1}$



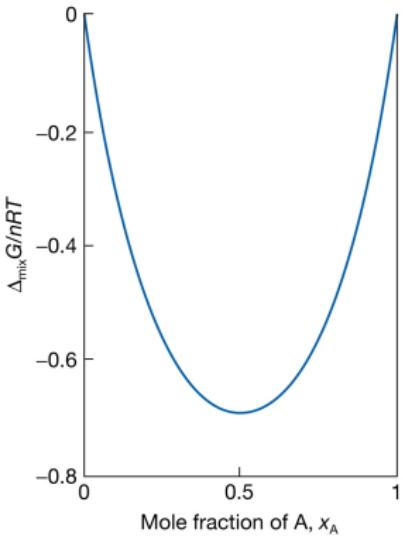
$$dV_A = -\frac{n_B}{n_A} dV_B, \text{ say } B \equiv K_2SO_4$$

$$\text{or, } V_A = V_A^{\text{pure}} - 9.108 \int_0^{V_B} \frac{n_B}{n_A} x^{-\frac{1}{2}} dx$$

$$\text{and } \frac{n_B}{n_A} = \frac{x}{1000/18} = \frac{18x}{1000}$$

$$\begin{aligned} \therefore V_{m,H_2O} &= 18.079 - 18 \times 9.108 \int_0^{V_B} x^{\frac{1}{2}} dx \\ &= 18.079 - 0.1094 x^{\frac{3}{2}} \end{aligned}$$

## Gibbs energy of mixing of perfect gases



$$\mu = \mu^\ominus + RT \ln p$$

$$\text{Before mixing } G_i = n_A \mu_A + n_B \mu_B$$

$$= n_A (\mu_A^\ominus + RT \ln p) + n_B (\mu_B^\ominus + RT \ln p)$$

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

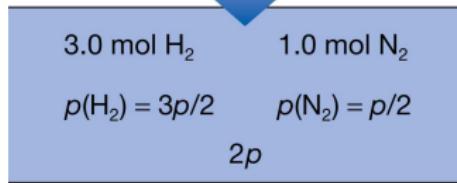
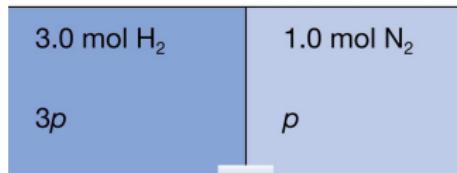
$$= n_A (\mu_A^\ominus + RT \ln p_A) + n_B (\mu_B^\ominus + RT \ln p_B)$$

$$\therefore \Delta_{\text{mix}} G = G_f - G_i$$

$$= n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

$$= nRT (x_A \ln x_A + x_B \ln x_B)$$

Ex. : initial pressures not the same :



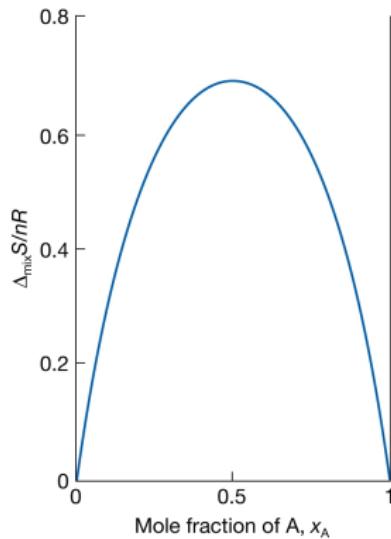
$$G_i = 3 (\mu_{H_2}^\ominus + RT \ln 3p) + 1 (\mu_{N_2}^\ominus + RT \ln p)$$

$$G_f = 3 (\mu_{H_2}^\ominus + RT \ln \frac{3}{2}p) + n_B (\mu_{N_2}^\ominus + RT \ln \frac{p}{2})$$

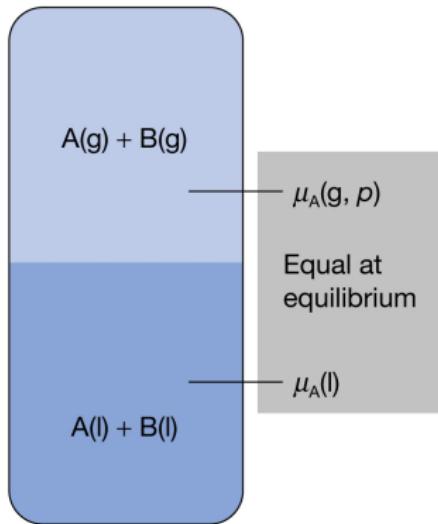
$$\begin{aligned}\therefore \Delta_{\text{mix}} G &= G_f - G_i \\ &= -4RT \ln 2 = -6.9 \text{ kJ}\end{aligned}$$

for a mixture of perfect gases initially at the same pressure,

$$\Delta_{\text{mix}}S = - \left( \frac{\partial \Delta_{\text{mix}}G}{\partial T} \right)_{p, n_A, n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$



## Ideal solutions



\*  $\equiv$  pure substance

$\mu_A^*$  = chemical potential of pure A

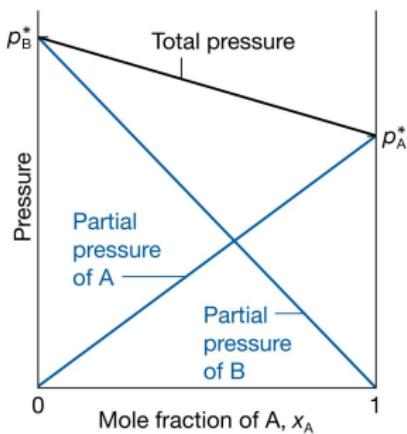
$\mu_A^*(l)$  = chemical potential of pure liquid A

$$\mu_A^* = \mu_A^\ominus + RT \ln p_A^*$$

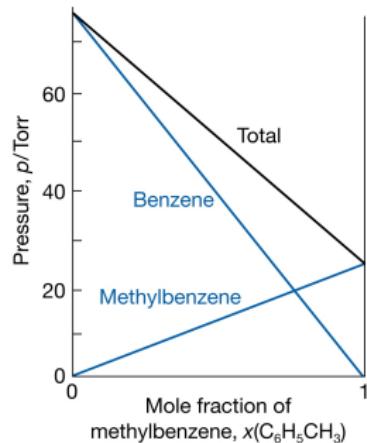
$$\text{soln. : } \mu_A = \mu_A^\ominus + RT \ln p_A$$

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

Ideal solutions - Raoult's law:  $p_A = x_A p_A^* \implies \mu_A = \mu_A^* + RT \ln x_A$



Some mixtures obey Raoult's law very well especially when the components are structurally similar



Mixtures that obey the law throughout from pure A to pure B are called **ideal solutions**

molecular origin of Raoult's law : effect of solute on entropy of solution

- ▶ pure solvent : molecules have a certain disorder and corresponding entropy
- ▶ vapour pressure represents tendency to reach a higher entropy
- ▶ solution : has a greater disorder than pure solvent because we cannot be sure that a molecule chosen at random will be a solvent molecule
- ▶  $\therefore S_{\text{soln.}} > S_{\text{pure solvent}}$   $\therefore$  solution has lower tendency to acquire an even higher entropy by solvent vaporizing
- ▶  $\therefore$  vapour pressure of solvent in solution  $<$  that of pure solvent
- ▶ vapour pressure of solvent in the solution is lower than that of pure solvent

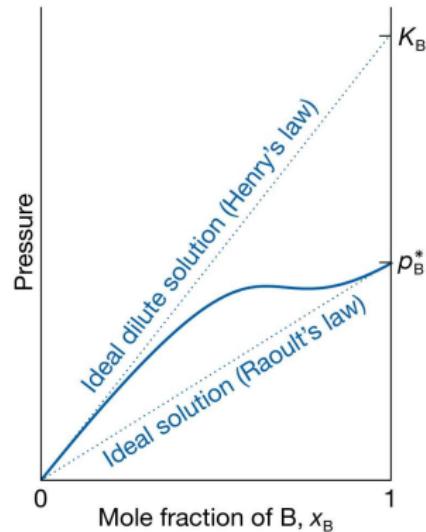
## Ideal-dilute solutions

although vapour pressure of solute  
 $\propto$  mole fraction

constant of proportionality  
 $\neq$  vapour pressure of pure substance  
Henry's law :  $p_B = x_B K_B$

For practical applications, expressed in  
terms of molality,  $b$ ,

$$p_B = b_B K_B$$

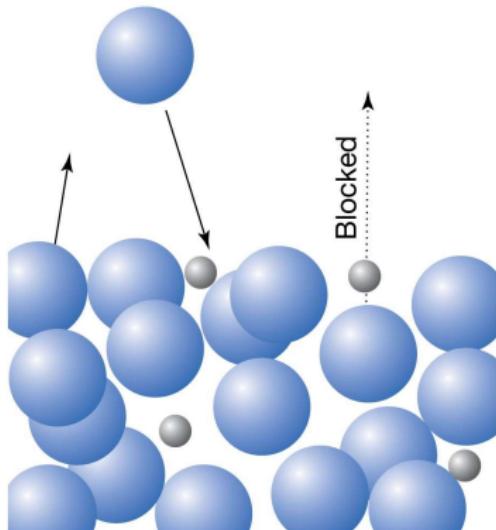


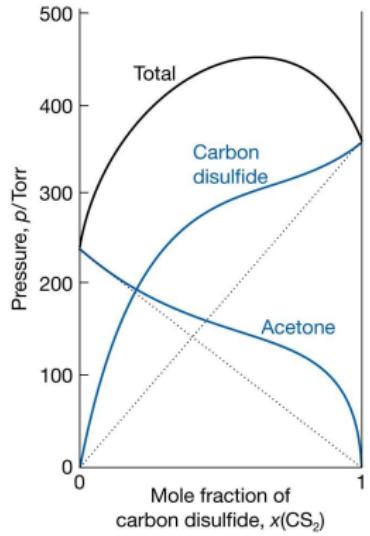
Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are called ideal-dilute solutions

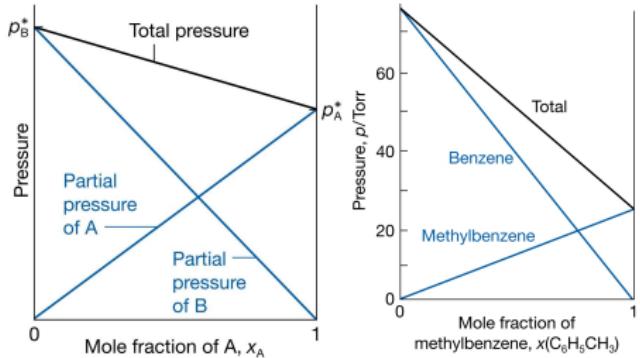
why this difference in behaviour of solute and solvent at low concentrations?

solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure

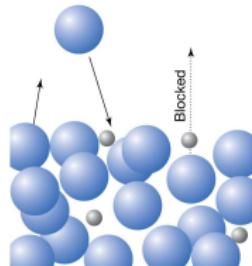
solvent behaves like a slightly modified pure liquid, but the solute behaves entirely differently from its pure state unless the solvent and solute molecules happen to be very similar

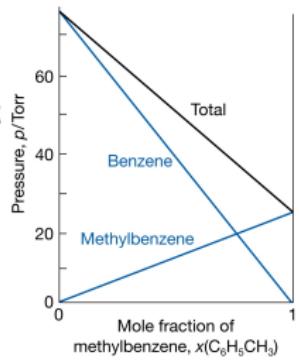
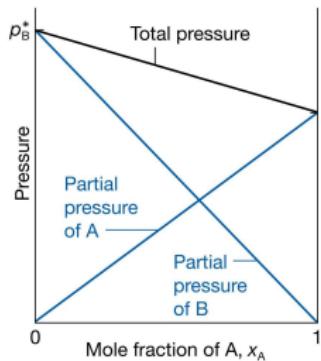




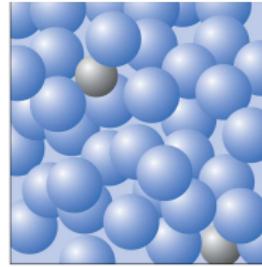
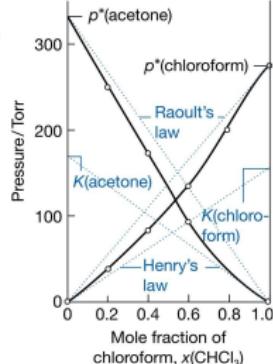
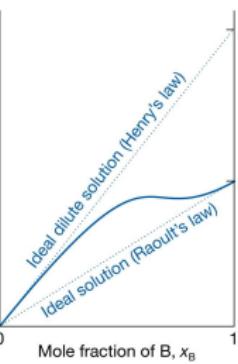
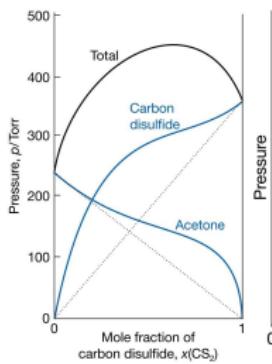
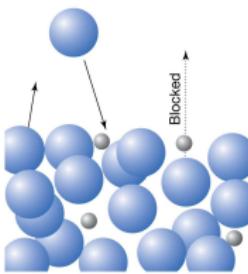


vaporisation (blocked by solute)  
& condensation (not hindered)





vaporisation (blocked by solute)  
& condensation (not hindered)



dilute solution  
solvent mols - similar environ as pure liq.  
solute mols - very different environ

chemical potentials of liquids

Ideal solutions : Raoult's law

$$\mu_A^* = \mu_A^\ominus + RT \ln p_A^*$$

also  $\mu_A = \mu_A^\ominus + RT \ln p_A$

or,  $\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} = \mu_A^* + RT \ln x_A$  :

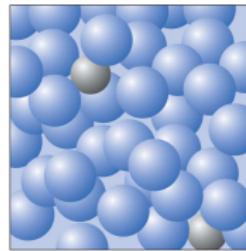
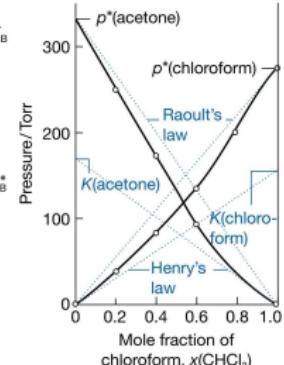
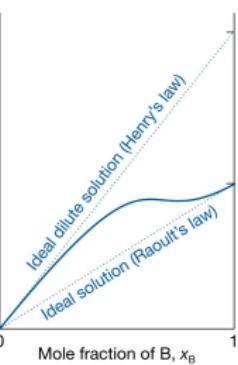
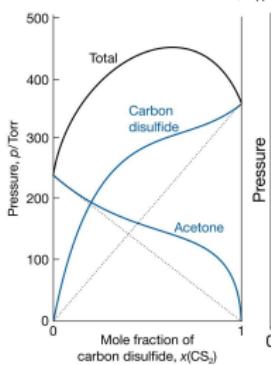
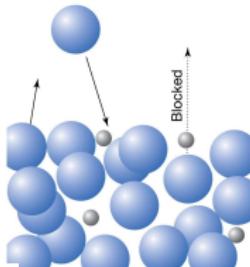
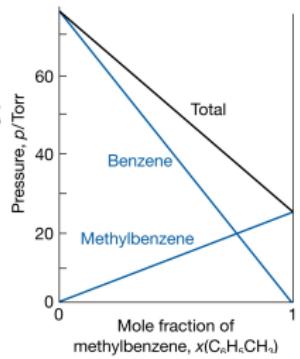
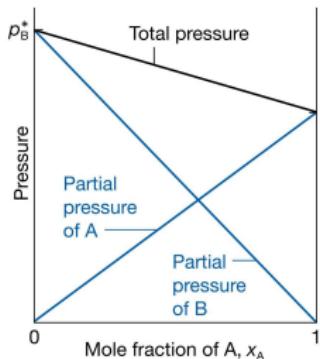
Ideal-dilute solutions :

Henry's law :  $p_B = x_B K_B$

For practical applications, expressed in terms of molality,  $b$ ,

$$p_B = b_B K_B$$

vaporisation (blocked by solute)  
& condensation (not hindered)



dilute solution  
solvent mols - similar environ as pure liq.  
solute mols - very different environ

## Liquid mixtures

Ideal solutions :

$$\text{Before mix : } G_i = n_A \mu_A^* + n_B \mu_B^*$$

$$\text{After : } G_f = n_A (\mu_A^* + RT \ln x_A) + n_B (\mu_B^* + RT \ln x_B)$$

- ▶  $\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B)$
- ▶  $\Delta_{\text{mix}} S = - \left( \frac{\partial \Delta_{\text{mix}} G}{\partial T} \right)_p = -nR (x_A \ln x_A + x_B \ln x_B)$
- ▶  $\therefore \Delta_{\text{mix}} H = \Delta G_{\text{mix}} + T \Delta_{\text{mix}} S = 0$
- ▶  $\Delta_{\text{mix}} V = \left( \frac{\partial \Delta_{\text{mix}} G}{\partial p} \right)_T = 0$
- ▶ solution ideality means something different from gas perfection
- ▶ perfect gas : no forces acting between molecules
- ▶ ideal solutions : average energy of A–B interactions same as average energy of A–A and B–B interactions in pure liquids

Excess functions :

$$X^E = \Delta_{\text{mix}} X - \Delta_{\text{mix}} X^{\text{ideal}}$$

$$S^E = \Delta_{\text{mix}} S - \Delta_{\text{mix}} S^{\text{ideal}}$$

$$H^E = \Delta_{\text{mix}} H - \Delta_{\text{mix}} H^{\text{ideal}} = \Delta_{\text{mix}} H$$

$H^E > 0 \implies$  A–B interactions weaker than  
A–A and B–B interactions

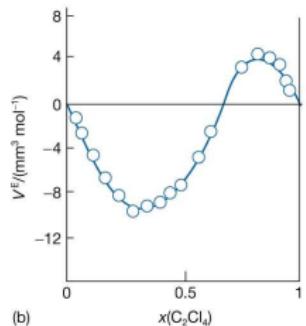
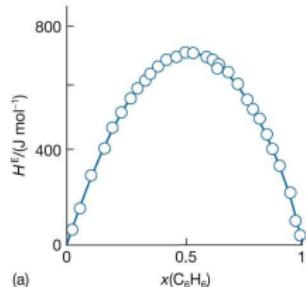
$$V^E = \Delta_{\text{mix}} V - \Delta_{\text{mix}} V^{\text{ideal}} = \Delta_{\text{mix}} V$$

(a) symmetrical shape  $\implies$  similar strengths  
of the A–A and B–B interactions

(b) high mole fractions of cyclopentane  $\implies$   
solution contracts as  $C_2Cl_4$  added

because ring structure of cyclopentane results  
in inefficient packing but, as  $C_2Cl_4$  is added,  
molecules pack together more tightly

high mole fractions of  $C_2Cl_4$  : solution expands as cyclopentane is added because  
 $C_2Cl_4$  molecules are nearly flat and pack efficiently in pure liquid but become  
disrupted as bulky ring cyclopentane is added



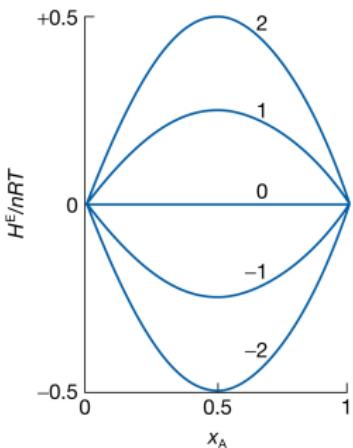
(a) benzene/cyclohexane

(b)  $C_2Cl_4$ /cyclopentane

Models : Regular solution :  $H^E \neq 0$  but  $S^E = 0$   
 solution in which two kinds of molecules are distributed randomly (as in ideal solution) but have different energies of interactions with each other

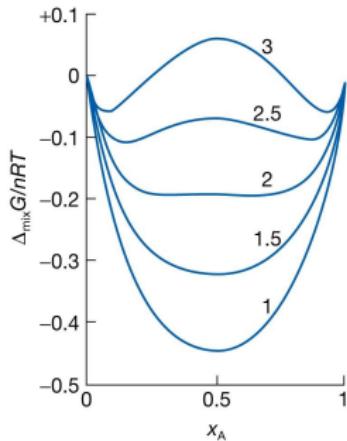
$$H^E = n\xi RT x_A x_B; \Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B)$$

$\xi$  : dimensionless measure of energy of AB interactions relative to A-A and B-B  
 $\xi < 0 \implies$  exothermic mixing :A-B interactions more favourable than A-A and B-B interactions



$\xi > 0 \implies$  endothermic mixing

graphs labeled by  $\xi$



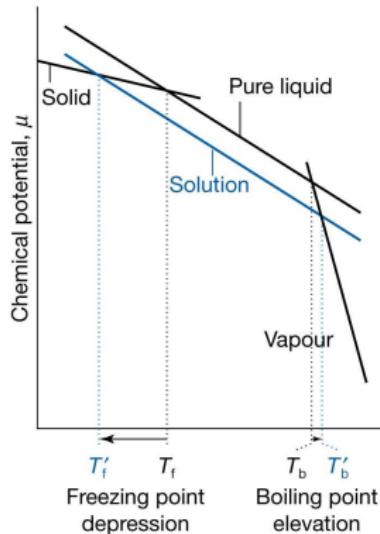
for  $\xi > 2$ , two minima in  $G_{\text{mix}}$

## Colligative properties

- ▶ lowering of vapour pressure
- ▶ elevation of boiling point
- ▶ depression of freezing point
- ▶ osmotic pressure
- ▶ these arise from presence of a solute
- ▶ In dilute solutions these properties depend only on number of solute particles present, not their identity
- ▶ For this reason, they are called colligative properties ('depending on the collection')
- ▶ assume :
  - ▶ solute not volatile : does not contribute to vapour
  - ▶ solute does not dissolve in solid solvent, i.e., pure solid solvent separates when solution is frozen

colligative properties stem from reduction of  $\mu$ (liquid solvent) due to presence of solute

- ▶ ideal-dilute solution : reduction from  $\mu_{\text{pure solvent}}^*$  to  $\mu^* + RT \ln x$
- ▶ no direct influence of solute on  $\mu_{\text{solvent vapour}}^*$  and  $\mu_{\text{solid solvent}}^*$ 
  - ▶ because solute appears in neither vapour nor solid



reduction in chemical potential of solvent  $\Rightarrow$   
liq-vap equilibr. at higher  $T$  (boiling point raised)  
solid-liq equilibr. at lower  $T$  (freezing point lowered)

molecular origin of the lowering of chemical potential :

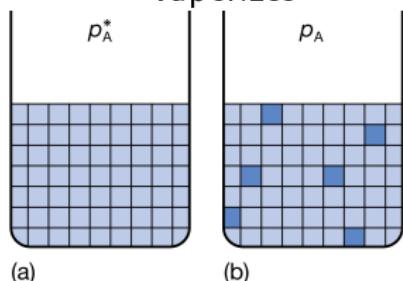
It occurs even in ideal solution ( $\Delta_{\text{mix}} H = 0$ )

$\therefore$  It is not due to energy of interaction of solute and solvent

If not enthalpy effect : must be entropy effect

vapour pressure of pure liquid reflects tendency of solution towards greater entropy :

achieved if liquid vaporizes



When solute present : additional contribution to  $S_{\text{liq in soln}}$  even in an ideal solution

$\therefore S_{\text{liq in soln}} > S_{\text{pure liq}}$ ,  $\therefore$  weaker tendency to form gas

effect of solute : lowered vapour pressure

$\therefore$  higher boiling point

Similarly enhanced molecular randomness of solution opposes the tendency to freeze

$\therefore$  lower temperature reached before equilibrium between solid and solution is achieved

$\implies$  freezing point lowered

quantitative discussion:

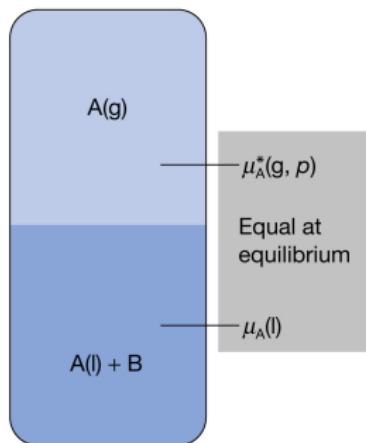
look for the temperature at which, at 1 atm, one phase (pure solvent vapour or solid solvent) has same chemical potential as solvent in the solution

$\Leftrightarrow$  new equilibr. temperature for phase transition : new boiling/freezing point

Elevation of boiling pt.

equilibr.  $\implies$

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$



$$\ln x_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{\text{vap}} G}{RT} \quad (\text{vap} \equiv \text{vaporisation})$$

$$\frac{d \ln x_A}{dT} = \frac{1}{R} \frac{d(\Delta_{\text{vap}} G / T)}{dT} = -\frac{\Delta_{\text{vap}} H}{RT^2}$$

$$\int_0^{\ln x_A} d \ln x_A = -\frac{\Delta_{\text{vap}} H}{R} \int_{T^*}^T \frac{dT}{T^2}$$

$$\therefore \ln(1 - x_B) = -\frac{\Delta_{\text{vap}} H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$$

$$\text{assume : } x_B \ll 1 \implies \ln(1 - x_B) = -x_B$$

$$\therefore x_B = \frac{\Delta_{\text{vap}} H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$$

with  $T \approx T^*$

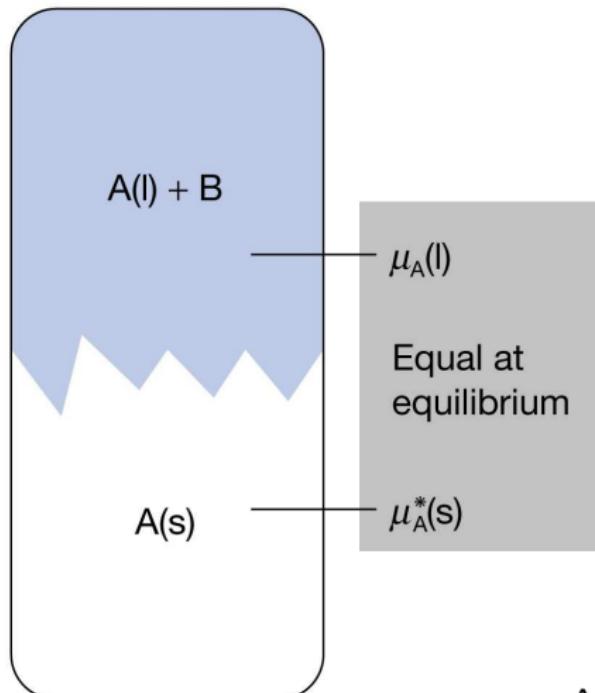
$$\Delta T = K x_B; \quad K = \frac{RT^{*2}}{\Delta_{\text{vap}} H}$$

$$\text{or, } \Delta T = K_b b$$

	$K_f$ (K.kg.mol $^{-1}$ )	$K_b$ (K.kg.mol $^{-1}$ )
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

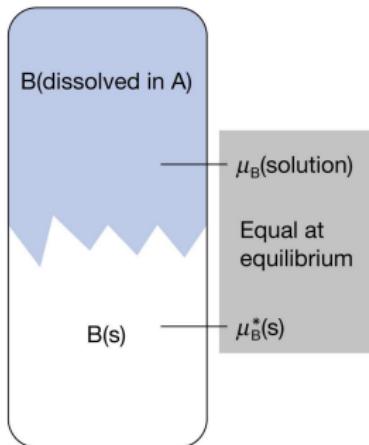
Depression of freezing pt.

$$\text{equilibr.} \implies \mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$



$$\Delta T = K_f b; \quad K_f = \frac{RT_f^2}{\Delta_{\text{fus}} H}$$

solubility :

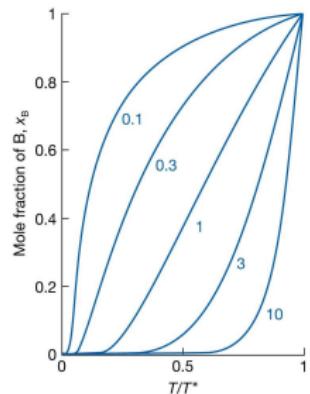


$$\ln x_B = \frac{\mu_B^*(\text{s}) - \mu_B^*(\text{l})}{RT} = -\frac{\Delta_{\text{fus}} G}{RT}$$

$$\frac{d \ln x_B}{dT} = \frac{1}{R} \frac{d(\Delta_{\text{fus}} G/T)}{dT} = \frac{\Delta_{\text{fus}} H}{RT^2}$$

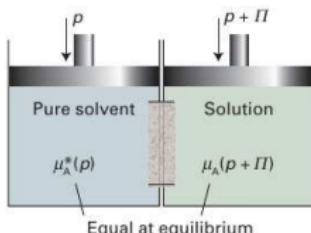
$$\int_0^{\ln x_B} d \ln x_B = \frac{\Delta_{\text{fus}} H}{R} \int_{T_f}^T \frac{dT}{T^2}$$

$$\therefore \ln x_B = \frac{\Delta_{\text{fus}} H}{R} \left( \frac{1}{T_f} - \frac{1}{T} \right)$$



label :  $\frac{\Delta_{\text{fus}} H}{RT^*}$   
 $T^*$ =freezing temp.  
 of solute

Osmosis : spontaneous passage of pure solvent into a solution separated from it by semipermeable membrane, permeable to solvent but not to the solute



equilibr.  $\implies$

$\mu_{\text{solvent}}$  must be same  
on each side of  
membrane

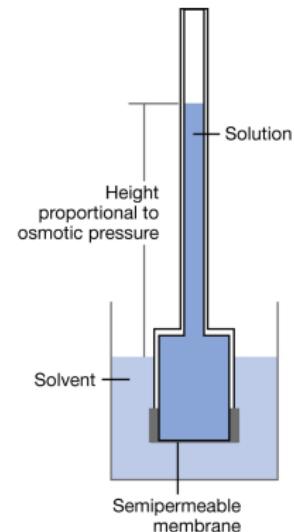
$\mu_{\text{solvent}}$  is lowered by  
the solute, but is  
restored to its 'pure'  
value by application  
of pressure

osmotic pressure

$\Pi$  = pressure that must be  
applied to solution to stop the  
influx of solvent

ex. : transport of fluids  
through cell membranes,  
dialysis, osmometry

(determination of molar mass)



$$\text{van't Hoff eqn. : } \Pi = [B] RT$$

$$[B] = \frac{n_B}{V}, \text{ molar concn.}$$

$$\begin{aligned}\mu_A^*(p) = \mu_A(x_A, p + \Pi) &= \underbrace{\mu_A^*(p + \Pi)}_{\mu_A^*(p) + \int_p^{p+\Pi} V_m dp} + RT \ln x_A \\ \implies -RT \ln x_A &= \int_p^{p+\Pi} V_m dp\end{aligned}$$

or, for  $x_B \ll 1$ ,  $RTx_B = \Pi V_m$

using  $x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$  and  $n_A V_m = V$ , we get,  $\Pi = [B] RT$

For more realistic solutions,  $\Pi = [J] RT \{1 + B[J] + \dots\}$  (caution : notation  $[B]$  replaced by  $[J]$  and  $B$  is a virial like coefficient)

Solved Ex. : given  $\Pi$  for solns of PVC in cyclohexanone at 298 K,  
 pressures expressed in terms of the heights of solution (mass density  $\rho = 0.980\text{ g cm}^{-3}$ ) in balance with osmotic pressure

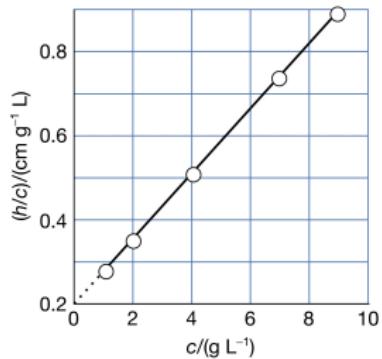
Task : Determine molar mass of polymer

$c/(g \text{ dm}^{-3})$	1.0	2.0	4.0	7.0	9.0
$h/\text{cm}$	0.28	0.71	2.01	5.10	8.0

$$\Pi = \rho gh = RT \cdot \frac{c}{M} \left[ 1 + B \frac{c}{M} + \dots \right]$$

$$\text{or, } \frac{h}{c} = \frac{RT}{\rho g M} + \frac{RT}{\rho g M^2} c + \dots$$

$$M = \frac{RT}{\rho g} \times \frac{1}{0.2} = 130\text{ kg/mol}$$

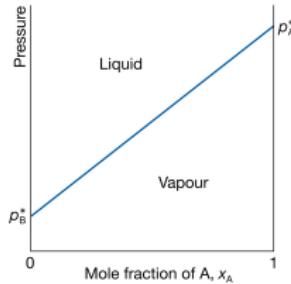


## Phase diagrams of binary systems

$$p_A = x_A p_A^*, \quad p_B = x_B p_B^*$$

$$\begin{aligned} p &= p_A + p_B \\ &= x_A p_A^* + x_B p_B^* \\ &= p_B^* + (p_A^* - p_B^*) x_A \end{aligned}$$

Ideal binary mixture



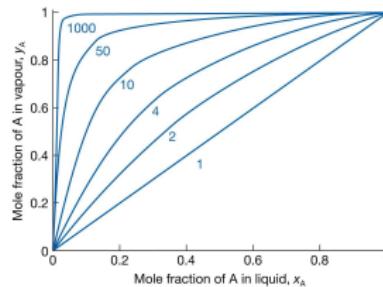
composition of vapour :

$$y_A = \frac{p_A}{p}; \quad y_B = \frac{p_B}{p}$$

ideal mix. :

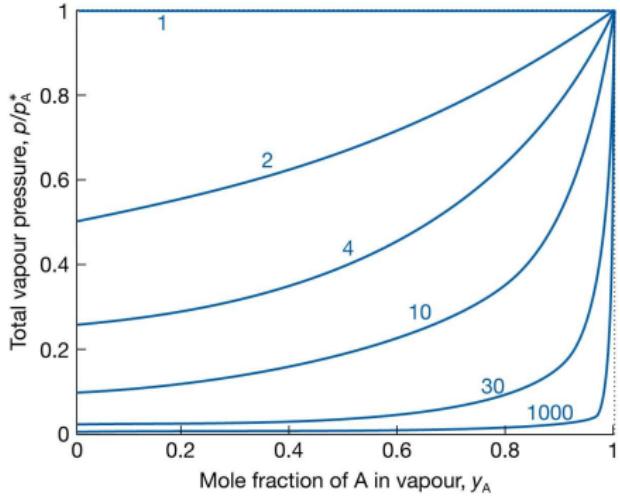
$$y_A = \frac{p_A}{p_B^* + (p_A^* - p_B^*) x_A}$$

$$y_B = 1 - y_A$$



label :  $\frac{p_A^*}{p_B^*}$

$$\text{label : } \frac{p_A^*}{p_B^*}$$



$$y_A = \frac{p_A}{p_B^* + (p_A^* - p_B^*)x_A}$$

$$y_B = 1 - y_A$$

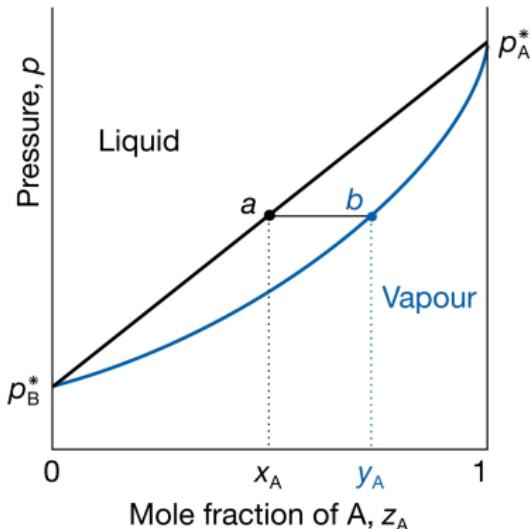
$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}$$

combined plot :

point a : vapour pressure of a mixture of composition  $x_A$

point b : composition of vapour that is in equilibrium with liquid at that pressure

horizontal axis shows overall composition,  $z_A$ , of system (mole fraction of how mixture is prepared)

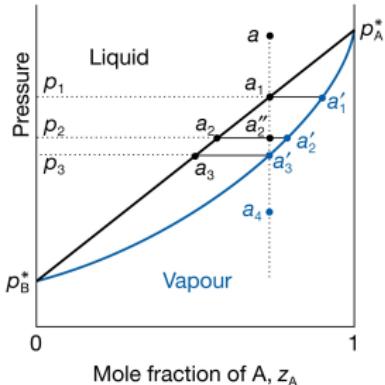


all points down to solid diagonal : system under such high pressure that only liquid phase exists (applied pressure > vapour pressure), so  $z_A = x_A$ , composition of liquid

all points below lower curve : system under such low pressure that only vapour exists (applied pressure < vapour pressure), so  $z_A = y_A$

Points between the two lines : system has two phases, liquid and vapour

consider effect of lowering the pressure by drawing out a piston on a liquid mixture of overall composition at pt. **a**



composition of liquid is same as initially; at this pressure there is virtually no vapour present; line joining two points representing phases in equilibrium is called a **tie line**

tiny amount of vapour that is present has the composition **a1'**

consider lowering pressure to  $p_2$ , taking overall composition represented by the point **a2''**

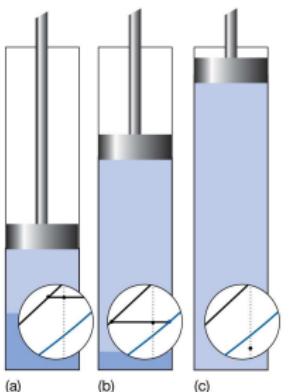
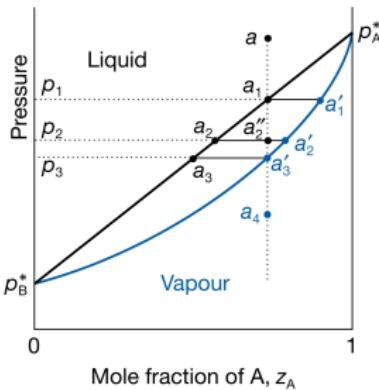
This new pressure < vapour pressure of original liquid, so it vaporizes until the vapour pressure of the remaining liquid falls to  $p_2$

composition of such a liquid must be **a2**

composition of vapour in equilibrium with that liquid must be given by the point  $a2'$  at the other end of the tie line

Lowering pressure does not change overall composition, system moves down vertical line that passes through **a**: **isopleth** (equal abundance)

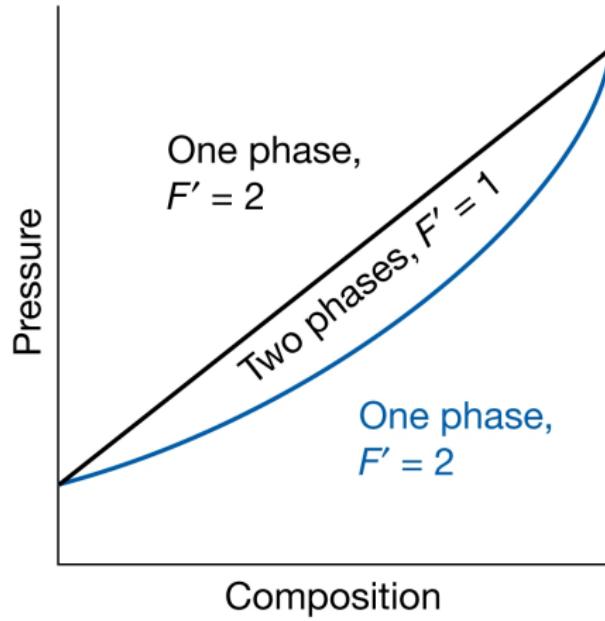
At **a1** liquid can exist in equilibrium with its vapour composition of the vapour phase is given by point **a1'**



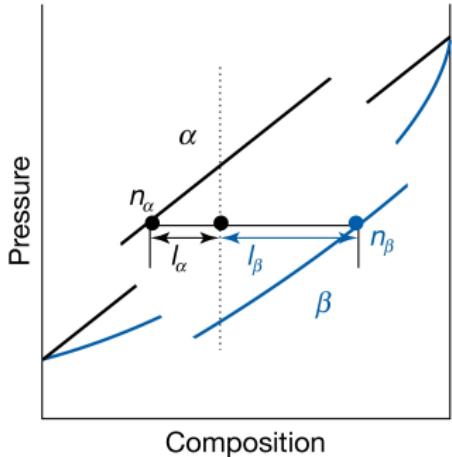
If pressure is reduced to  $p_3$ , readjustment in composition takes place, and now the compositions of the liquid and vapour are represented by the points **a3** and **a3'**, respectively

**a3'**: system with composition of vapour same as overall composition, so amount of liquid present is tiny with composition a3

further decrease in pressure takes the system to a4; only vapour is present and its composition same as initial overall composition of original liquid



## The lever rule



$$n_\alpha l_\alpha = n_\beta l_\beta$$

$n_\alpha$  = amount of phase  $\alpha$

$n_\beta$  = amount of phase  $\beta$

In the case illustrated  $\therefore l_\beta \approx 2l_\alpha$   
 $\therefore$  amount of phase  $\alpha \approx 2 \times$  amount of phase  $\beta$

Proof :

total #moles of A and B :  $n = n_\alpha + n_\beta$

amount of A in phase  $\alpha = n_\alpha x_{A,\alpha}$

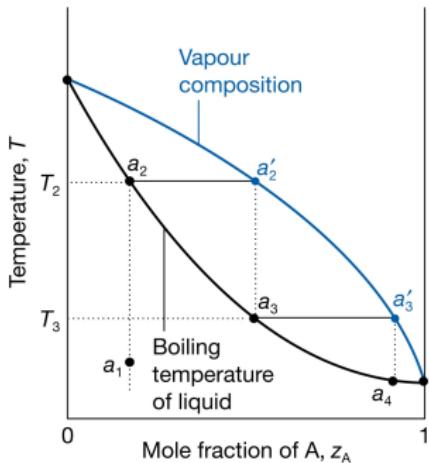
amount of A in phase  $\beta = n_\beta x_{A,\beta}$

$$\therefore n_A = n_\alpha x_{A,\alpha} + n_\beta x_{A,\beta}$$

$$\text{but } n_A = nz_A = (n_\alpha + n_\beta) z_A$$

$$\therefore n_\alpha (x_{A,\alpha} - z_A) = n_\beta (z_A - x_{A,\beta})$$

## Temperature–composition diagrams : distillation of mixtures

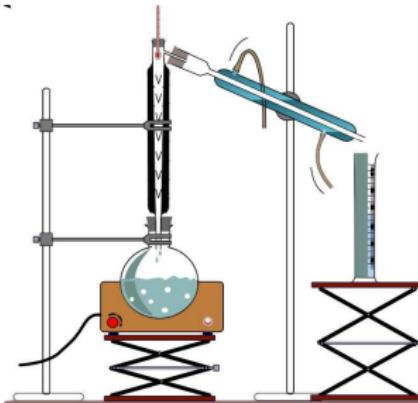
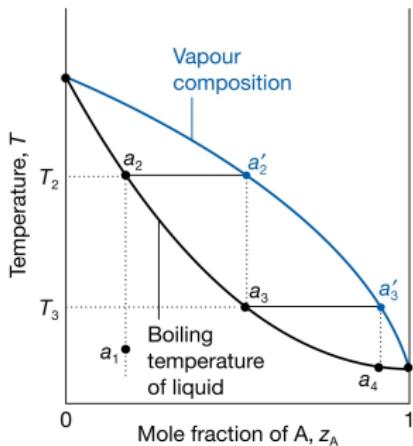


If liquid of composition **a1** heated - it boils at temperature **T2**

Then liquid has composition **a2** (same as **a1**) and vapour (trace) has composition **a2'**  
vapour is richer in more volatile component A  
(lower boiling point)

**a2'** : vapour's composition at boiling point.

Read boiling temperature (**T2**) of original mixture from location of the tie line joining **a2** and **a2'**



simple distillation : vapour withdrawn and condensed

**fractional distillation** : boiling and condensation cycle repeated successively

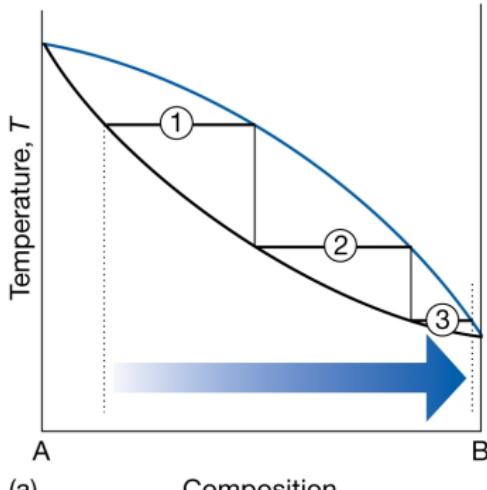
- technique used to separate volatile liquids

follow the changes that occur when the first condensate of composition **a3** is reheated

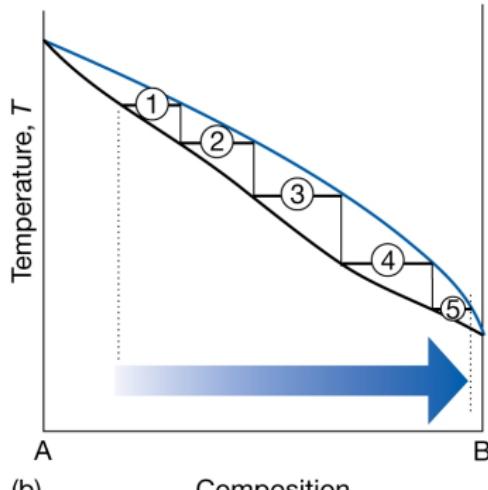
This mixture boils at **T3** and yields a vapour of composition **a3'**, which is even richer in the more volatile component. Vapour is drawn off, and the first drop condenses to a liquid of composition **a4**

cycle repeated until almost pure A obtained in vapour and pure B remains in liquid

Efficiency of a fractionating column is expressed in terms of  
number of theoretical plates = #effective vaporization and condensation step



(a) Composition



(b) Composition

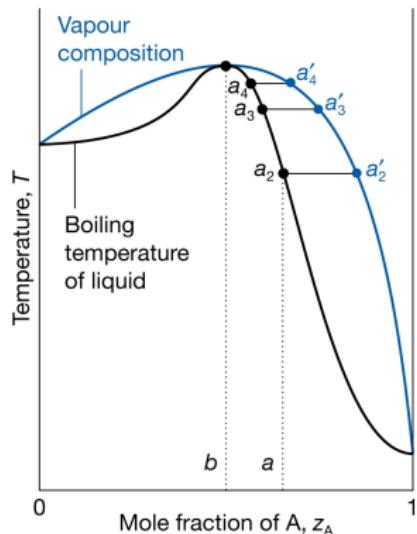
to achieve degree of separation shown in (a) fractionating column must correspond to 3 theoretical plates

to achieve same separation for system (b), in which components have more similar partial pressures, fractionating column must have 5 theoretical plates

**Azeotropes** : Many liquids have temperature–composition phase diagrams resembling the ideal version, but in a number of important cases there are marked deviations

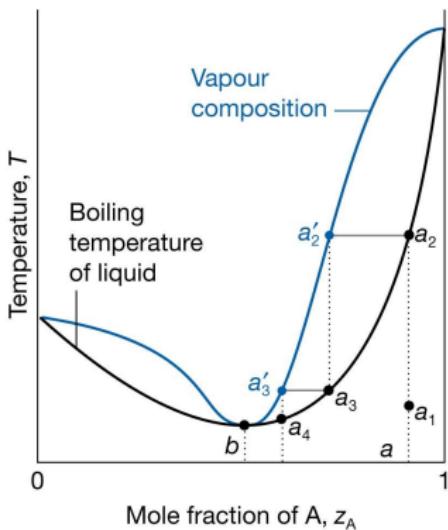
A maximum in phase diagram may occur when favourable interactions between A and B molecules reduce vapour pressure of mixture below the ideal value and raise its boiling temperature: in effect, A–B interactions stabilize the liquid

Ex. :  $\text{CHCl}_3/\text{propanone}$  and  $\text{HNO}_3/\text{H}_2\text{O}$



In such cases excess Gibbs energy,  $G^E < 0$   
- more favourable to mixing than ideal

Minimum indicates that the mixture is destabilized relative to ideal solution, A–B interactions unfavourable; boiling temperature is lowered  
Ex. : dioxane/water and ethanol/water

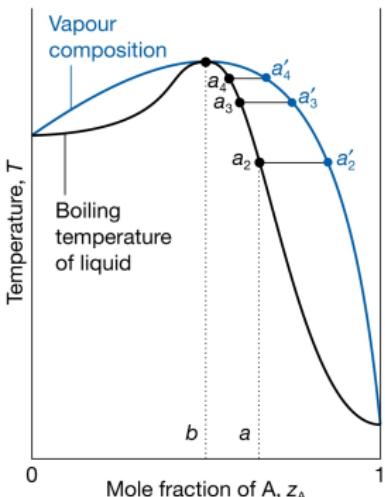


For such mixtures  $G^E > 0$  (less favourable to mixing than ideal), and there may be contributions from both enthalpy and entropy effects.

Deviations from ideality are not always so strong as to lead to a maximum or minimum in the phase diagram, but when they do there are important consequences for distillation

Consider liq. composition

a on right of maximum vapour ( $a'_2$ ) of boiling mixture ( $a_2$ ) richer in A



vapour removed (and condensed elsewhere) : remaining liquid richer in B ( $a_3$ ), and vapour in equilibrium has composition  $a'_3$

As vapour is removed, composition of the boiling liquid shifts to a point  $a_4$  and composition of vapour shifts to  $a'_4$

as evaporation proceeds, composition of remaining liquid shifts towards B as A is drawn off

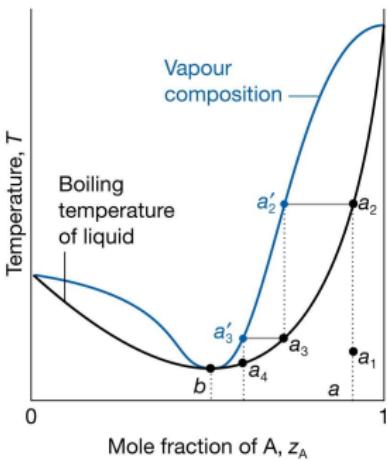
boiling point rises, and vapour becomes richer in B so much A is evaporated that liq. reaches composition b, vapour has same composition as liq.

Evaporation occurs without change of composition :

**azeotrope**

Ex. : HCl/H<sub>2</sub>O azeotropic at 80% by mass of water, boils at 108.6°C

Consider liq. composition  $a_1$  on right of minimum



vapour ( $a'_2$ ) of boiling mixture ( $a_2$ ) poorer in A

vapour removed (and condensed elsewhere) : remaining liquid poorer in A ( $a_3$ ), and vapour in equilibrium has composition  $a'_3$

As vapour is removed, composition of the boiling liquid shifts to a point  $a_4$

as evaporation proceeds, composition of remaining liquid shifts towards B as A is drawn off

boiling point falls, and vapour becomes richer in A

so much A is evaporated that liq. reaches composition  $b$ , vapour has same composition as liq.

Evaporation occurs without change of composition :

### azeotrope

Ex. : ethanol/H<sub>2</sub>O azeotropic at 4% by mass of water, boils at 78°C

When azeotropic composition reaches, distillation cannot separate the liquids

- ▶ because the condensate has same composition as azeotropic liquid

Immiscible liquids (ex. octane/H<sub>2</sub>O)

At equilib., tiny bit of A dissolved in B, and similarly a tiny bit of B dissolved in A  
both liquids saturated with the other component (a)

$$\text{total vapour pressure } p = p_A^* + p_B^*$$

If  $T$  is raised s.t. total vapour pressure=atmospheric pressure,  
boiling commences



a)

and dissolved substances are purged from solution

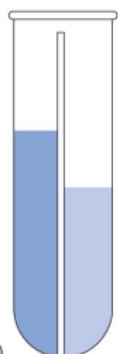
boiling results in vigorous agitation of mixture

each component is kept saturated in the other component

purging continues as the very dilute solutions are replenished

intimate contact is essential: immiscible liquids heated in a container

(b) would not boil at same temperature



(b)

intimate contact is essential: immiscible liquids heated in a container

(b) would not boil at same temperature

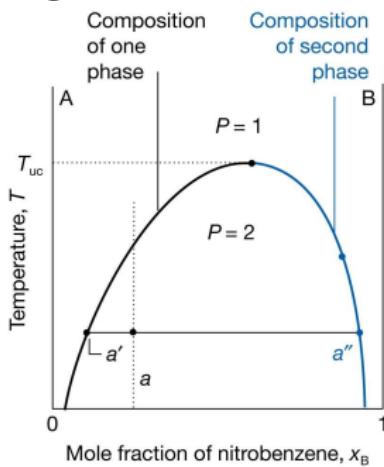
presence of saturated solutions means that 'mixture' boils at lower  $T$  than either component alone

because boiling begins when total vap. press. reaches 1 atm, not when either vap. press. reaches 1 atm

This distinction is basis of steam distillation, which enables some heat-sensitive, water-insoluble organic compounds to be distilled at lower  $T$  than their normal boiling point

Liquid–liquid phase diagrams:  
small amount of B is  
added to A at temp.  $T$

Liq. B dissolves completely  
binary system has  
single phase



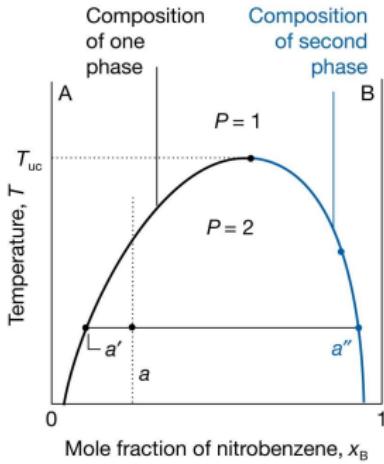
more B added, stage comes when no more dissolves  
sample has two phases in equilibrium

- most abundant : consisting of A saturated  
with B : point  $a'$
  - minor : trace of B saturated with A : point  $a''$
- relative abundances given by lever rule

When more B added, A dissolves in it slightly  
compositions of phases in equilibr. :  $a'$  and  $a''$   
A stage reaches when so much B is present that it  
can dissolve all the A

system reverts to a single phase  
addition of more B now simply dilutes the solution,  
and a single phase remains

composition of the two phases at equilib. varies with the temperature  
For hexane and nitrobenzene, raising  $T$  increases their miscibility



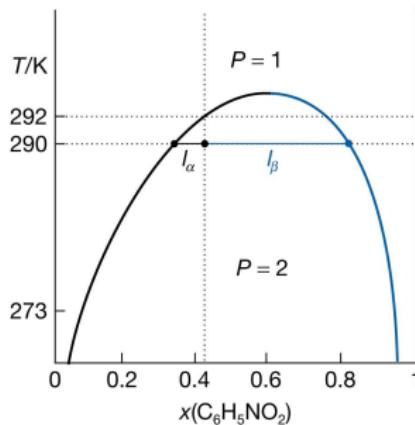
two-phase region therefore covers a narrower range of composition because each phase in equilibr. is richer in its minor component:

A-rich phase is richer in B and B-rich phase is richer in A

construct entire phase diagram by repeating observations at different  $T$  and drawing the envelope of two-phase region

solved ex. : mixture of 50 g of hexane ( $0.58 \text{ mol } \text{C}_6\text{H}_{14}$ ) and 50 g of nitrobenzene ( $0.41 \text{ mol } \text{C}_6\text{H}_5\text{NO}_2$ ) prepared at 290 K

What are the compositions of phases, and in what proportions do they occur? To what temperature must the sample be heated in order to obtain single phase?



horizontal tie line cuts phase boundary at

$x_N = 0.35$  and  $x_N = 0.83$ ,

$$\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha} = \frac{0.83 - 0.41}{0.41 - 0.35} = 7$$

there is about 7 times more hexane-rich phase than nitrobenzene-rich phase

Heating to 292 K takes it into single-phase region

phase diagram constructed experimentally : conclusions not based on assumpns. of ideality

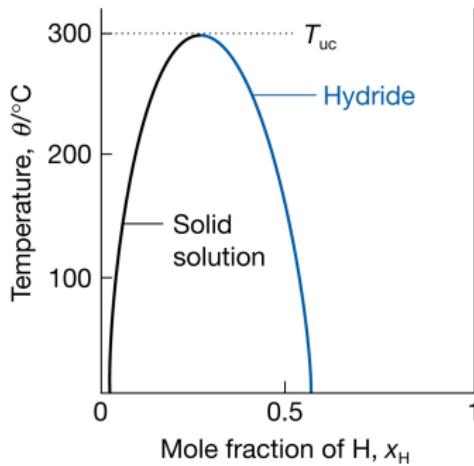
$x_N = 0.41$ ,  $T = 290 \text{ K}$   
occurs in two-phase region

would be modified if system subjected to different pressure

Critical solution temperatures :

upper critical solution temperature,  $T_{uc}$  (upper consolute temperature) : highest temperature at which phase separation occurs

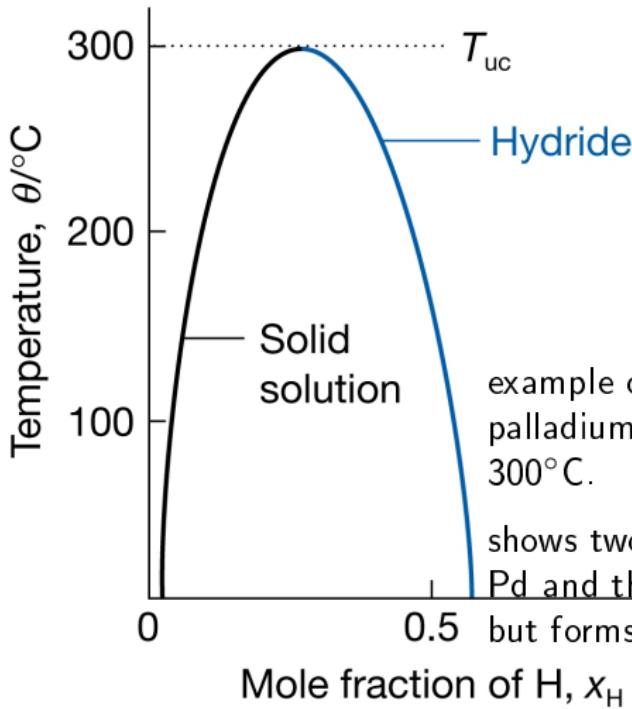
Above  $T_{uc}$  two components are fully miscible



$T_{uc}$  exists because greater thermal motion overcomes any potential energy advantage in molecules of one type being close together

ex. :nitrobenzene/hexane system shown

example of solid solution : Pd/  $H_2$  system, which shows two phases, one a solid solution of  $H_2$  in Pd and the other a Pd-hydride, up to 300°C but forms single phase at higher  $T$



example of solid solution : palladium and palladium hydride, upper critical temperature :  $300^\circ\text{C}$ .

shows two phases, one a solid solution of  $\text{H}_2$  in Pd and the other a Pd-hydride, up to  $300^\circ\text{C}$   
but forms single phase at higher  $T$

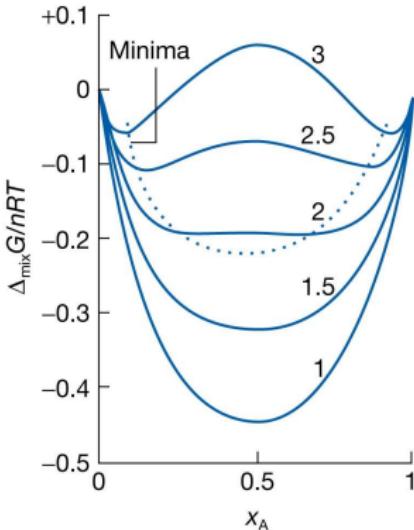
thermodynamic interpretation of  $T_{uc}$ :

model of a real solution : Regular solution :  $H^E \neq 0$  but  $S^E = 0$

$H^E = n\xi RTx_Ax_B$  : For  $\xi > 2$ ,  $\Delta_{\text{mix}}G$  has two minima

As a result, for  $\xi > 2$ , we expect phase separation to occur

compositions corresponding to minima are obtained by looking for  $\frac{\partial \Delta_{\text{mix}}G}{\partial x} = 0$

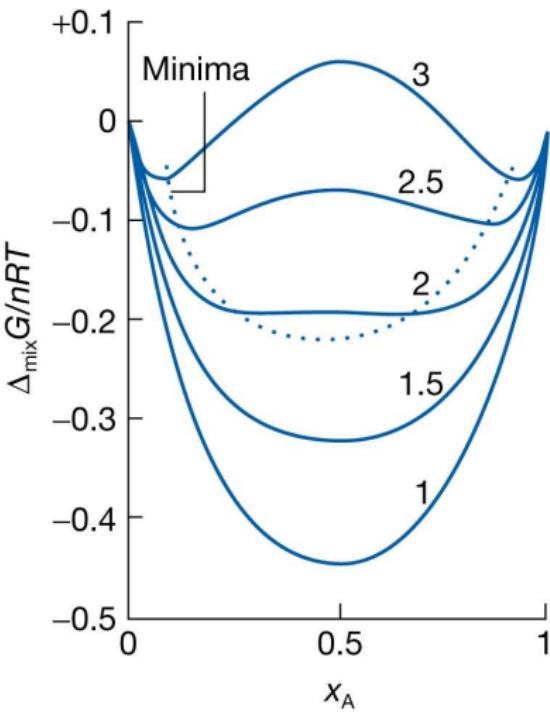
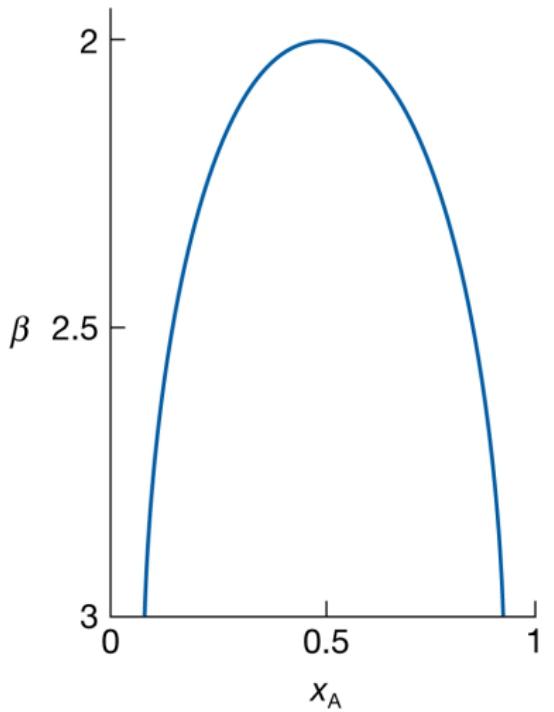


using  $\Delta_{\text{mix}}G =$

$$nRT(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B)$$

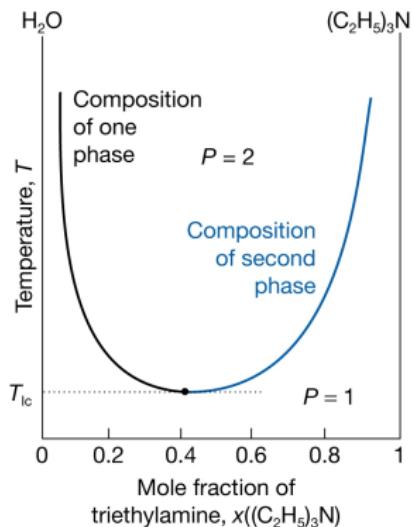
$$\text{we have, } \ln \frac{x}{1-x} + \xi(1-2x) = 0$$

as  $\xi$  decreases (increase in  $T$ ),  
two minima move together and  
merge when  $\xi = 2$



Some systems show a lower critical solution temperature,  $T_{lc}$   
(lower consolute temperature)

below which they mix in all proportions and above which they form two phases  
ex. : water/triethylamine

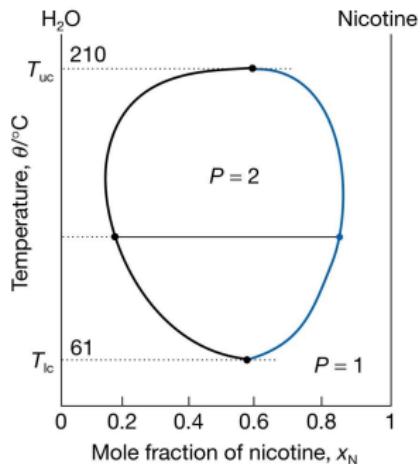


at low temperatures the two components are more miscible because they form a weak complex;  
at higher temperatures the complexes break up  
and the two components are less miscible

Some systems have both  $T_{uc}$  and  $T_{lc}$   
just as in the case of ordinary partially miscible liquids

They occur because, after weak complexes have been disrupted, leading to partial miscibility, thermal motion at higher  $T$  homogenizes the mixture again

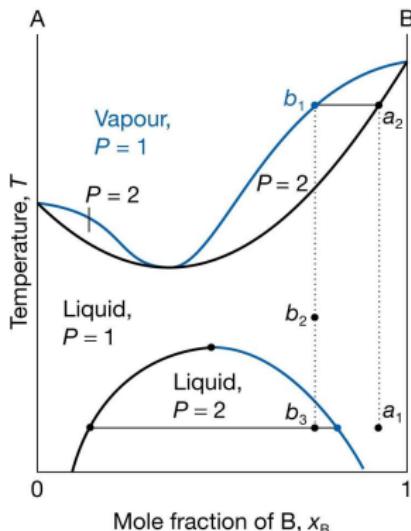
ex. : nicotine/water, partially miscible between  $61^\circ\text{C}$  and  $210^\circ\text{C}$



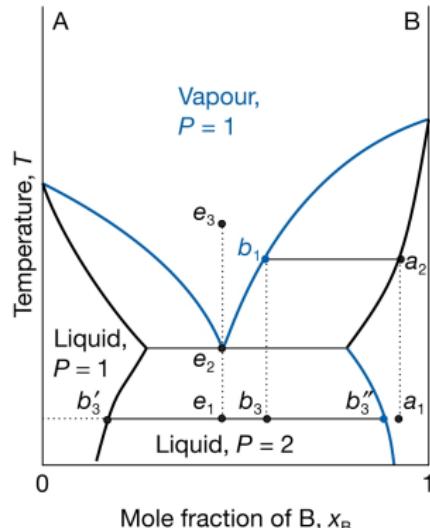
distillation of partially miscible liquids with low-boiling azeotrope

- combination quite common because both properties reflect tendency of the two kinds of molecule to avoid each other

i) fully miscible before they boil



ii) boiling before mixing complete - no  $T_{uc}$



$T_{uc} <$  boiling point at all compositions  
mixture forms low-boiling azeotrope

ex. : changes occurring when mixture boiled and vapour condensed

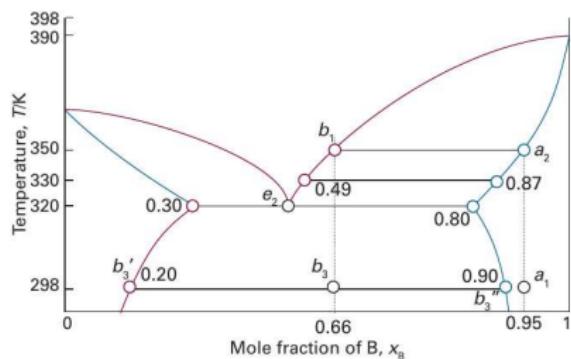
a<sub>1</sub> :  $x_B = 0.95$  - when heated, boils at 350K

b<sub>1</sub> : vapour  $x_B = 0.66$

330K : liq.  $x_B = 0.87$ ; vapour  $x_B = 0.49$ ;  
liq/vap = 1 : 4.4

320K : three phases; (i) liq.  $x_B = 0.3$ ;  
(ii) liq.  $x_B = 0.8$ ; (iii) vap  
ratio of phases = 0.92 : 1 :  $\approx 0$

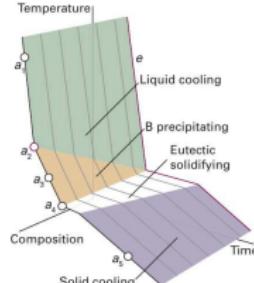
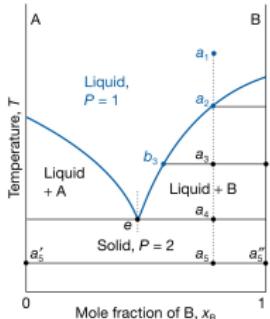
298K : two phases; ratio = 0.94 : 1



Liquid–solid phase diagrams : guides the design of important industrial processes,  
e.g., manufacture of LCDs and semiconductors

solid and liquid phases may both be present at  $T$  below boiling point  
almost immiscible solids and their completely miscible liquids : **Eutectics**  
cooling curves

$a_1 \rightarrow a_2$  : system  
enters two-phase  
region ‘Liquid+B’  
Pure solid B comes  
out and remaining  
liquid is richer in A



$a_2 \rightarrow a_3$  : More solid B forms, and relative amounts of the solid and liquid (in equilibrium) are given by lever rule

At this stage there are roughly equal amounts of each

Liquid phase richer in A than before ( $b_3$ ) because some B is deposited

$a_3 \rightarrow a_4$ : At the end, less liquid than at  $a_3$  - composition e  
liquid freezes to give two-phase system : pure B + pure A

isopleth through e corresponds to eutectic composition, the mixture  
with lowest melting point

isopleth a : cooling rate  
slows at  $a_2$  as solid B  
deposits from solution

complete halt at  $a_4$   
while eutectic solidifies

halt longest for  
eutectic isopleth, e  
eutectic halt shortens  
again for compositions  
beyond e - richer in A

## Examples of eutectics

1. solder : technologically important eutectic  
mass composition  $\approx$  67 % Sn and 33 % Pb - melts at 183°C
2. 23 % NaCl and 77% H<sub>2</sub>O by mass, melts at -21.1°C

Reacting systems : ex.  $\text{Ga} + \text{As} \rightleftharpoons \text{GaAs}$

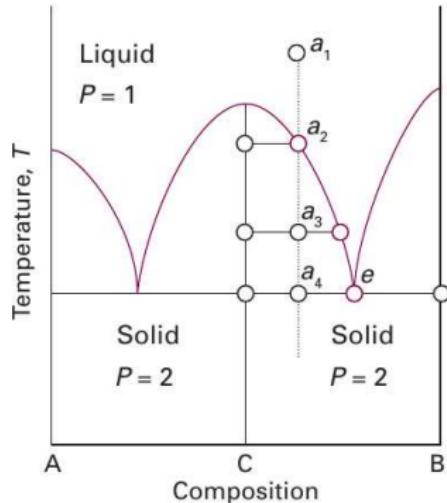
system prepared by mixing excess B with A consists of C and unreacted B : binary B, C system, which forms a eutectic

change from earlier eutectic phase diagram :  
whole phase diagram is squeezed into  
compositions lying between equal amounts of A  
and B ( $x_B = 0.5$ ) , marked C and pure B

solid deposited on cooling along isopleth  $a$  is C

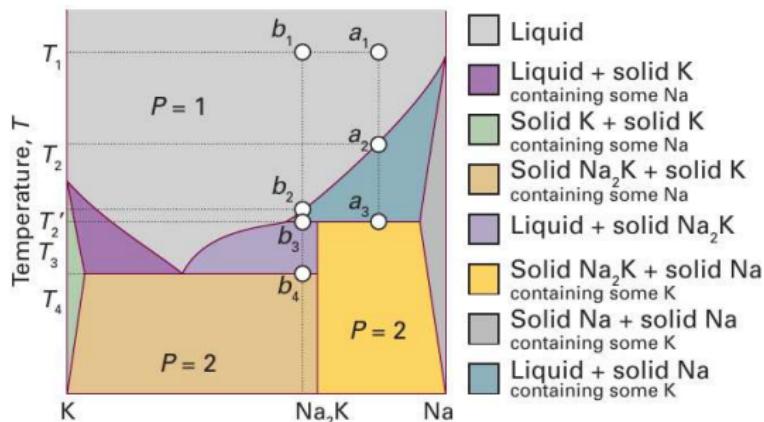
At  $T < a_4$  there are two solid phases, C and B

pure compound C melts **congruently** :  
composition of liquid it forms is same as that of  
solid compound



Incongruent melting : In some cases the compound C is not stable as a liquid

Ex. : alloy Na<sub>2</sub>K, which survives only as a solid



chemical potential of an ideal solvent :

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} = \mu_A^* + RT \ln x_A = \mu_{A,\text{modified}}^* + RT \ln b_A$$

general form for real or ideal solvent :  $\mu_A = \mu_A^* + RT \ln a_A; \quad a_A = \frac{p_A}{p_A^*}$

activity = activity coefficient  $\times$  molar concentration relative to standard value

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

activity coefficient,  $\gamma$  :  $a_A = \gamma_A x_A$

$$\left\{ \begin{array}{l} \text{as } x_A \rightarrow 1 \\ \gamma_A \rightarrow 1 \\ a_A \rightarrow x_A \end{array} \right.$$

$$\boxed{\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A}$$

standard state of solvent:  $x_A = 1$

In terms of molality,  $a_j = \gamma_j \frac{b_j}{b_j^\ominus}$

**Table 5.3** Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^*, a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K, a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 0$
		(2) A hypothetical state of the solute at molality $b^*$	$a = \gamma b/b^*$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

solute: it approaches ideal dilute solution as  $x_B \rightarrow 0$  (not 1).

Ideal-dilute:  $\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} + RT \ln x_B = \mu_B^\ominus + RT \ln x_B$

Real:  $\mu_B = \mu_B^\ominus + RT \ln a_B; a_B = \frac{p_B}{K_B}; a_B = \gamma_B x_B; \left\{ \begin{array}{l} \gamma_B \rightarrow 1 \\ \text{as } x_B \rightarrow 0; (\text{not 1}) \end{array} \right.$

in terms of molalities: selection of standard state is arbitrary

ideal-dilute:  $\mu_B = \mu_B^\ominus + RT \ln b_B$

Real:  $\mu_B = \mu_B^\ominus + RT \ln a_B; a_B = \gamma_B \frac{b_B}{b_B^\ominus}; \left\{ \begin{array}{l} \gamma_B \rightarrow 1 \\ \text{as } b_B \rightarrow 0; (\text{not 1}) \\ b_B^\ominus = 1 \text{ mol/kg} \end{array} \right.$

$\left\{ \begin{array}{l} b_B \rightarrow 0 \\ \text{as } \mu_B \rightarrow -\infty \end{array} \right. : \text{difficult to remove last traces of soln.}$

General expression:  $\boxed{\mu = \mu^\ominus + RT \ln a = \mu^{\text{ideal}} + RT \ln \gamma}$

biological standard state:  $a_{H^+} = 10^{-7}$ ;  $pH = 7$

$$\mu(H^+) = \mu^\ominus(H^+) + RT \ln a(H^+) = \mu^\ominus(H^+) - (RT \ln 10) \times pH$$

$$\mu^\oplus(H^+) = \mu^\ominus(H^+) - 7RT \ln 10$$

At 298 K,  $7RT \ln 10 = 39.96 \text{ kJ mol}^{-1}$

two standard values differ by about  $40 \text{ kJ mol}^{-1}$

## Chemical equilibrium

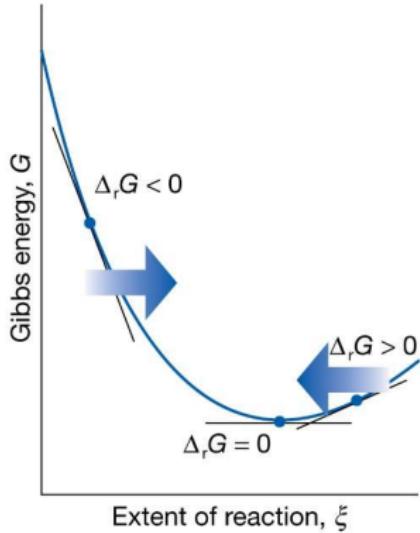
- ▶ Consider  $A \rightleftharpoons B$ ,
  - ▶ e.g., pentane  $\rightleftharpoons$  2-methylbutane or L-alanine  $\rightleftharpoons$  D-alanine
- ▶ infinitesimal amount  $d\xi$  of A turns into B
  - ▶ change in amount of A,  $dn_A = -d\xi$
  - ▶ and change in amount of B,  $dn_B = d\xi$
- ▶ If extent of reaction changes by a finite amount  $\Delta\xi$ 
  - ▶ change in amount of A,  $\Delta n_A = -\Delta\xi$
  - ▶ and change in amount of B,  $\Delta n_B = \Delta\xi$
- ▶ reaction Gibbs energy :  $\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p, T}$ ;  $\xi$  measures extent of reaction
  - ▶  $\Delta_r G$  is a derivative

suppose the reaction advances by  $d\xi$ ,

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

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

= difference between chemical potentials of reactants and products  
**at the composition of the reaction mixture**



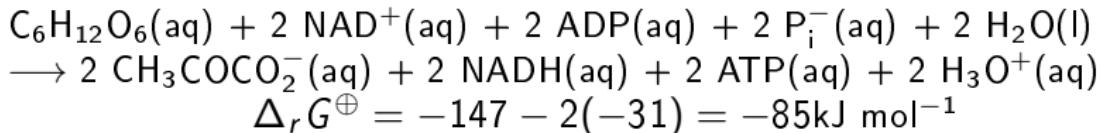
- ▶ As reaction advances :  
slope of  $G$  changes
- ▶ Exergonic:  
 $\Delta_r G < 0 \implies$  forward reaction spontaneous
- ▶ Endergonic:  
 $\Delta_r G > 0 \implies$  reverse reaction spontaneous
- ▶ Equilibrium corresponds to zero slope  
 $\Delta_r G = 0 \implies$  foot of the valley : reaction at equilibrium

coupling of exergonic and endergonic reactions :

- ▶  $\text{ATP}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{ADP}(\text{aq}) + \text{P}_i^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ 
  - ▶  $\Delta_r G^\oplus = -31 \text{ kJ mol}^{-1}$ ;  $\Delta_r H^\oplus = -20 \text{ kJ mol}^{-1}$ ;  $\Delta_r S^\oplus = 34 \text{ J K}^{-1} \text{ mol}^{-1}$
  - ▶  $\because \Delta_r S^\oplus$  is large,  $\Delta_r G^\oplus$  is sensitive to temperature
- ▶ ATP acts as a phosphate donor to a number of acceptors (e.g., glucose), but is recharged by more powerful phosphate donors in a number of biochemical processes
  - ▶ Synthesis of ATP is Endergonic  $\Delta_r G^\oplus = 31 \text{ kJ mol}^{-1}$
- ▶ To synthesize it in cells, we must couple the reverse reaction with an exergonic reaction

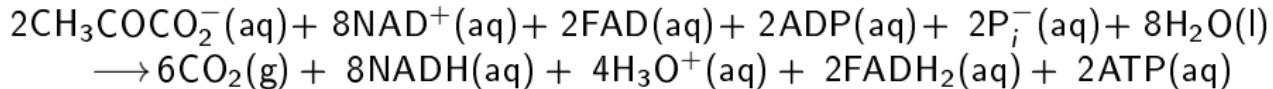
At blood temperature,  $\Delta_r G^\oplus = -147 \text{ kJ mol}^{-1}$  for oxidation of glucose by  $\text{NAD}^+$

- ▶ coupled reaction :



$$\Delta_{\text{combustion}} G^\oplus(\text{glucose}) = -2880 \text{ kJ mol}^{-1}$$

- ▶ so terminating its oxidation at pyruvate is a poor use of resources
- ▶ In presence of  $\text{O}_2$ , pyruvate is oxidized further during the citric acid cycle:



- ▶ The NADH and  $\text{FADH}_2$  go on to reduce  $\text{O}_2$  during oxidative phosphorylation, which also produces ATP
- ▶ citric acid cycle and oxidative phosphorylation generate as many as 38 ATP molecules for each glucose molecule consumed
  - ▶ Each mole of ATP molecules extracts 31 kJ from the 2880 kJ supplied by 1 mol  $\text{C}_6\text{H}_{12}\text{O}_6$  (180 g of glucose)
  - ▶ so 1178 kJ is stored for later use
  - ▶ ∴ aerobic oxidation of glucose is much more efficient than glycolysis

In the cell, each ATP molecule is used to drive an endergonic reaction for which  $\Delta_r G^\oplus \geq 31 \text{ kJ mol}^{-1}$

- ▶ actual cell composition may be far from standard, and ATP reaction may be much more potent
- ▶ e.g., biosynthesis of sucrose from glucose and fructose can be driven by plant enzymes because reaction is endergonic  $\Delta_r G^\oplus = 23 \text{ kJ mol}^{-1}$
- ▶ biosynthesis of proteins is strongly endergonic, not only due to enthalpy change but also for large decrease in entropy that occurs when many amino acids are assembled into precisely determined sequence
- ▶ e.g., formation of peptide link is endergonic, with  $\Delta_r G^\oplus = 17 \text{ kJ mol}^{-1}$
- ▶ but biosynthesis occurs indirectly and is equivalent to consumption of 3 ATP molecules for each link

In moderately small protein like myoglobin, with about 150 peptide links, construction alone requires 450 ATP molecules

- ▶  $\therefore 12 \text{ mol of glucose} \implies \text{for 1 mol of protein molecules}$

Perfect gas equilibria :

When A and B are perfect gases

$$\begin{aligned}\Delta_r G &= \mu_B - \mu_A = (\mu_B^\ominus + RT \ln p_B) - (\mu_A^\ominus + RT \ln p_A) \\ &= \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A} = \Delta_r G^\ominus + RT \ln Q; \quad Q = \text{reaction quotient}\end{aligned}$$

and  $\Delta_r G^\ominus = \Delta_f G_m^\ominus(B) - \Delta_f G_m^\ominus(A)$  = standard reaction Gibbs energy

At equilibrium,  $\Delta_r G^\ominus = 0 \implies \Delta_r G^\ominus + RT \ln K$  with  $K = \left(\frac{p_B}{p_A}\right)_\text{equilibr}$

In general, for a reaction  $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$ ,  $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$

$\Delta_r G^\ominus = \nu_C \mu_C^\ominus + \nu_D \mu_D^\ominus - \nu_A \mu_A^\ominus - \nu_B \mu_{AB}^\ominus$  and  $Q = \frac{p_D^{\nu_D} p_C^{\nu_C}}{p_A^{\nu_A} p_B^{\nu_B}}$  if A, ..., D are perfect gases

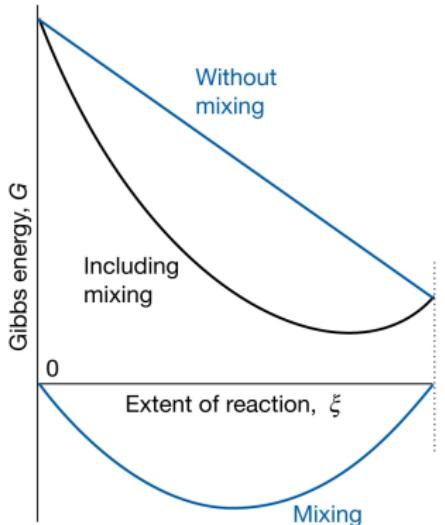
At equilibrium:  $\Delta_r G = 0 \xrightarrow{Q=K} \Delta_r G^\ominus = -RT \ln K$

For real gases, pressures replaced by fugacities and more generally for arbitrary phases, by activities.

$$Q = \frac{\text{activities of products raised to powers of stoichiometric coefficients}}{\text{activities of reactants raised to powers of stoichiometric coefficients}}$$

Writing  $\nu_s$  for reactants as negative integers,  $Q = \prod_j a_j^{\nu_j}$

In molecular terms, the minimum at  $\Delta_r G^\ominus = 0$  stems from  $\Delta_{\text{mix}} G$



- ▶ If mixing of reactants + products ignored  
     $\Rightarrow G$  changes linearly from initial (pure reactants) to final value (pure products)
- ▶ slope =  $\Delta_r G^\ominus$ .
- ▶ as products are produced : further contribution to  $G$  arising from mixing (lowest curve)
- ▶  $\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B)$
- ▶ sum of two contributions has a minimum
  - ▶ corresponds to equilibrium composition

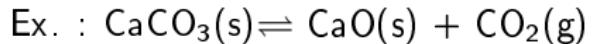
dependence of  $\Delta_r G$  on  $Q$  :  $dG = \sum_j \mu_j d\eta_j = \sum_j \nu_j \mu_j d\xi$

$$\begin{aligned}\Delta_r G &= \left( \frac{\partial G}{\partial \xi} \right)_{p, T} = \sum_j \nu_j \mu_j = \underbrace{\sum_j \nu_j \mu_j^\ominus}_{\Delta_r G^\ominus} + RT \sum_j \nu_j \ln a_j = \Delta_r G^\ominus + RT \ln \overbrace{\prod_j a_j^{\nu_j}}^Q \\ &= \Delta_r G^\ominus + RT \ln Q\end{aligned}$$

$$K = \left( \prod_j a_j^{\nu_j} \right)_{\text{equil}} ; \Delta_r G^\ominus = -RT \ln K$$

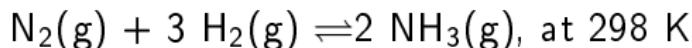
In elementary applications, activities are often replaced by:

- ▶ molalities, by replacing  $a_j$  by  $\frac{b_j}{b^\ominus}$  where  $b^\ominus = 1 \text{ mol kg}^{-1}$
- ▶ molar concentrations, by replacing  $a_j$  by  $\frac{[J]}{c^\ominus}$ , where  $c^\ominus = 1 \text{ mol dm}^{-3}$
- ▶ partial pressures, by replacing  $a_j$  by  $\frac{p_j}{p^\ominus}$ , where  $p^\ominus = 1 \text{ bar}$



$$K = a_{\text{CaCO}_3(s)}^{-1} \cdot a_{\text{CaO}(s)} \cdot a_{\text{CO}_2(g)} = \frac{\overbrace{a_{\text{CaO}(s)} \cdot a_{\text{CO}_2(g)}}^{=1}}{\underbrace{a_{\text{CaCO}_3(s)}}_{=1}} = a_{\text{CO}_2(g)}$$

Provided  $\text{CO}_2$  can be treated as a perfect gas,  $K = \frac{p_{\text{CO}_2(g)}}{p^\ominus} = p_{\text{CO}_2(g)}$   
=numerical value of decomposition vapour pressure of calcium carbonate



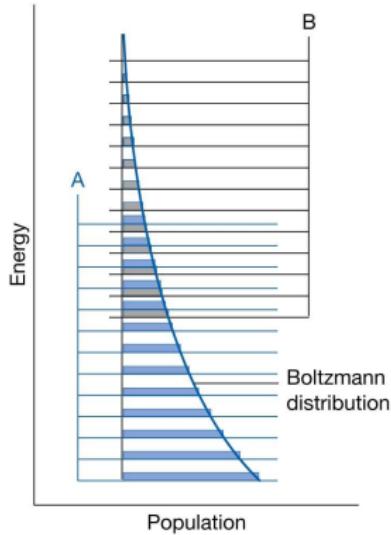
$$\begin{aligned}\Delta_r G^\ominus &= 2\Delta_f G^\ominus(\text{NH}_3, \text{g}) - [\Delta_f G^\ominus(\text{N}_2, \text{g}) + 3\Delta_f G^\ominus(\text{H}_2, \text{g})] \\ &= 2\Delta_f G^\ominus(\text{NH}_3, \text{g}) = 2 \times (-16.5) \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta_r G^\ominus = 2\Delta_f G^\ominus(\text{NH}_3, \text{g}) - [\Delta_f G^\ominus(\text{N}_2, \text{g}) + 3\Delta_f G^\ominus(\text{H}_2, \text{g})]$$

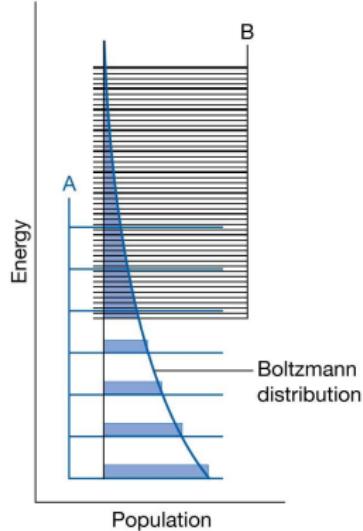
$$\therefore \ln K = -\frac{2 \times (-16.5 \times 10^3)}{8.3145 \times 298} = 6.1 \times 10^5$$

$$K = \frac{a_D^{\nu_D} a_C^{\nu_C}}{a_A^{\nu_A} a_B^{\nu_B}} = \frac{\gamma_D^{\nu_D} \gamma_C^{\nu_C}}{\gamma_A^{\nu_A} \gamma_B^{\nu_B}} \times \frac{b_D^{\nu_D} b_C^{\nu_C}}{b_A^{\nu_A} b_B^{\nu_B}} = K_\gamma K_b, \text{ where } b_j \equiv \frac{b_j}{b_j^\ominus}$$

molecular interpretation :  $K = e^{-\frac{\Delta_r H^\ominus}{RT}} \cdot e^{\frac{\Delta_r S^\ominus}{RT}}$



Species A dominant



Species B dominant

biological standard state:  $a_{H^+} = 10^{-7}$ ;  $pH = 7$

For reaction:  $R + \nu H^+(aq) \rightarrow P$

$$\Delta_r G = \Delta_r G^\ominus + RT \ln \frac{a_P}{a_R a_H^\nu} = \Delta_r G^\ominus + RT \ln \frac{a_P}{a_R} - \nu RT \ln a_{H^+}$$

In the biological standard state, both P and R are at unit activity

$$\therefore \Delta_r G = \Delta_r G^\ominus - \nu RT \ln 10 \log a_{H^+} = \Delta_r G^\ominus + \nu RT \ln 10 \cdot pH$$

with  $pH = 7$ ,  $\Delta_r G^\oplus = \Delta_r G^\ominus + 7\nu RT \ln 10$

response of equilibria to the conditions

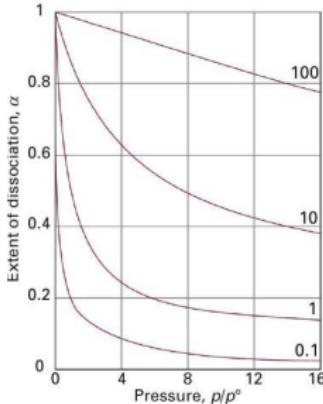
Le Chatelier's principle :

A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance

How equilibria respond to changes of pressure

Consider reaction  $A \rightleftharpoons 2B$

$$\alpha = \sqrt{\frac{1}{1 + \frac{4p}{K_p^\ominus}}}$$



even though  $K$  is independent of pressure  
amounts of  $A$  and  $B$  do depend on pressure  
as  $p$  is increased,  $\alpha$  decreases

in accord with Le Chatelier's principle

label :  $K$

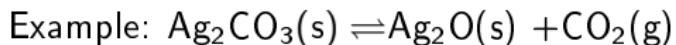
effect of increase in pressure on ammonia synthesis

$$K = \frac{p_{\text{NH}_3}^2 p^\ominus^2}{p_{\text{N}_2} p_{\text{H}_2}^3} = \frac{x_{\text{NH}_3}^2 p^2 p^\ominus^2}{x_{\text{N}_2} x_{\text{H}_2}^3 p^4} = \frac{K_x p^\ominus^2}{p^2}$$

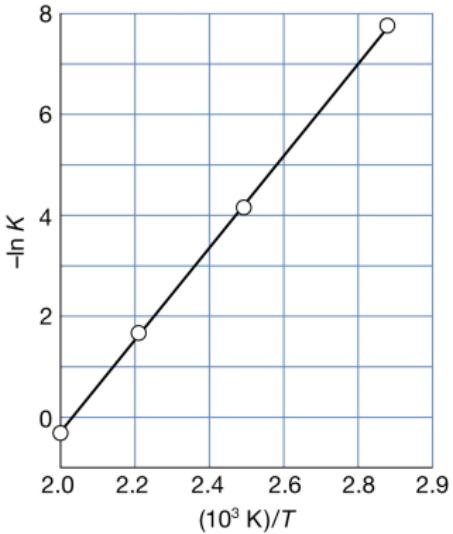
response of equilibria to changes of temperature

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$$

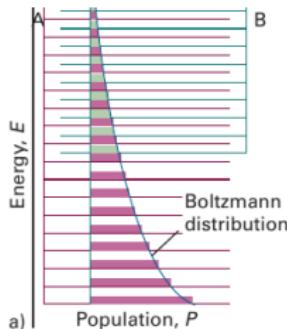
or,  $\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_r H^\ominus}{R}$



K vs. T(K)



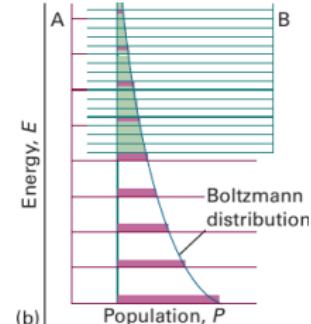
At a given temperature, there is a specific distribution of populations, and hence specific composition of reaction mixture



usually dominant species in a mixture at equilibrium is the one with lower set of energy levels

In a reaction, entropy plays a role as well as energy

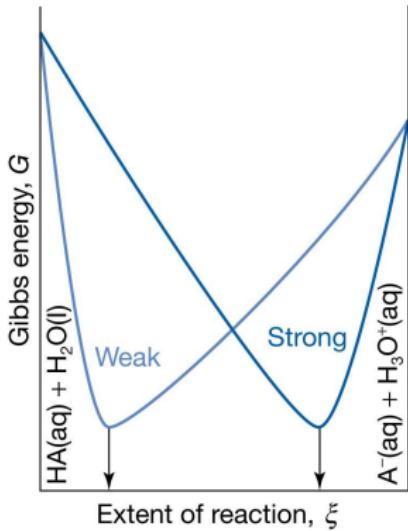
an endothermic reaction



B energy levels lie higher than the A energy levels, but they are much more closely spaced  $\Rightarrow$  their total population may be considerable and B could even dominate in the reaction mixture at equilibrium

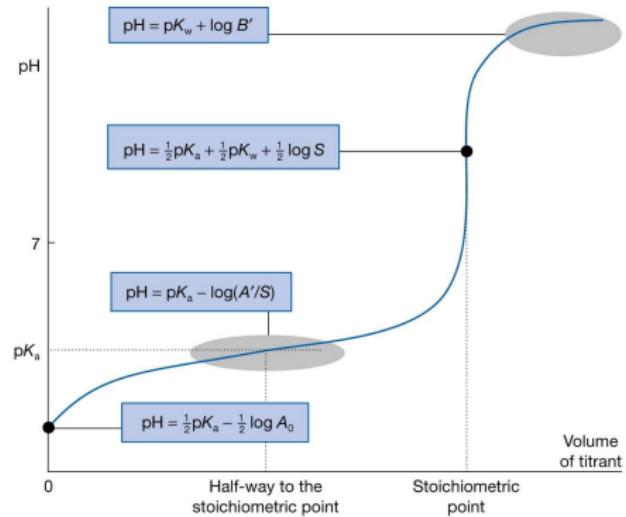
Closely spaced energy levels correlate with high entropy, so entropy effects dominate

$$K = e^{-\frac{\Delta_f H^\ominus}{RT}} e^{-\frac{\Delta_f S^\ominus}{R}}$$



- ▶ strong acids and bases : minimum Gibbs free energy of the solution lies close to products
- ▶ weak acids:  $pH = \frac{1}{2}pK_a - \frac{1}{2}\log[HA]$
- ▶ weak base:  $pH = pK_w - \frac{1}{2}pK_b + \frac{1}{2}\log[B]$

## Titration of weak acid with strong base



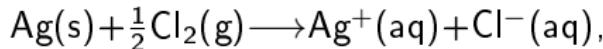
## **Equilibrium electrochemistry**

**thermodynamic properties of ions in solutions:**

convenient defn.:  $\Delta_f G^\ominus(H^+, \text{aq}) = 0$  at all temps.

For the rxn.,  $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow H^+(aq) + Cl^-(aq)$ ,  $\Delta_r G^\ominus = -131.23 \text{ kJ/mol}$

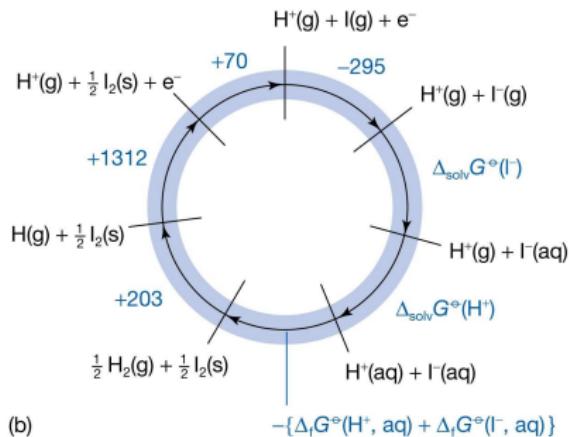
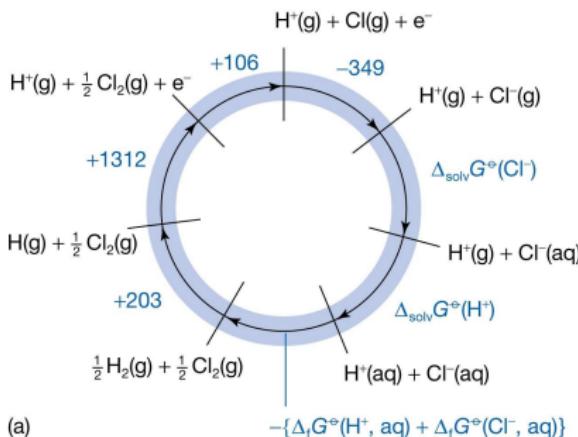
$\Delta_r G^\ominus = \Delta_f G^\ominus(H^+, \text{aq}) + \Delta_f G^\ominus(Cl^-, \text{aq}) = \Delta_f G^\ominus(Cl^-, \text{aq}) = -131.23 \text{ kJ/mol}$



$\Delta_r G^\ominus = \Delta_f G^\ominus(Ag^+, \text{aq}) + \Delta_f G^\ominus(Cl^-, \text{aq}) = -54.12 \text{ kJ/mol} \implies$

$\Delta_f G^\ominus(Ag^+, \text{aq}) = 77.11 \text{ kJ/mol.}$

solvation of (a) chloride and (b) iodide ions:  
 entropy terms for formation of  $\text{H}^+$  and  $\text{Cl}^-$  cancel each other out



Born equation for Gibbs energy of solvation of individual ions

$$\Delta_f G^\ominus(\text{Cl}^-, \text{aq}) =$$

$$1272 \text{ kJ mol}^{-1} + \Delta_{\text{solv}}G^\ominus(\text{H}^+) + \Delta_{\text{solv}}G^\ominus(\text{Cl}^-)$$

for constant  $p$ ,  $T$ ,     $\Delta G =$ non- $pV$  work :  
electrical work of transferring an ion from vacuum into a solvent  
depends on **dielectric constant** of the medium

entropy terms : Standard entropies of ions:  $S^\ominus(H^+, \text{aq})=0$

## Activities of ions in solns

consider  $M^+X^-$ :  $G_m^{\text{ideal}} = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}}$

$$G_m = \mu_+ + \mu_- = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}} + RT \ln \gamma_+ + RT \ln \gamma_- = G_m^{\text{ideal}} + RT \ln \gamma_+ \gamma_-$$

deviations from ideality are in the last term

$$\text{mean activity coefficient: } \gamma_{\pm} = \sqrt{\gamma_+ \gamma_-}$$

Redefine:  $\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_{\pm}$  and  $\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_{\pm}$   
nonideality shared equally

compound  $M_p X_q$ :  $G_m = p\mu_+ + q\mu_- = G_m^{\text{ideal}} + pRT \ln \gamma_+ + qRT \ln \gamma_-$

mean activity coefficient:  $\gamma_{\pm} = [(\gamma_+)^p (\gamma_-)^q]^{\frac{1}{s}}$ , where  $s = p + q$

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

same expression for  $G_m$  as before but both types of ion now share equal responsibility for non-ideality

Debye-Hückel limiting law (1923):

Long range Coulomb force  $\Rightarrow$  dominant cause of nonideal behaviour

opposite charged ions attract one another

overall neutral solution

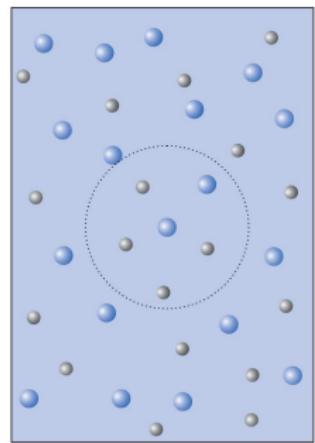
near any given ion there is an excess of counterions

Time averaged **Counter ionic atmosphere** of charge

$\equiv$  net charge equal in magnitude but opposite in sign to that on the central ion

Free energy of central ion lowered because of interactions with ionic atmosphere

$$G_m - G_m^{\text{ideal}} = RT \ln \gamma_{\pm}$$



Debye Hückel limiting law:  $\log \gamma_{\pm} = -|z_+ z_-| A \sqrt{I}$

$A = 0.509$  for aqueous soln at 298K;

$$I = \frac{1}{2} \sum_i z_i^2 \left( \frac{b_i}{b^\ominus} \right)$$

For solution with ions at molalities  $b_+$  and  $b_-$ ,  $I = \frac{1}{2b^\ominus} (b_+ z_+^2 + b_- z_-^2)$

ex. 1: 5 mmol kg<sup>-1</sup> of KCl (aq) at 25°C;  $b = 5 \times 10^{-3}$  molal

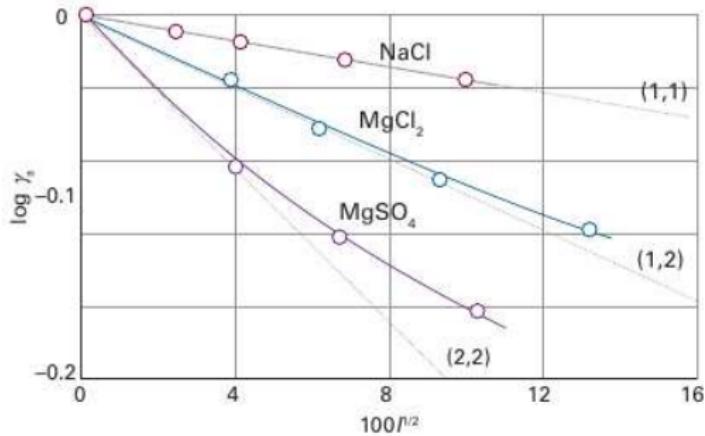
$$I = \frac{1}{2b^\ominus} (b_+ 1^2 + b_- (-1)^2) = \frac{b}{b^\ominus}$$

$$\log \gamma_{\pm} = -0.509 \cdot \sqrt{5 \times 10^{-3}} = -0.03 \implies \gamma_{\pm} = 0.927$$

ex. 2 : 1 mmol kg<sup>-1</sup> of CaCl<sub>2</sub> (aq) at 25°C

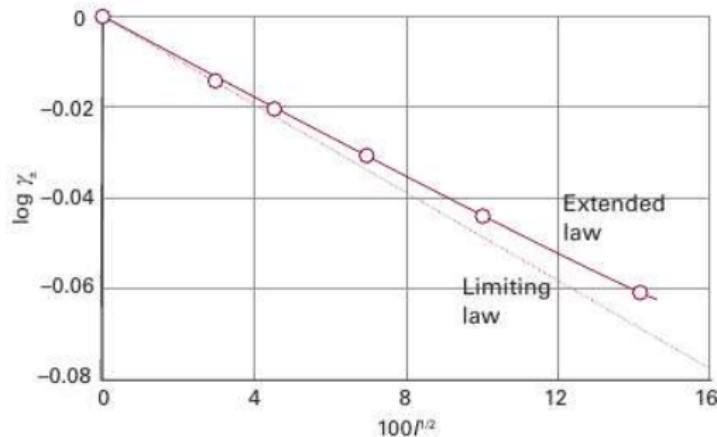
$$I = \frac{1}{2b^\ominus} (b_+ 2^2 + b_- (-1)^2) = \frac{3b}{b^\ominus}; \dots$$

## activity coefficient vs. ionic strength



Extended Debye Hückel law:  $\log \gamma_{\pm} = -\frac{|z_+ z_-| A \sqrt{I}}{1 + B \sqrt{I}}$ ;

Davies eqn. :  $\log \gamma_{\pm} = -\frac{|z_+ z_-| A \sqrt{I}}{1 + B \sqrt{I}} + C.I$



Plot for 1:1 electrolyte

Derivation of Debye Hückel law:

task : establish relation between

work needed to charge an ion and its chemical potential

then relate that work to ion's interaction with

atmosphere of counter ions assembled around it

three competing factors contribute to counterionic atmosphere:

1. attraction between oppositely charged ions
2. repulsion of like-charged ions
3. distributing effect of thermal motion

Work of charging :

$G_m - G_m^{\text{ideal}} = w_{\text{electr}}$ , electrical work of charging neutral atoms  
in an ideal solution to make them ions

$$\text{For } M_p X_q, w_{\text{electr}} = \underbrace{(p\mu_+ + q\mu_-)}_{G_m, \text{ charged}} - \underbrace{(p\mu_+^{\text{ideal}} + q\mu_-^{\text{ideal}})}_{G_m^{\text{ideal}}, \text{ uncharged}}$$
$$= p(\mu_+ - \mu_+^{\text{ideal}}) + q(\mu_- - \mu_-^{\text{ideal}})$$

using  $\mu_+ - \mu_+^{\text{ideal}} = \mu_- - \mu_-^{\text{ideal}} = RT \ln \gamma_{\pm}$ , we have  $\ln \gamma_{\pm} = \frac{w_{\text{electr}}}{sRT}$

first find final distribution of ions

then find work for charging them in that distribution

Ex.  $\gamma_{\pm} = 0.927$  for 5 mmol kg<sup>-1</sup> of KCl (aq) at 25°C

∴ average work involved in charging ions in their environment in solution

$$= sRT \ln \gamma_{\pm} = 2 \times 8.3145 \times 298 \times \ln 0.927 = -0.38 \text{ kJ mol}^{-1}$$

## Potential due to charge distribution :

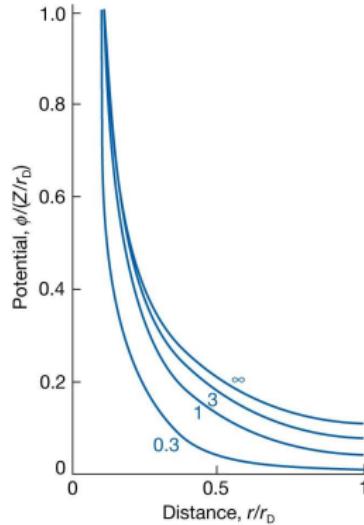
Coulomb potential at distance  $r$  from isolated ion of charge  $z_i e$ ,

$$\phi_i = \frac{Z_i}{r}, \text{ where } Z_i = \frac{z_i e}{4\pi\epsilon}$$

Ionic atmosphere causes potential to decay with distance more sharply than this expression implies

Shielded Coulomb potential,  $\phi_i = \frac{Z_i}{r} e^{-\frac{r}{r_D}}$ ,  
where  $r_D$  = Debye length : characteristic distance depending on nature and concentration of ions

## Potential as a function of distance from central ion



The labels are different values of  $r_D$

Calculating  $r_D$  :

$$\text{Poisson eqn. : } \nabla^2 \phi = -\frac{\rho}{\varepsilon}$$

For spherically symmetric environment,  $\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\phi}{dr} \right) = -\frac{\rho}{\varepsilon}$

Substituting,  $\phi_i = \frac{z_i}{r} e^{-\frac{r}{r_D}}$ , we get,  $r_D^2 = -\frac{\varepsilon \phi_i}{\rho_i}$

To solve this we need to relate  $\rho_i$  and  $\phi_i$

energy of an ion depends on its closeness to central ion

find Boltzmann probability for an ion to be found at each distance

energy of ion  $j$  of charge  $z_j e$  at a distance where it experiences potential  $\phi_i$  of central ion relative to when far away in bulk solution = charge  $\times$  potential =  $z_j e \cdot \phi_i$

∴ for molar concentration of ions at distance  $r$ ,  $c_j$  and in bulk  $c_j^0$ :  $\frac{c_j}{c_j^0} = e^{-\frac{z_j e \phi_i}{kT}}$

charge density,  $\rho_i$  at distance  $r$  from ion  $i$

= molar concn. of each type of ion  $\times$  charge per mole of ions,  $z_i e N_A (= z_i F)$

$$\rho_i = c_+ z_+ F + c_- z_- F = c_+^0 z_+ F e^{-\frac{z_+ e \phi_i}{kT}} + c_-^0 z_- F e^{-\frac{z_- e \phi_i}{kT}}$$

$$\approx c_+^0 z_+ F \left( 1 - \frac{z_+ e \phi_i}{kT} + \dots \right) + c_-^0 z_- F \left( 1 - \frac{z_- e \phi_i}{kT} + \dots \right) =$$

$$\overbrace{(c_+^0 z_+ + c_-^0 z_-)}^0 F - (c_+^0 z_+^2 + c_-^0 z_-^2) \frac{F e \phi_i}{kT} \stackrel{(c=b\rho)}{=} - \underbrace{(b_+^0 z_+^2 + b_-^0 z_-^2)}_{2lb^\ominus} \frac{\rho F^2 \phi_i}{RT} = - \frac{2lb^\ominus \rho F^2 \phi_i}{RT}$$

$$\therefore r_D = \sqrt{-\frac{\varepsilon \phi_i}{\rho_i}} = \sqrt{\frac{\varepsilon RT}{2lb^\ominus \rho F^2}}$$

Ex.: aq. soln. of ionic strength 0.1 and density 1.0 g cm<sup>-3</sup> at 25°C;  $\epsilon_r = 80.1$

$$r_D = \sqrt{\frac{80.1 \times 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \times 8.1345 \times 298}{2 \times 0.1 \times 1000 \times 96490^2}} = 0.972 \text{ nm}$$

Activity coefficient ( $\ln \gamma_{\pm} = \frac{w_{\text{electr}}}{sRT}$ ): need to evaluate  $w_{\text{electr}}$

To calculate work of charging central ion we need to know potential at the ion due to its atmosphere,  $\phi_{\text{atmos}}$

$\phi_{\text{atmos}}$  = difference between total potential,  $\phi = \frac{Z_i e}{r} e^{-\frac{r}{r_D}}$ , and potential due to central ion itself

$$= \phi - \phi_{\text{central ion}} = Z_i \left( \frac{e^{-\frac{r}{r_D}}}{r} - \frac{1}{r} \right); \quad Z_i = \frac{z_i e}{4\pi\epsilon}$$

$$\text{at } r = 0, \phi_{\text{atmos}}(0) = Z_i \left( \frac{1 - \frac{r}{r_D} + \dots}{r} - \frac{1}{r} \right) = -\frac{Z_i}{r_D}$$

potential due to ionic atmosphere  $\equiv$  potential arising from single charge of equal magnitude but opposite sign to that of central ion and located at distance  $r_D$  from the ion

If the charge of the central ion were  $Q$  and not  $z_i e$ , then potential due to its atmosphere,

$$\phi_{\text{atmos}}(0) = -\frac{Q}{4\pi\epsilon r_D}$$

Work of adding a charge  $dQ$  to a region of potential  $\phi_{\text{atmos}}(0)$ ,

$$dw_{\text{electr}} = \phi_{\text{atmos}}(0)dQ$$

$\therefore$  total work of fully charging 1 mole of ions in presence of the atmosphere,

$$w_{\text{electr}} = N_A \int_0^{z_i e} \phi_{\text{atmos}}(0)dQ = -\frac{N_A}{4\pi\epsilon r_D} \int_0^{z_i e} QdQ = -\frac{N_A z_i^2 e^2}{8\pi\epsilon r_D} = -\frac{z_i^2 F^2}{8N_A \pi \epsilon r_D}$$

total work of charging  $p$  cations and  $q$  anions in the presence of their atmospheres,

$$w_{\text{electr}} = pw_+ + qw_-$$

$$\therefore \ln \gamma_{\pm} = \frac{w_{\text{electr}}}{sRT} = \frac{(pz_+^2 + qz_-^2)F^2}{8N_A \pi s RT \varepsilon r_D}$$

$$\text{and } pz_+^2 + qz_-^2 = \overbrace{pz_+}^{-qz_-} \cdot z_+ + \overbrace{qz_-}^{-pz_+} z_- = -(p+q)z_+z_- = s|z_+z_-|$$

$$\therefore \ln \gamma_{\pm} = -\frac{|z_+z_-|F^2}{8\pi N_A R T \varepsilon r_D}$$

using  $r_D = \sqrt{\frac{\varepsilon RT}{2lb^\ominus \rho F^2}}$ , we have,

$$\ln \gamma_{\pm} = -\frac{|z_+z_-|F^2}{8\pi N_A R T \varepsilon} \sqrt{\frac{2lb^\ominus \rho F^2}{\varepsilon RT}} = -\frac{F^3}{4\pi N_A} \sqrt{\frac{\rho b^\ominus}{2\varepsilon^3 R^3 T^3}} |z_+z_-| \sqrt{I}$$

$$\text{Finally, } \log \gamma_{\pm} = -A |z_+z_-| \sqrt{I}$$

## **Electrochemical cell :**

consists of two electrodes, or metallic conductors, in contact with an electrolyte, an ionic conductor (solution, liquid, or solid).

Electrode and its electrolyte comprise electrode compartment

Two electrodes may share same compartment

Any 'inert metal' shown acts as a source or sink of electrons  
and has no other part in reaction other than as a catalyst

If electrolytes are different,  
the two compartments may be joined by

salt bridge : tube containing a concentrated electrolyte solution (potassium chloride in agar jelly) that completes electrical circuit and enables cell to function

**galvanic cell** : produces electricity as a result of spontaneous reaction

**electrolytic cell** : non-spontaneous reaction driven by external source of current

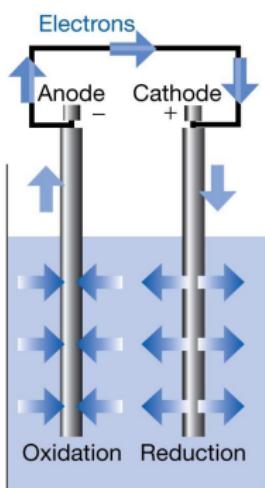
		Electrode type	Designation	Redox couple	Half-reaction
(a)		Metal/metal ion	M(s) M+(aq)	M+/M	$M^+(aq) + e^- \rightarrow M(s)$
(b)		Gas	Pt(s) X2(g) X+(aq)	X+/X2	$X^+(aq) + e^- \rightarrow \frac{1}{2} X_2(g)$
(c)		Pt(s) X2(g) X-(aq)	X2/X-	$\frac{1}{2} X_2(g) + e^- \rightarrow X^-(aq)$	
(d)		Metal/insoluble salt	M(s) MX(s) X-(aq)	MX/M,X-	$MX(s) + e^- \rightarrow M(s) + X^-(aq)$
		Redox	Pt(s) M+(aq),M2+(aq)	M2+/M+	$M^{2+}(aq) + e^- \rightarrow M^+(aq)$

## Half reactions and electrodes:

redox reaction is expressed as difference of two reduction half-reactions (conceptual reactions showing gain of electrons)

reactions that are not redox reactions may be expressed as the difference of two reduction half-reaction

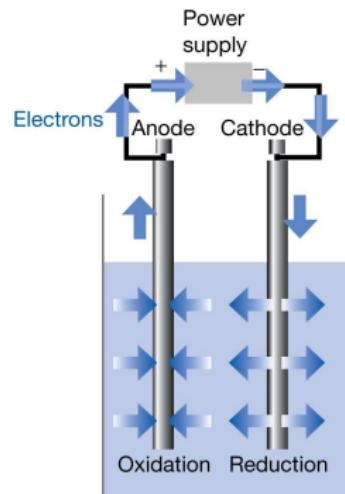
reduced/oxidized species in half-reaction form redox couple



Galvanic cell

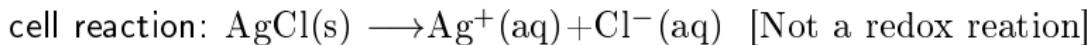
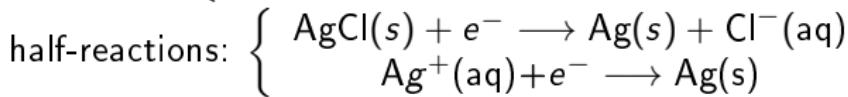
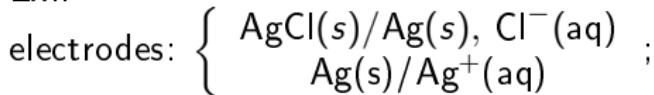
couple : Ox/Red

corresponding reduction half-reaction :  $Ox + \nu e^- \longrightarrow Red$



electrolytic cell

Ex.:



reaction quotient :  $aA + bB \longrightarrow cC + dD$ ;

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}; \quad \Delta G = \Delta G^\ominus + RT \ln Q; \quad \Delta G^\ominus = -RT \ln K$$

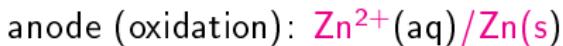
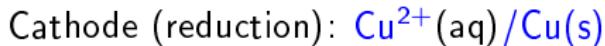
reaction quotient for half-reaction:

Ex. 1 : reduction of  $O_2$  to  $H_2O$  in acid soln. :  $O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O(l)$

$$Q = \frac{a_{H_2O}^2}{a_{H^+}^4 a_{O_2}} \approx \frac{p^\ominus}{a_{H^+}^4 p_{O_2}}$$

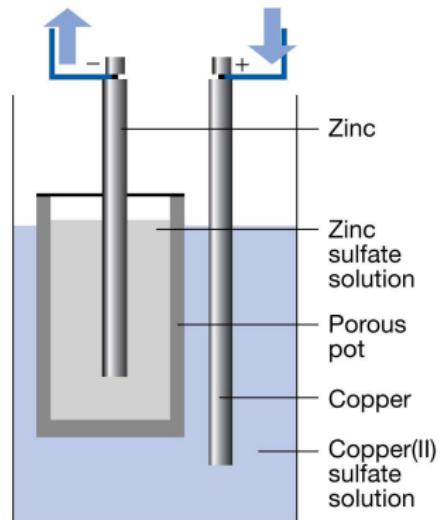
Ex. 2: chlorine gas electrode :  $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq); \quad Q = \frac{p^\ominus a_{Cl^-}^2}{p_{Cl_2}}$

Daniell cell:



Electrons leave zinc electrode (through a wire)  
and enter again through copper electrode

cell reaction :



## Liquid junction potential:

In a cell with two different electrolyte solutions in contact

as in Daniell cell

$\exists$  additional source of potential difference

across interface of two electrolytes

$\Rightarrow$  liquid junction potential,  $E_{lj}$

Another example of junction potential :

between different concentrations of HCl

At junction, mobile  $H^+$  ions diffuse into more dilute solution.

Bulkier  $Cl^-$  ions follow, but initially do so more slowly, which results in potential difference at junction.

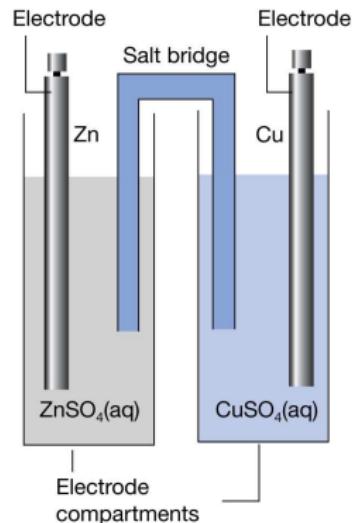
After brief initial period, ions diffuse at same rates

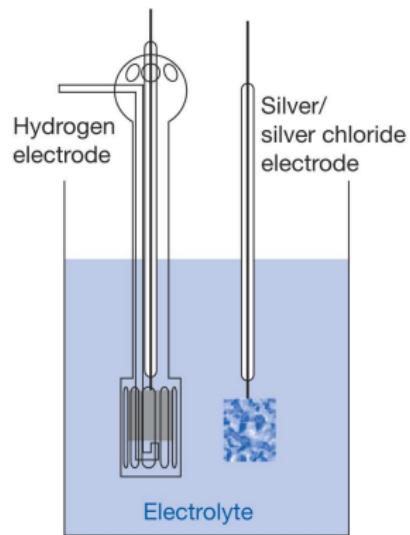
Electrolyte concentration cells always have a liquid junction;  
electrode concentration cells do not.

salt bridge:

Contribution of liquid junction to potential is reduced by  $\approx$  1-2 mV by joining electrolyte compartments through a salt bridge

liquid junction potentials at either end are largely independent of concentrations of two dilute solutions, and so nearly cancel



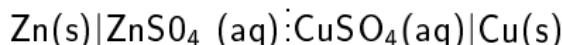


Notation:

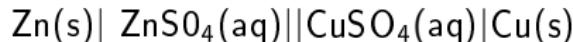
phase boundaries denoted by a vertical bar:

two electrodes share same electrolyte:  $\text{Pt(s)}|\text{H}_2\text{(g)}|\text{HCl(aq)}|\text{AgCl(s)}|\text{Ag(s)}$

Liquid junction denoted by :



Double vertical line, ||, denotes interface for which it is assumed that junction potential is eliminated



Example of electrolyte concentration cell in which liquid junction potential is assumed eliminated :



EMF: cell potential

Current produced by galvanic cell from spontaneous chemical reaction

Cell reaction :

right-hand electrode is cathode

spontaneous reaction : reduction taking place in right-hand compartment

If left-hand electrode is cathode,

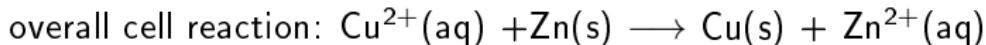
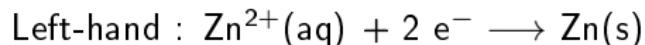
then reverse of corresponding cell reaction is spontaneous

To write cell reaction corresponding to a cell diagram,  
first write right-hand half-reaction as reduction  
(because we have assumed it spontaneous)

Then subtract from it left-hand reduction half-reaction : right-left  
( by implication, that electrode is site of oxidation)

Ex. cell :  $\text{Zn(s)} \mid \text{ZnSO}_4(\text{aq}) \parallel \text{CuSO}_4(\text{aq}) \mid \text{Cu(s)}$

two electrodes and their reduction half-reactions are:



## Nernst eq.

when overall cell reaction has not reached chemical equilibrium  
electrical work can be done as reaction drives electrons through external circuit  
potential difference between electrodes = cell potential measured in volts

1. **large cell potential** : given number of electrons traveling between electrodes can do large amount of electrical work
2. **small cell potential** : same #electrons do small amount of work
3. overall reaction at equilibrium : no work, and **cell potential = 0**

$w_{e,\max} = \Delta G$  = Gibbs energy of the cell reaction,  $\Delta_r G$

cell must operate reversibly : only then it produces max. work

$\Delta_r G$  is a property relating to specified composition of reaction mixture  
∴ cell must operate reversibly at specific, constant composition

these conditions are achieved by measuring cell potential when balanced by exactly opposing source of potential

then **cell reaction is reversible**, **composition constant**, and **no current flows**

in effect, **cell reaction is poised for change, but not actually changing**

Resulting potential difference  $\equiv$  electromotive force (emf), E, of the cell

key connection between electrical measurements and thermodynamic properties  
relation between  $\Delta_r G$  and emf :

$$-\nu FE = \Delta_r G$$

$$F = eN_A$$

$\nu$  = stoichiometric coefficient of electrons in half-reactions into which cell reaction is divided

At constant  $T, p$ , when reaction advances by  $d\xi$ ,

amounts of reactants and products change by

$$dn_j = \nu_j d\xi$$

$$\text{and } dG = \sum_j \mu_j dn_j = \sum_j \mu_j \nu_j d\xi \implies \Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_j \mu_j \nu_j$$

or,  $dG = \Delta_r G d\xi$

Max. non-expansion (electrical) work

as reaction advances by  $d\xi$  at constant temperature and pressure

$$= \Delta_r G \cdot d\xi$$

as reaction advances by  $d\xi$ ,

then  $\nu d\xi$  electrons must travel from anode to cathode

charge transported between electrodes when this change occurs per mole

$$= -\nu e N_A d\xi = -\nu F d\xi$$

Work done when an infinitesimal charge  $-\nu F d\xi$  travels from anode to cathode

$$= \text{charge} \times \text{potential difference } (E) = -\nu F E d\xi$$

$$\therefore \boxed{\Delta_r G = -\nu F E}$$

$$\Delta_r G < 0$$

for a spontaneous cell reaction

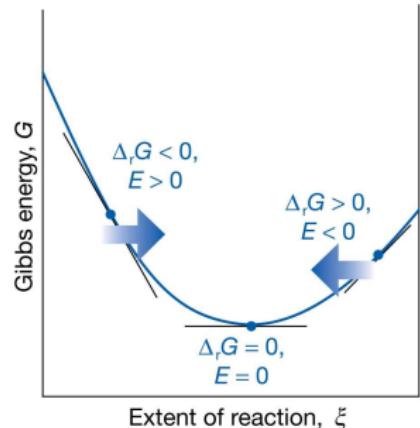
corresponds to  $E > 0$

It is plausible that a reaction far from equilibrium (slope steep)

has a strong tendency to drive electrons through an external circuit

When slope  $\approx 0$  (cell reaction close to equilibrium), emf is small

driving power of a cell (emf)  $\propto$  slope of Gibbs energy w r t extent of reaction



Ex. :  $\Delta_r G = -10^2$  kJ /mol;  $\nu = 1$ ,

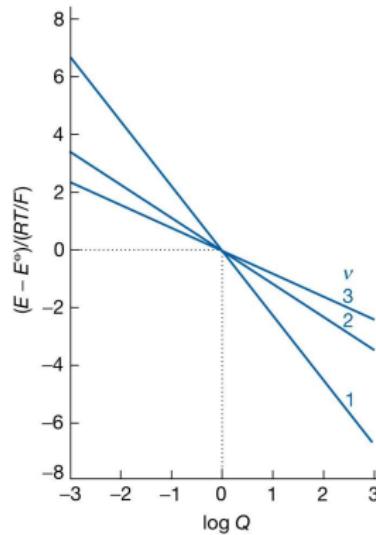
$$\text{then } E = -\frac{\Delta_r G}{\nu F} = -\frac{10^2}{96485} \approx 1 \text{ V.}$$

From,  $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$ ,

$$\text{Nernst eq.: } E = E^\ominus - \frac{RT}{\nu F} \ln Q$$

$$= E^\ominus - \frac{25.7 \text{mV}}{\nu} \ln Q = E^\ominus - \frac{59.2 \text{mV}}{\nu} \log Q$$

Variation of cell emf with value of reaction quotient for cell reaction for different values of  $\nu$  (#electrons transferred)



At 298 K,  $\frac{RT}{F} = 25.69$  mV, vertical scale refers to multiples of this value

important application of Nernst equation:

determination of pH and, with a suitable choice of electrodes, of concentration of other ions

Standard emf can be interpreted as emf when all reactants/products in cell reaction are in standard states,

for then all activities are 1, so  $Q = 1$  and  $\ln Q = 0$

Standard emf is merely a disguised form of  $\Delta_r G$  :

should always be kept in mind and it underlies all its applications

## Cells at equilibrium

Suppose reaction has reached equilibrium;

then  $Q = K$ , where  $K$  is the equilibrium constant of cell reaction

a chemical reaction at equilibrium cannot do work

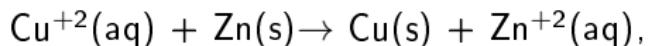
and hence it generates zero potential difference between electrodes of a galvanic cell

setting  $E = 0$  and  $Q = K$  in Nernst equation gives

$$\ln K = \frac{\nu F E^\ominus}{RT}$$

Standard emf of the Daniell cell is +1.10 V,

equilibrium constant for the cell reaction



for which  $\nu = 2$ , is

$$K = 1.5 \times 10^{37} \text{ at } 298 \text{ K.}$$

displacement of copper by zinc goes virtually to completion

an emf of about 1 V is easily measurable

but corresponds to equilibrium constant that is impossible to measure by direct chemical analysis

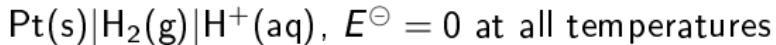
## Standard potentials :

galvanic cell is a combination of two electrodes,  
each one making a characteristic contribution to overall cell potential

It is not possible to measure contribution of a single electrode

**define one electrode potential as zero and assign values to others on that basis**

specially selected electrode : **standard hydrogen electrode (SHE):**



standard :  $a_{\text{H}^+} = 1$  ( $\text{pH} = 0$ ) and  $p_{\text{H}_2(\text{g})} = 1\text{bar}$  (more precisely, fugacity)

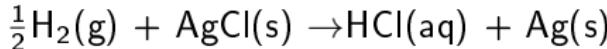
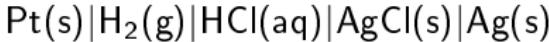
$E^\ominus$  of another couple is assigned by constructing a cell in which it is right-hand electrode and SHE is left-hand electrode

## Procedure for measuring a standard potential :

Plot :  $E + \frac{2RT}{F} \ln b$  vs.  $\sqrt{b}$   
 extrapolated to  $b = 0$  gives  $E^\ominus$   
 Once  $E^\ominus$  known,  $\gamma_\pm$  can be obtained

consider  $\text{AgCl}(s) \mid \text{Ag}(s)$  electrode.

Measurement made on the 'Harned cell':



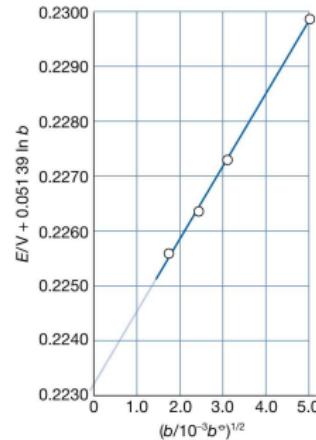
$$\text{Nernst eq.: } E = E^\ominus - \frac{RT}{F} \ln \frac{a_{\text{H}^+} a_{\text{Cl}^-}}{a_{\text{H}_2}^{\frac{1}{2}}}$$

$$= E^\ominus - \frac{RT}{F} \ln (a_{\text{H}^+} a_{\text{Cl}^-})$$

$$\text{or, } E = E^\ominus - \frac{RT}{F} \ln b^2 - \frac{RT}{F} \ln \gamma_\pm^2$$

$$\implies E + \frac{2RT}{F} \ln b = E^\ominus - \frac{2RT}{F} \ln \gamma_\pm$$

$$= E^\ominus + C\sqrt{b}$$



$b/(10^{-3}b^\ominus)$	3.215	5.619	9.138	25.63
$\{b/(10^{-3}b^\ominus)\}^{1/2}$	1.793	2.370	3.023	5.063
$E_{\text{cell}}/\text{V}$	0.520 53	0.492 57	0.468 60	0.418 24
$y/\text{V}$	0.2256	0.2263	0.2273	0.2299

Exercise:

**Self-test 7.9** The data below are for the cell  $\text{Pt(s)}|\text{H}_2(\text{g}, p^\ominus)|\text{HBr(aq, } b)\text{||AgBr(s)}|\text{Ag(s)}$  at 25°C. Determine the standard emf of the cell.

$b/(10^{-4} b^\ominus)$	4.042	8.444	37.19	
$E/\text{V}$	0.47381	0.43636	0.36173	[0.071 V]

## Standard electrode potentials:

Couple	$E^\ominus/V$
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{Cu}^{2+}(\text{aq}) + 2 \text{ e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g})$	0
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{Zn}^{2+}(\text{aq}) + 2 \text{ e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71

Standard potentials of electrodes are unchanged if chemical equation for cell reaction or a half-reaction is multiplied by a numerical factor

Numerical factor increases value of the standard Gibbs energy for the reaction.  
it also increases number of electrons transferred by the same factor  
using  $\Delta_r G = -\nu F E$ , value of  $E^\ominus$  remains unchanged.

practical consequence : cell emf independent of physical size of the cell

$\implies$  cell emf is an intensive property

Evaluating a standard potential from two others:

Given:  $E_{\text{Cu}^{2+}/\text{Cu}}^{\ominus} = +0.340\text{V}$ ,  $E_{\text{Cu}^{+}/\text{Cu}}^{\ominus} = +0.522\text{ V}$ ,

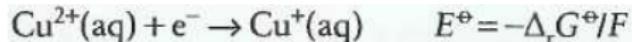
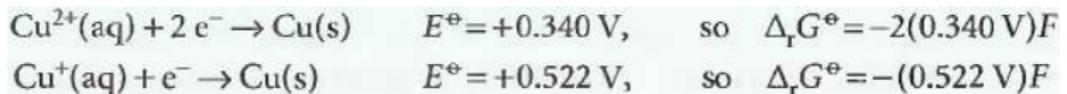
evaluate:  $E_{\text{Cu}^{2+}/\text{Cu}^{+}}^{\ominus}$

First, note :  $\Delta_r G$  may be added

$\therefore$  convert  $E^{\ominus}$  values to  $\Delta_r G^{\ominus}$  by using  $\Delta_r G^{\ominus} = -\nu F E^{\ominus}$

add them appropriately

and convert overall  $\Delta_r G^{\ominus}$  to required  $E^{\ominus}$



$$\Delta_r G^\ominus = \Delta_r G^\ominus(\text{a}) - \Delta_r G^\ominus(\text{b}) = -(-0.158 \text{ V}) \times F$$

generalisation:  $v_c E^\ominus(c) = v_a E^\ominus(a) + v_b E^\ominus(b)$

## Electrochemical series:

For redox couples,

$\text{Ox}_L/\text{Red}_L$  and  $\text{Ox}_R/\text{Red}_R$

and cell:

$\text{Red}_L, \text{Ox}_L || \text{Red}_R, \text{Ox}_R$

$$E^\ominus = E_R^\ominus - E_L^\ominus$$

cell reaction:



is spontaneous as written

$$\text{if } E^\ominus > 0, \quad \therefore E_R^\ominus > E_L^\ominus$$

$\because \text{Red}_L$  reduces  $\text{Ox}_R$ ,

$\therefore \text{Red}_L$  has a thermodynamic

tendency to reduce  $\text{Ox}_R$  if  $E_L^\ominus < E_R^\ominus$

example:



$$\because E_{\text{Zn}^{2+}/\text{Zn}}^\ominus = -0.76\text{V}$$

$$< E_{\text{Cu}^{2+}/\text{Cu}}^\ominus = 0.340\text{V}$$

zinc has tendency to reduce  
 $\text{Cu}^{2+}$  ions in aqueous solution

**low reduces high**

## The electrochemical series:

*Least strongly reducing*

Gold  
Platinum  
Silver  
Mercury  
Copper  
(Hydrogen)  
Lead  
Tin  
Nickel  
Iron  
Zinc  
Chromium  
Aluminium  
Magnesium  
Sodium  
Calcium  
Potassium  
*Most strongly reducing*

## Determination of activity coeffs:

$\gamma_{\pm}$  is determined by measuring cell emf with ions at concentration of interest.

e.g., mean activity coefficient of the ions in HCl of molality  $b$  in Harned cell

$$\ln \gamma_{\pm} = \frac{E^{\ominus} - E}{2RT/F} - \ln b$$

## Determination of equilibrium consts:

standard emf

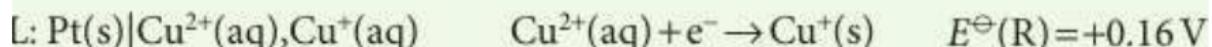
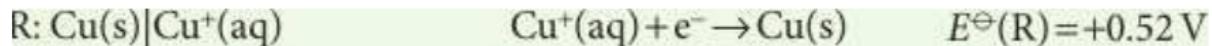
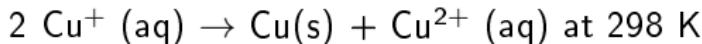
= standard potential of right-hand electrode  
– standard potential of left-hand electrode

$$E^\ominus = E^\ominus(\text{right}) - E^\ominus(\text{left})$$

if  $E^\ominus > 0$ , then corresponding cell reaction has  $K > 1$

Find K.

Disproportionation reaction : a species is both oxidized and reduced

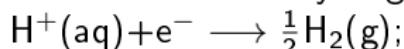


$$E^\ominus = +0.52V - 0.16V = +0.36V$$

$$\Rightarrow \ln K = \frac{0.36V}{0.025693V} = 1.2 \times 10^6$$

## Measurement of pH

Half-reaction of a hydrogen electrode:

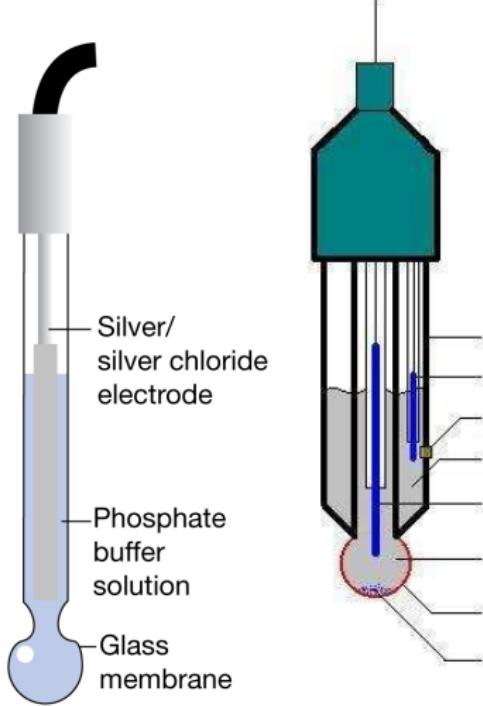


$$E(\text{H}^+/\text{H}_2) = \frac{RT}{F} \ln a_{\text{H}^+} = -\frac{RT \ln 10}{F} \text{pH} = -59.16 \times \text{pH} \text{ in mV.}$$

Dip a hydrogen electrode and a standard electrode like calomel in a solution and measure the emf

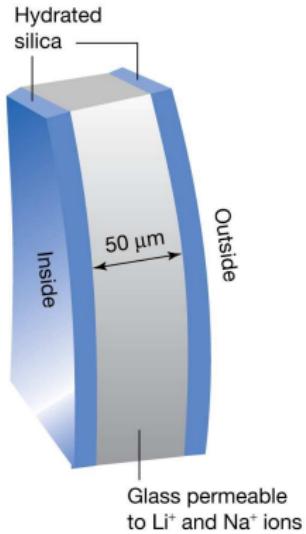
$$\text{Then } \text{pH} = -\frac{E + E(\text{cal})}{59.16}$$

SCE :  $\text{Cl}^-(4\text{M})|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg}(\text{l})|\text{Pt}$ ;  $E^\ominus = 0.27\text{V}$



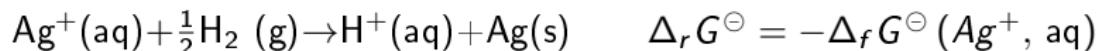
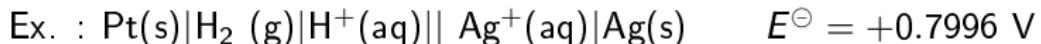
1. sensing part of electrode, bulb made from specific glass
2. internal electrode, usually silver chloride or calomel electrode
3. internal solution, usually  $\text{pH}=7$  buffered solution of 0.1 mol/L KCl for pH electrodes
4. with silver chloride electrode, small amount of AgCl can precipitate inside glass electrode
5. reference electrode, usually same as 2
6. reference internal solution, usually 0.1 mol/L KCl
7. junction with studied solution, usually ceramics or capillary with asbestos or quartz fiber
8. body of electrode, made from non-conductive glass or plastics





## Determination of thermodynamic functions

$$\Delta_r G^\ominus = -\nu F E^\ominus$$



$\therefore \nu = 1, \Delta_f G^\ominus (\text{Ag}^+, \text{aq}) = -(-FE^\ominus) = 9.6485 \times 10^4 \times 0.7996 = 77.15 \text{ kJ mol}^{-1}$

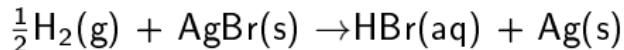
using  $\left(\frac{\partial G}{\partial T}\right)_p = -S, \quad \frac{dE^\ominus}{dT} = \frac{\Delta_r S^\ominus}{\nu F}$

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T \Delta_r S^\ominus = -\nu F \left( E^\ominus - T \frac{dE^\ominus}{dT} \right)$$

it is a non-calorimetric method for measuring  $\Delta_r H^\ominus$

with  $\Delta_f H^\ominus (\text{H}^+, \text{aq}) = 0$ , obtain  $\Delta_f H^\ominus$  of other ions in solution

Ex. : Pt(s)|H<sub>2</sub>(g)|HBr(aq)|AgBr(s)|Ag(s)



$$E^\ominus = 0.07131 - 4.99 \times 10^{-4}(T - 298) - 3.45 \times 10^{-6}(T - 298)^2$$

task:  $\Delta_r G^\ominus = ?$ ;  $\Delta_r H^\ominus = ?$   $\Delta_r S^\ominus = ?$

$$\Delta_r G^\ominus = -\nu F E^\ominus = -6.88 \text{ kJ mol}^{-1}$$

$$\text{At } 298\text{K, } \frac{dE^\ominus}{dT} = -4.99 \times 10^{-4} \text{ V K}^{-1}$$

$$\Delta_r S^\ominus = \nu F \frac{dE^\ominus}{dT} = -48.2 \text{ JK}^{-1}\text{mol}^{-1}; \quad \Delta_r H^\ominus = -21.2 \text{ kJ mol}^{-1}$$

difficulty: accurate measurement of small temperature coefficients

achievement: relating the apparently unrelated :

electrical measurements and thermal properties