



Lotka-Volterra (Prey-predator) mechanism:

universe : Fox (Y) and Rabbit (X) and grass (A) are the only components

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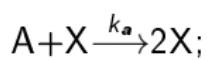
Various subprocesses are

- ▶ Rabbits consume grass to become more healthy and breed:
 $A + X \rightarrow 2X$,
- ▶ Foxes eat rabbits to be healthy and increase their population:
 $X + Y \rightarrow 2Y$
- ▶ Foxes die due to natural causes: $Y \rightarrow \Phi$
(Null denoting nonexistence- death or decay)

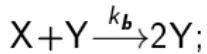
assume : amount of grass (A) is non-varying, constant.

These three “equations” constitute the model.

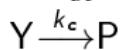




$$\frac{d[X]}{dt} = k_a[A][X] - k_b[X][Y];$$



$$\frac{d[Y]}{dt} = k_b[X][Y] - k_c[Y];$$



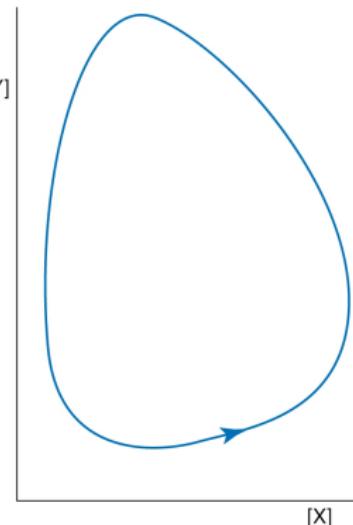
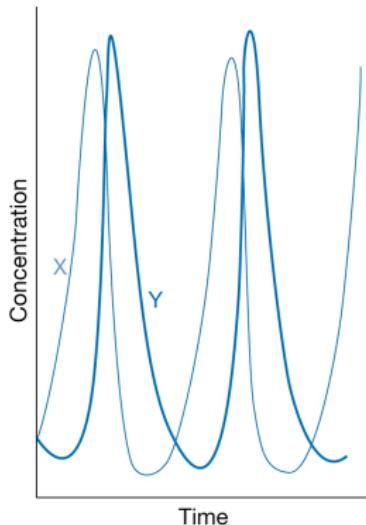
it is told to use these values.

$$\text{use } [X] = \frac{k_c}{k_b}x; [Y] = \frac{k_c}{k_b}y;$$

$$[A] = \frac{k_c}{k_a}y; t = \frac{1}{k_c}\tau$$

$$\frac{dx}{d\tau} = ax - xy$$

$$\frac{dy}{d\tau} = xy - y$$



For a general dynamical system, the solution for an initial state (X_0, Y_0) may be :
 $X(t) = X_0 + \Delta_x e^{\lambda t}$; and similar for Y
the behaviour depends on λ . Take $\Delta > 0$

real $\lambda > 0 \implies X(t)$ monotonic increasing function of t

real $\lambda < 0 \implies X(t)$ monotonic decreasing function of t

λ purely imaginary $\implies X(t)$ oscillatory function in t

$\lambda = p + iq$, where p and q are real \implies interesting scenarios where $p > 0$ or,
 $p < 0$ while $q \neq 0$.

$p > 0 \implies$ “spiraling out” phase portrait

$p < 0$ “spiraling in” behaviour. They spiral about a “limit point” or a “limit cycle”.

Finding steady states :

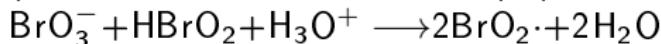
$$\frac{dx}{d\tau} = ax - xy = 0$$

$$\frac{dy}{d\tau} = xy - y = 0$$

$$\implies x = 1; \ y = a \text{ or, } x = y = 0$$

Belousov-Zhabotinski reaction

(KBrO₃, malonic acid, cerium (IV) salt in acidic solution):

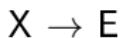
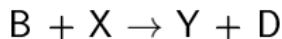
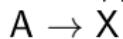


product HBrO₂ is a reactant in first step and provides a feedback mechanism that enhances rate of formation of HBrO₂

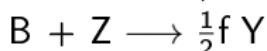
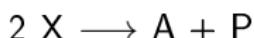
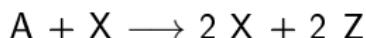
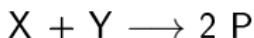
Examples of oscillatory systems:

1. Demand and supply [Economics]
- (2) process of sleep [Biology]
- (3) Belousov-Zhabotinskii reaction ("oscillatory reaction") [Chemistry]

<https://en.wikipedia.org/wiki/Brusselator>



<https://en.wikipedia.org/wiki/Oregonator>



Monika Sharma and Praveen Kumar,
Chemical Oscillations - Basic Principles and Examples,
Resonance, vol.11, #2, Feb 2006 p. 43-50
Chemical Oscillations - Mathematical Modelling,
Resonance, vol.11, #7, July 2006 p. 61-69



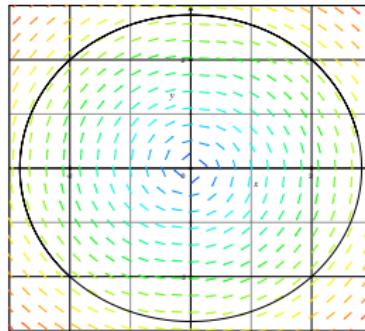
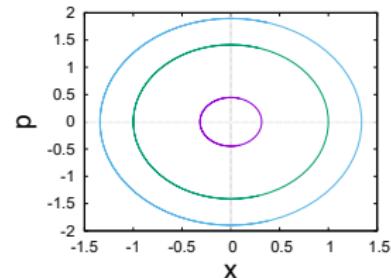
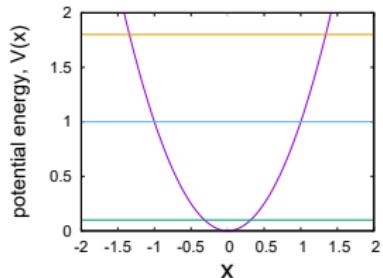
Motion of a particle attached to a spring

parabolic (simple harmonic) potential :

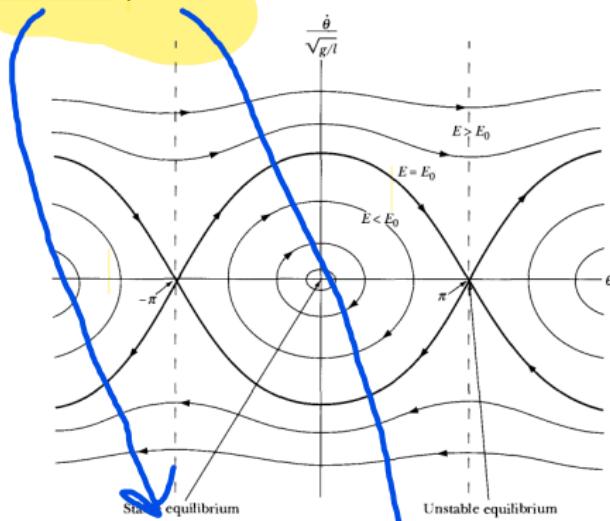
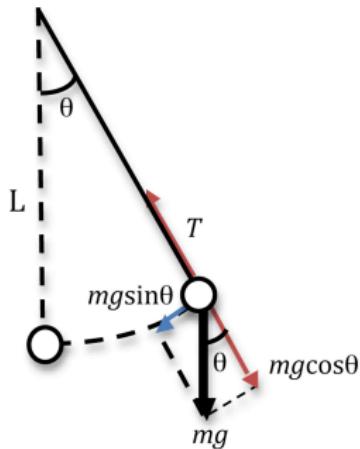
$$m\ddot{x} = -k(x - x_0)$$

$$\text{or, } \ddot{x} + \omega_o^2 x = 0 \quad (x_0 = 0; \omega_o^2 = \frac{k}{m})$$

phase plane portrait for : $\dot{x} = y$; $\dot{y} = -x$
 $y \equiv \text{momentum } p$; and constants are taken unity;



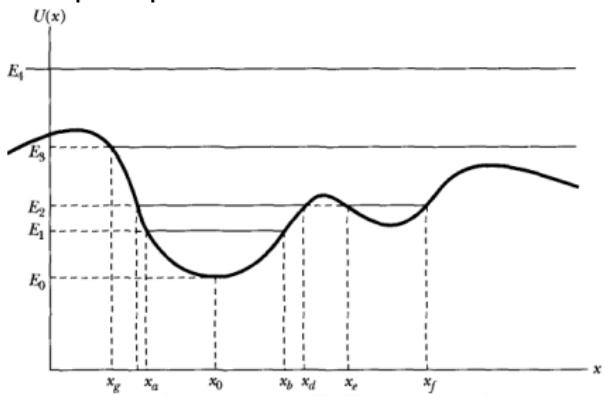
frictionless simple pendulum, $\ddot{\theta} = -\frac{g}{l} \sin \theta$, and its dynamics



$$\ddot{\theta} = \frac{d\dot{\theta}}{dt} = \frac{d\dot{\theta}}{d\theta} \frac{d\theta}{dt} = \frac{d}{d\theta} \left(\frac{1}{2} \dot{\theta}^2 \right) \text{ or, } \frac{d}{d\theta} \left(\frac{1}{2} \dot{\theta}^2 \right) + \omega^2 \sin \theta = 0; \quad \omega^2 = \frac{g}{l}$$

$$\text{integrating, } \frac{1}{2} \dot{\theta}^2 - \omega^2 \cos \theta = C \text{ or, } \dot{\theta} = \pm \sqrt{2(C + \omega^2 \cos \theta)}$$

complex potentials



$$\frac{1}{2}mv^2 \geq 0 \implies E \geq U$$

motion bounded for energies E_1 and E_2

For E_1 , motion **periodic** between
turning points x_a and x_b

For E_2 , motion periodic

- two possible regions :

$$x_c \leq x \leq x_d \text{ and } x_e \leq x \leq x_f$$



particle cannot "jump" from one "pocket" to the other

once in a pocket, it must remain there forever if energy = E_2

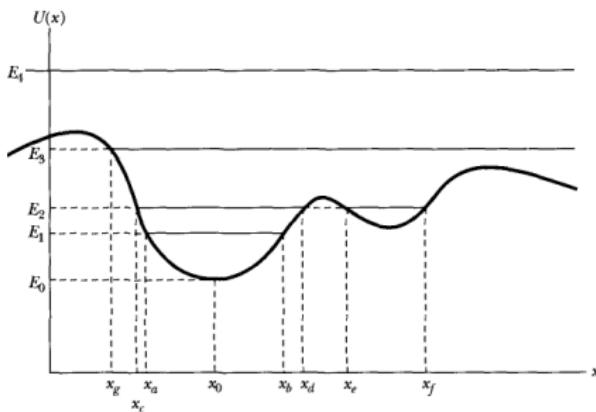
For E_0 , only one solution, $x = x_0$:
particle at rest with $T = 0$

For E_3 : particle comes in from infinity, stops and turns at $x = x_g$, and returns to infinity— like a tennis ball bouncing against a wall

For E_4 : motion unbounded and particle may be at any position

- speed varies as it depends on difference between E_4 and $U(x)$

If moving to right, it speeds up and slows down and continues to infinity



in region $x_a \leq x \leq x_b$

$$U(x) = -k(x-x_0)^2$$

particle with energy $\gtrsim E_0$ oscillates about equilibrium point $x = x_0$
particle placed at x_0 remains there

Equilibrium may be **stable**, **unstable**, or **neutral**

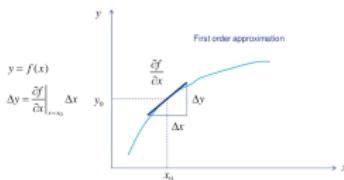
equilibrium at x_0 is **stable** because if particle is placed on either side of it, it would eventually return there

point at maximum between x_d and x_e is **unstable** equilibrium



Taylor series : a series expansion of a function $f(x)$ about a point $x = x_0$

$$f(x) = \underbrace{f(x_0) + f'(x_0)(x - x_0)}_{\text{unitary method}} + \frac{f''(x_0)}{2!}(x - x_0)^2 + \frac{f'''(x_0)}{3!}(x - x_0)^3 + \cdots + \frac{f^{(n)}(x_0)}{n!}(x - x_0)^n + \cdots$$



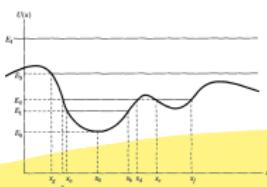
for arbitrary x_0 ,

$$f(x + a) = f(x) + f'(x)a + \frac{f''(x)}{2!}a^2 + \frac{f'''(x)}{3!}a^3 + \cdots + \frac{f^{(n)}(x)}{n!}a^n + \cdots$$

when $x_0 = 0$, it is called a Maclaurin series

$$f(x) = f(0) + f'(0)x + \frac{f''(0)}{2!}x^2 + \frac{f'''(0)}{3!}x^3 + \cdots + \frac{f^{(n)}(0)}{n!}x^n + \cdots$$

express potential $U(x)$ in a Taylor series about equilibrium point



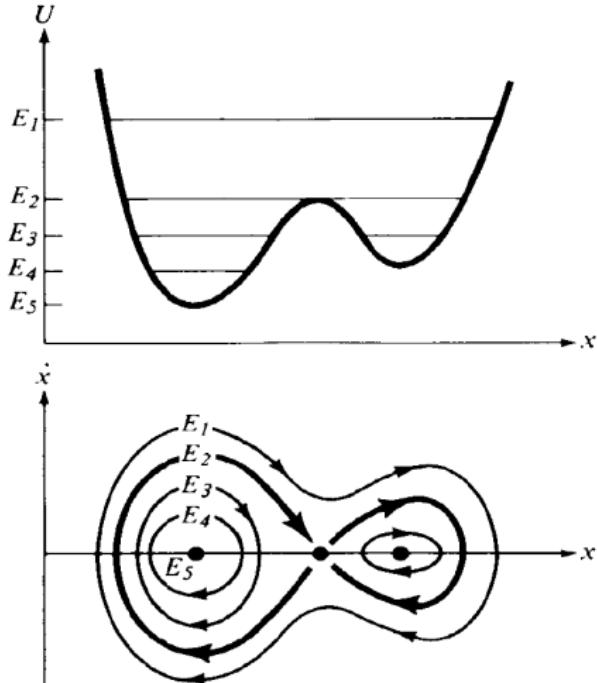
$$U(x) = U(x_0) + (x - x_0) \left. \frac{dU}{dx} \right|_{x_0} + \frac{(x - x_0)^2}{2!} \left. \frac{d^2 U}{dx^2} \right|_{x_0} + \frac{(x - x_0)^3}{3!} \left. \frac{d^3 U}{dx^3} \right|_{x_0} + \cdots$$

first order or linear term

$$\text{at equilibrium, } \left. \frac{dU}{dx} \right|_{x_0} = 0, \quad \therefore U(x) = U(x_0) + \frac{(x - x_0)^2}{2!} \left. \frac{d^2 U}{dx^2} \right|_{x_0} + \cdots$$

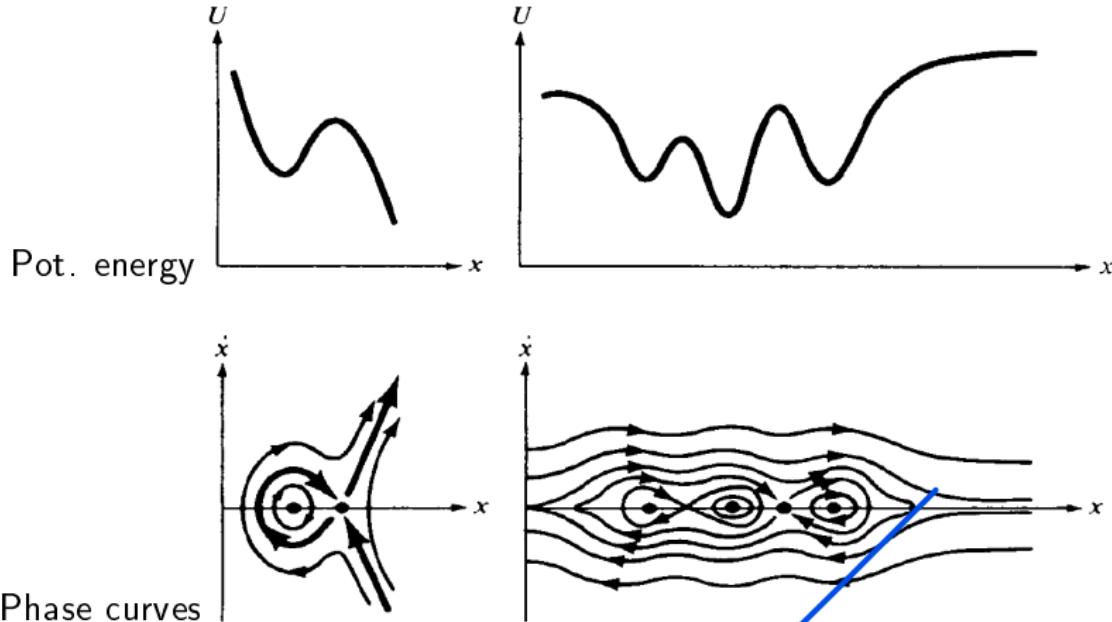
$\left. \frac{d^2 U}{dx^2} \right|_{x_0} > 0$: stable equilibrium; $\left. \frac{d^2 U}{dx^2} \right|_{x_0} < 0$: unstable equilibrium

Phase space description :



curve separating the two distinct dynamical behaviours is called **Separatrix**

- pay attention to the diagrams.



Nonlinear Oscillations and Chaos

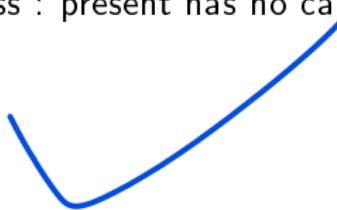
Laplace : if we know position and velocities of all particles in universe
then we know future for all time \Leftarrow determinism

knowing laws of nature is not enough. Much of nature seems to be chaotic

deterministic chaos (as opposed to randomness) : motion of a system whose time evolution has a sensitive dependence on initial conditions

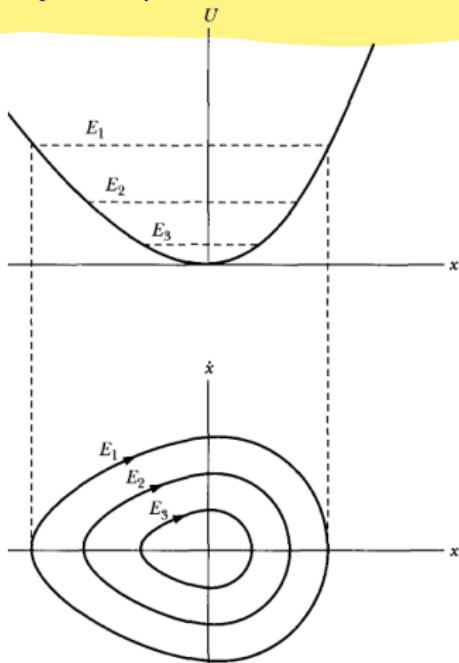
determinism : system develops from one moment to next, where present depends on past in a well-determined way through physical laws

random process : present has no causal connection to past (e.g., flipping of coin)



Phase Diagrams for Nonlinear Systems : $\dot{x} \propto \sqrt{E - U(x)}$

ex. : asymm. pot. - soft for $x < 0$ and hard for $x > 0$: no damping



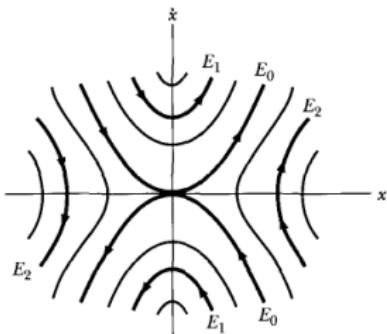
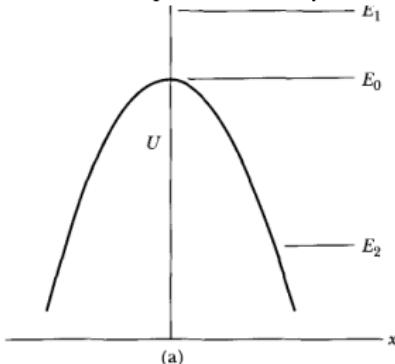
attractor : set of points (or point) in phase space toward which a system is 'attracted' when damping is present here, point $x = 0$ is an attractor

if total energy $E <$ height to which potential rises on either side of $x = 0$, then particle is 'trapped' in the potential well ($x_a < x < x_b$)

$x = 0$: stable equilibrium, $\frac{d^2 U}{dx^2} > 0$

small disturbance results in locally bounded motion

Inverted asymmetric potential



$x=0$ is unstable equilibrium : $\frac{d^2 U}{dx^2} < 0$

- If potential parabolic, $U(x) = -\frac{1}{2}kx^2$, then phase paths for energy E_0 are straight lines those corresponding to energies E_1 and E_2 are hyperbolas
- This is the limit to which phase paths approach if nonlinear term for force decreases in magnitude

look at E_0 , E_1 , E_2 very carefully.

van der Pol Equation : nonlinear oscillations in vacuum tube circuits

$$\ddot{x} + \mu(x^2 - a^2)\dot{x} + \omega_0^2 x = 0$$

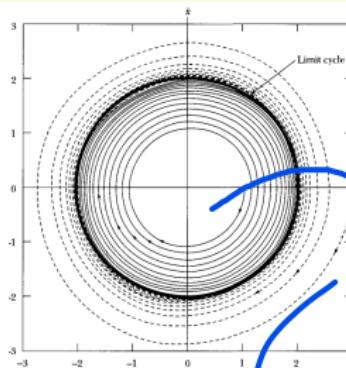
For $a = 1$ and $\omega_0 = 1$, we have $\ddot{x} + \mu(x^2 - 1)\dot{x} + x = 0$.

If $|x| > |a|$, then coefficient of \dot{x} is +ve and system is damped,
i.e., max. amplitude decreases in time

if $|x| < |a|$, then negative damping occurs, i.e., max. amplitude increases in time

$\therefore \exists$ soln. for which max. amplitude neither increases nor decreases with time

Such a curve in phase plane is called a limit cycle and is an attractor for the system

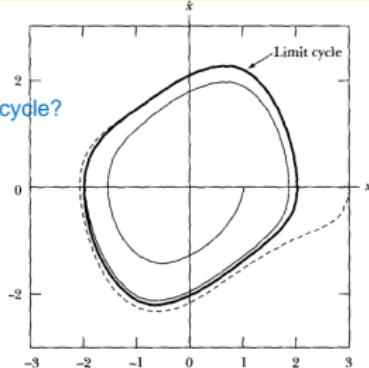


how to find limit cycle?

outward spiral inside limit cycle.

damping parameter $\mu = 0.05$

solution slowly approaches limit cycle



damping parameter $\mu = 0.5$

solution approaches limit cycle faster

inward spiral outside the limit cycle.

Phase paths outside the limit cycle spiral inward
and those inside the limit cycle spiral outward

limit cycle defines locally bounded **stable** motion

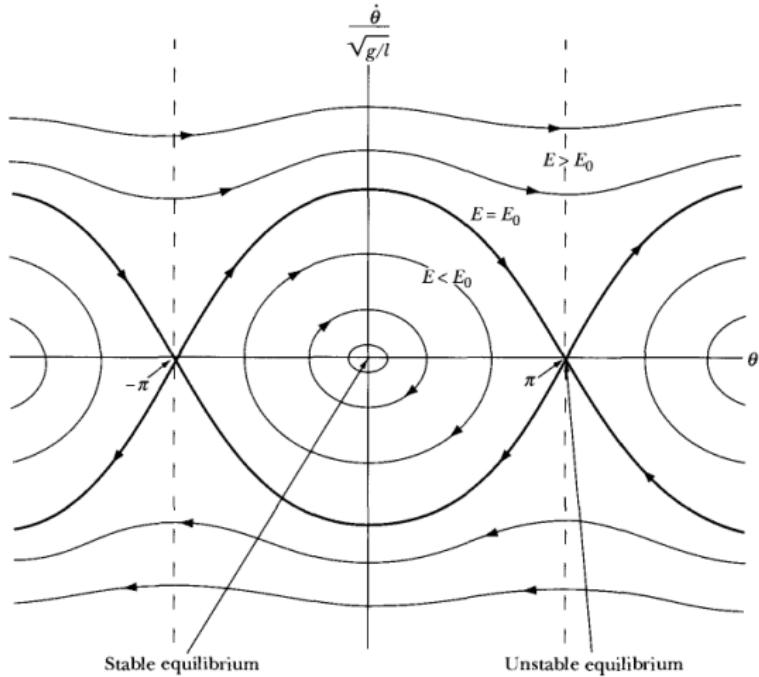
A system described by van der Pol's equation is **self-limiting**

i.e., once set into motion under conditions that lead to an increasing amplitude, it
is automatically prevented from growing without bound
system has this property whether the initial amplitude is greater or smaller than
critical (limiting) amplitude

For a small value of $\mu(0.05)$, x and \dot{x} are sinusoidal with time

for higher values of $\mu(0.5)$, sinusoidal shapes become skewed

Plane pendulum : phase diagram



map : use n to denote time sequence of a system
and x to denote a physical observable

describe progression of nonlinear system at a particular moment by investigating
how the $(n + 1)$ th state (or iterate) depends on the n th state

e.g., $x_{n+1} = (2x_n + 3)^2$

The relationship, $x_{n+1} = f(x_n)$, is called a map

Logistic equation : $f(a, x) = ax(1 - x)$

Logistic map : $x_{n+1} = ax_n(1 - x_n)$

biological application : population growth of fish in a pond

iterations, or n , represent fish population,

x_1 = #fish in the pond at the beginning

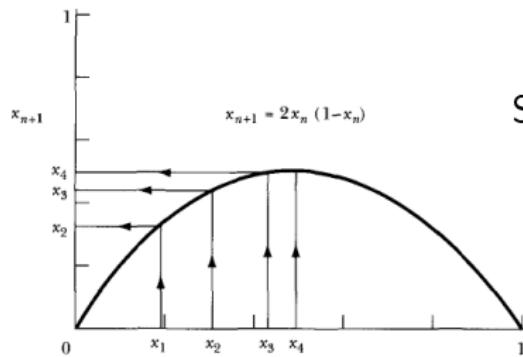
If x_1 is small, population grows rapidly in early years because of available resources

overpopulation may eventually deplete number of fish

population x_n is scaled so that its value fits in the interval $(0, 1)$

α is a model-dependent parameter representing average effects of environment

$$\alpha = 2$$



Start with initial value x_1 on horizontal axis,
move up until we intersect with the
$$curve x_{n+1} = 2x_n(1 - x_n)$$

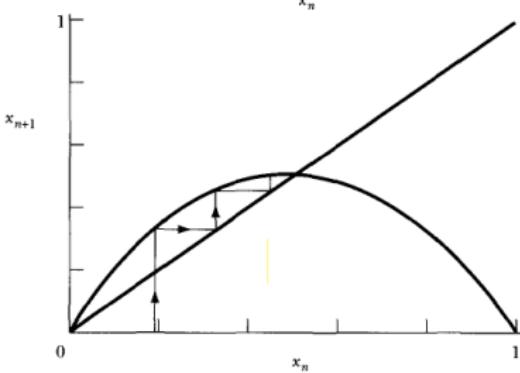
then move left where we find x_2 on the
vertical axis

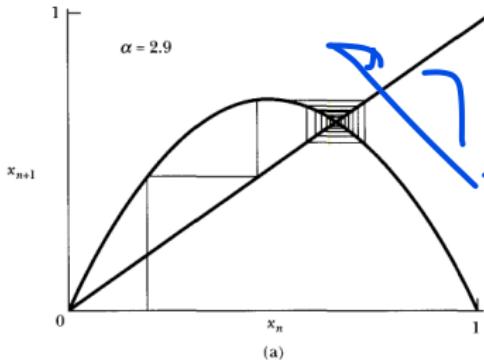
then start with x_2 on horizontal axis
and repeat the process to find x_3 on
vertical axis

after a few iterations, converge on $x=0.5$

fish population stabilizes at half its maximum

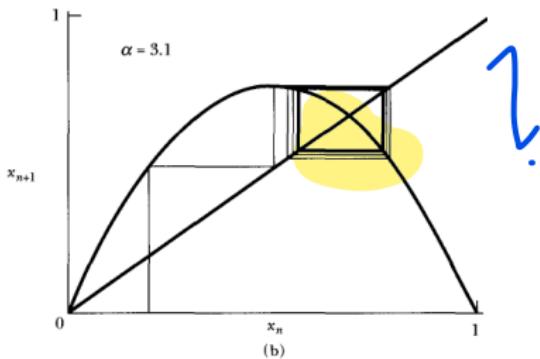
result is independent of initial value as
long as it is not 0 or 1





(a)

(a) $a \lesssim 3$ stable populations : solns. follow spiral path to final value



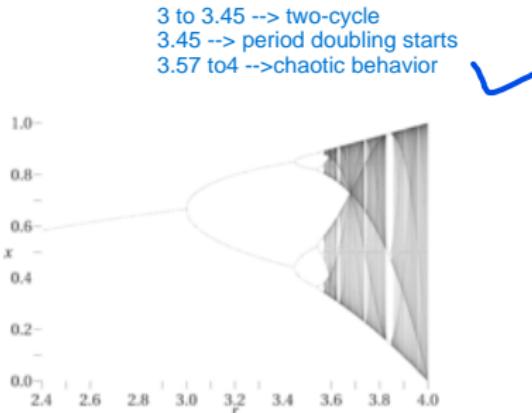
(b)

(b) $a \gtrsim 3$ multiple possible solutions depending on initial condition : solns. follow path converging to two points at which the square intersects the iteration line

Such a change in number of solutions to an equation, when a parameter such as α is varied, is called a **bifurcation**

In a bifurcation diagram, the value of the system's state variable "x" plotted on the y-axis represents the behavior to which the system converges at a particular parameter value "r."

bifurcation diagram :



Chaos occurs for many values of r between 3.57 and 4.0, but there are still windows of periodic motion, with an especially wide window around 3.84

interesting behavior occurs for $\alpha = 3.82831 \implies$ apparent periodic cycle of 3 units seems to occur for several periods, then it suddenly violently changes for some time, and then returns again to the 3-cycle

This intermittent behavior could prove devastating to a biological study operating over several years that suddenly turns chaotic without apparent reason

At $\alpha = 3.45$, two-cycle bifurcation evolves into a four cycle

bifurcation and period doubling continue up to an infinite number of cycles near $\alpha = 3.57$

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 $\leftarrow\leftarrow$ { physically meaningful B.C.
inter-particle interactions



molecular dynamics : monte carlo simulations



equilibrium properties

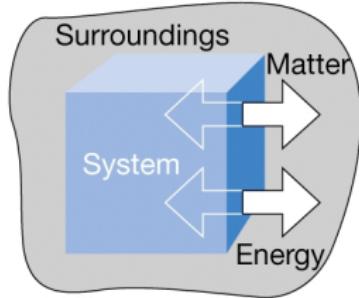
Thermodynamic space

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

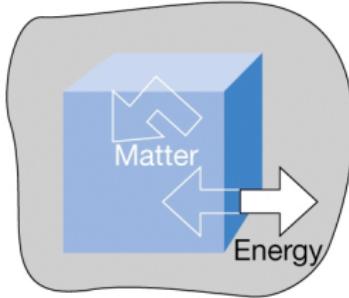
physical state of a sample of a substance, its physical condition
is defined by its physical properties

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

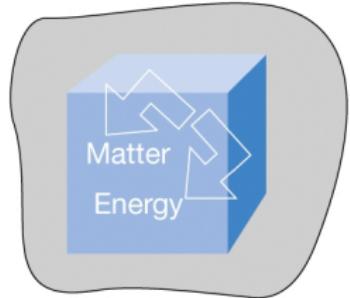
Thermodynamic systems :



(a) Open



(b) Closed



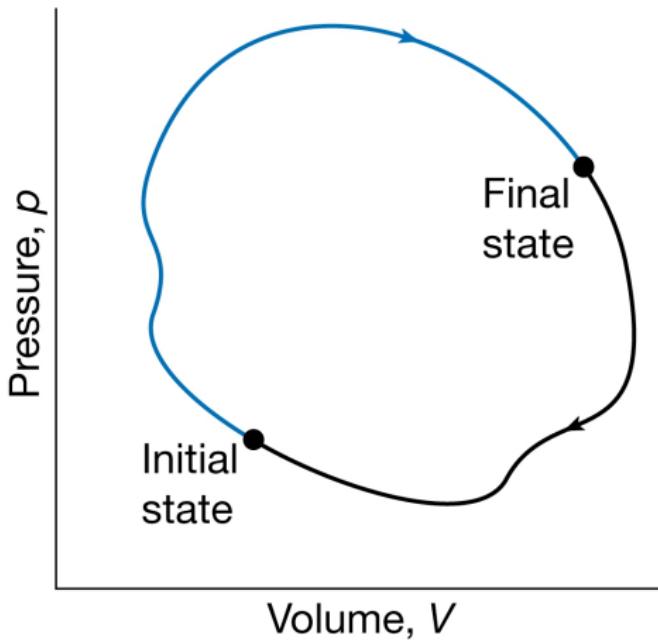
(c) Isolated

Variables, functions, processes, paths,

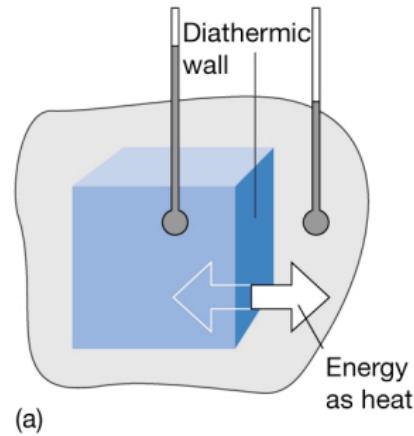
state functions

path functions

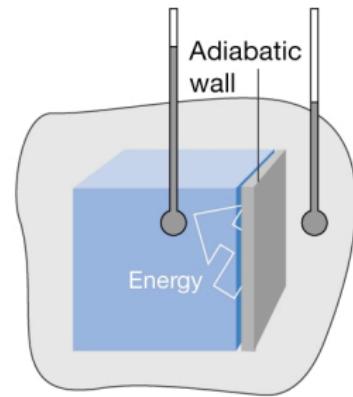
cyclic process : $\oint dX = 0$, if X is a state function



Heat flow - Diathermal and adiabatic walls :

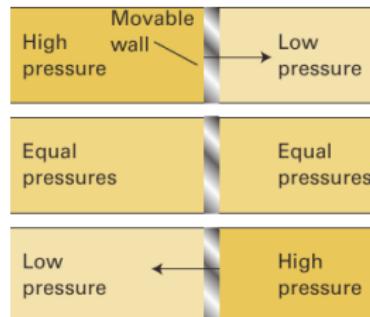


(a)



(b)

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

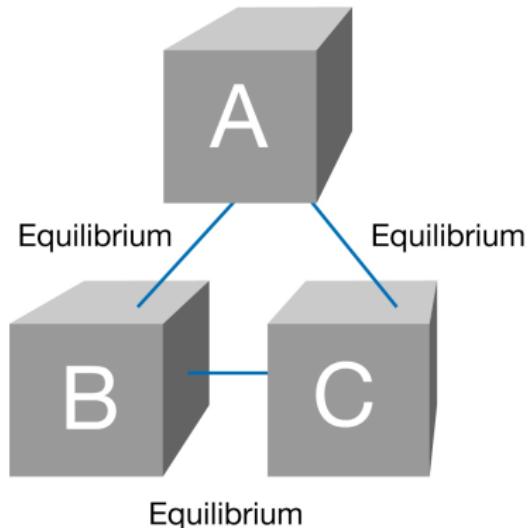


Mass flow : **Permeable** and **impermeable** walls

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 (≈ 1 atm) is already low enough for most gases to behave almost perfectly

 relates volume and pressure

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



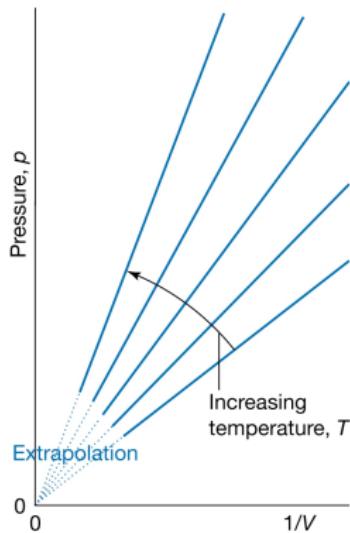
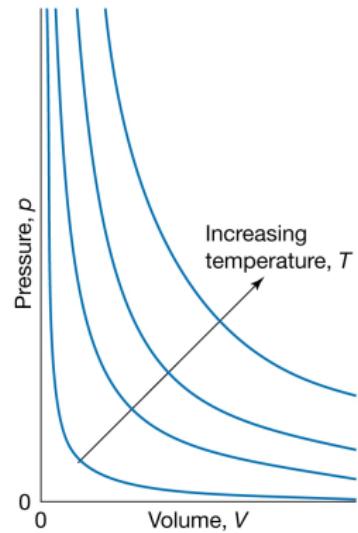
relates temperature and pressure

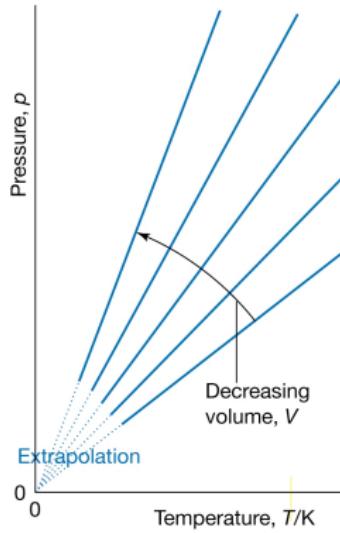
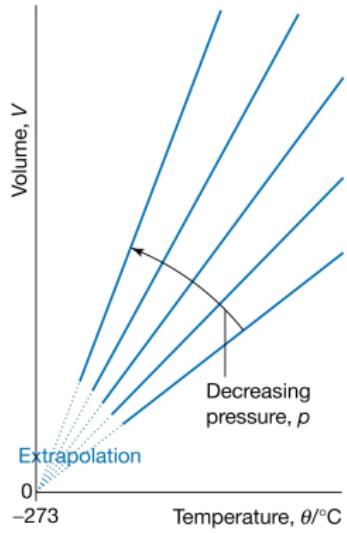
molecular explanation of Charles's law :

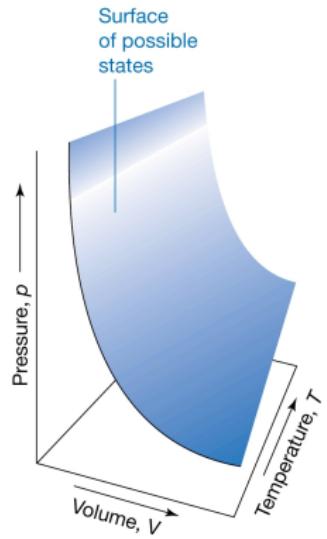
raising temperature of a gas increases average speed of molecules

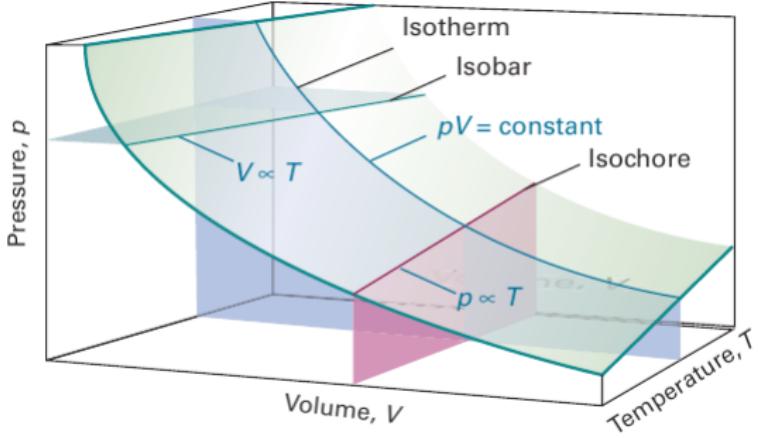
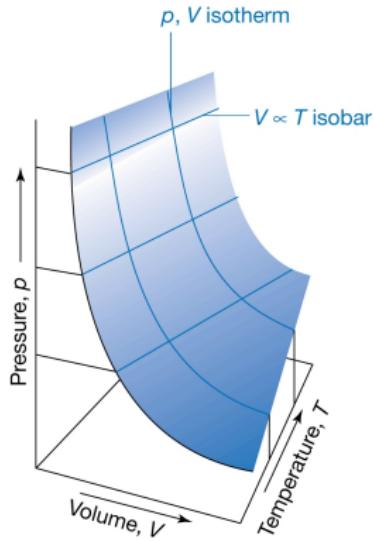
molecules collide with the walls more frequently and with greater impact
⇒ they exert a greater pressure on the walls of the container

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

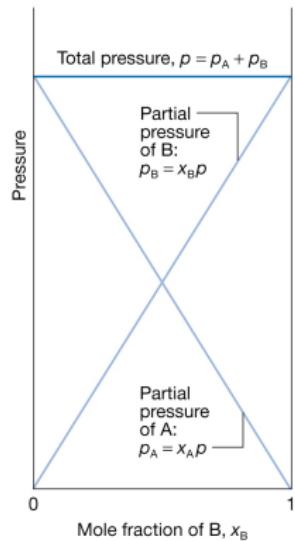




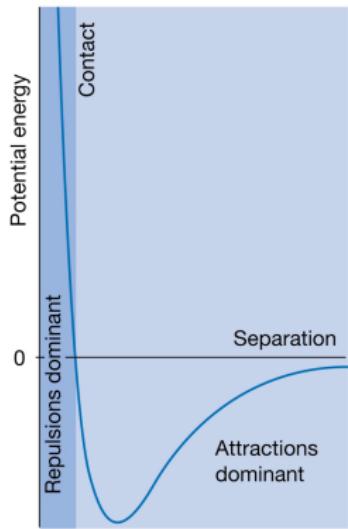




mixtures - partial pressures :



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 the molecules implies that instead of moving in a volume V they are restricted to a smaller volume $V - nb$
- ▶ where $nb \approx$ total volume taken up by molecules
- ▶ \Rightarrow perfect gas law should be replaced by $p = \frac{nRT}{V-nb}$ when repulsions are significant
- ▶ 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 = $4V_{\text{molecule}}$ $\therefore b = 4V_{\text{molecule}} \cdot N_A$

solved problem : Estimate the molar volume of CO₂ at 500 K and 100 atm by treating it as a van der Waals gas , given

$$\begin{cases} a = 3.592 \text{ dm}^6 \text{atmmol}^{-2} \\ b = 4.257 \times 10^{-2} \text{dm}^3 \text{mol}^{-1} \end{cases}$$

$$(V_m - b) V_m^2 p = R T V_m^2 - (V_m - b) a$$

get cubic eqn. for V_m :

$$x^3 - \left(b + \frac{RT}{p}\right)x^2 + \left(\frac{a}{p}\right)x - \frac{ab}{p} = 0$$

or, x = 0.366 dm³mol⁻¹ (perfect gas : 0.41dm³mol⁻¹)

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

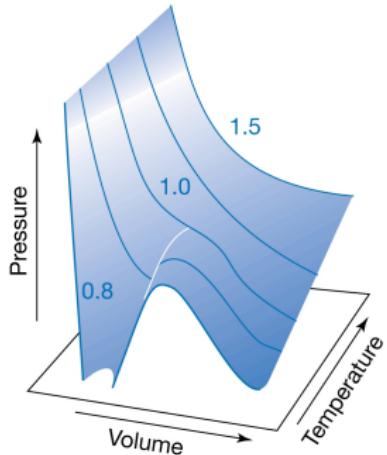
too optimistic to expect a single, simple expression to be equation of state of all substances

advantage :

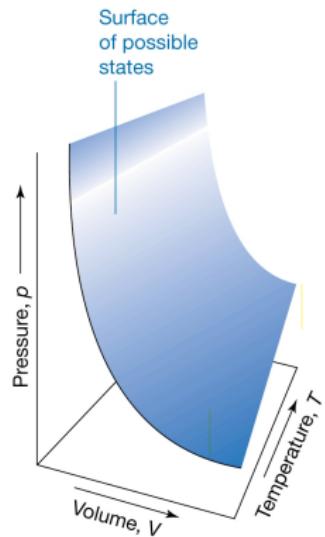
- ▶ analytical equation
- ▶ allows us to draw some general conclusions about real gases

Isotherms reflect consequences of interactions

van der Waals



perfect gas

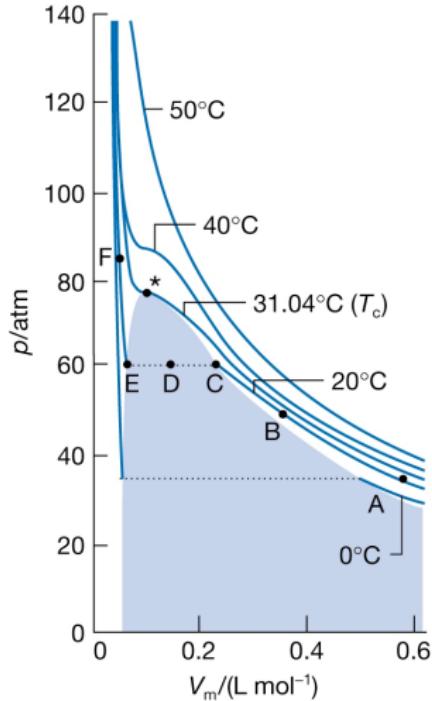


At low pressures - large volume : molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly

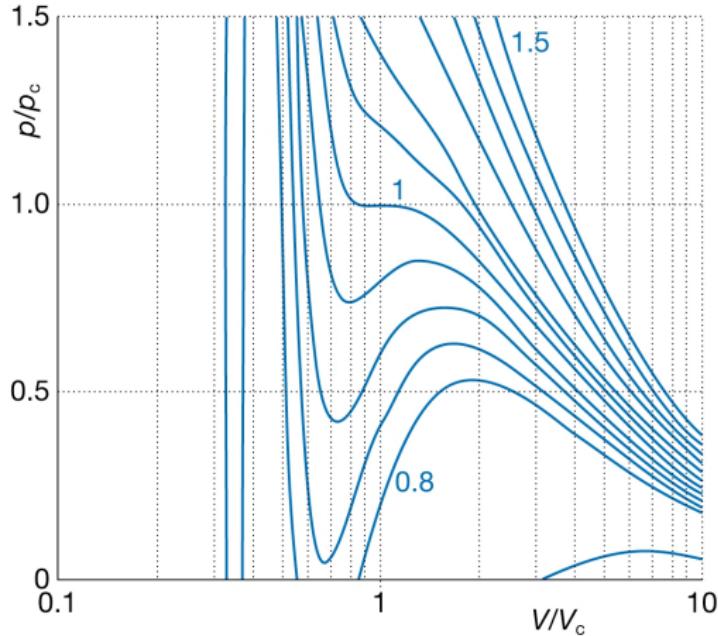
At moderate pressures, average separation of molecules is only a few molecular diameters
attractive forces dominate
gas is more compressible than a perfect gas because the forces help to draw the molecules together

At high pressures, average separation of molecules is small, repulsive forces dominate and the gas is less compressible because now the forces help to drive the molecules apart

experimental data for CO₂

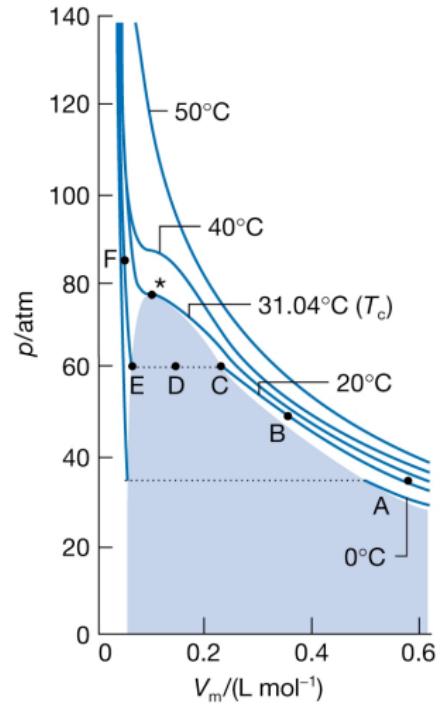


van der Waals isotherms at several values of $\frac{T}{T_c}$

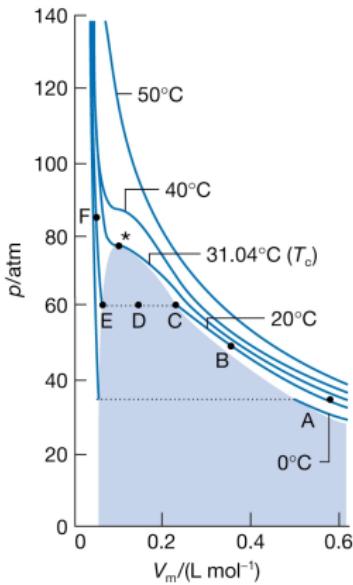


critical isotherm is for $\frac{T}{T_c} = 1$

experimental data for CO₂



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



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

At C (≈ 60 atm for CO_2), all similarity to perfect behaviour is lost, for suddenly the 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

pressure on line CDE, when both liquid and vapour are present in equilibrium, is the vapour pressure of liquid at the temperature of the experiment

At E, sample is entirely liquid and the piston rests on its 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 the presence of 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

The single phase that fills the entire volume when $T > T_c$ may be much denser than typical gas : supercritical fluid

features of the van der Waals eqn

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

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

(2) Liquids and gases coexist when cohesive and dispersing effects are in balance

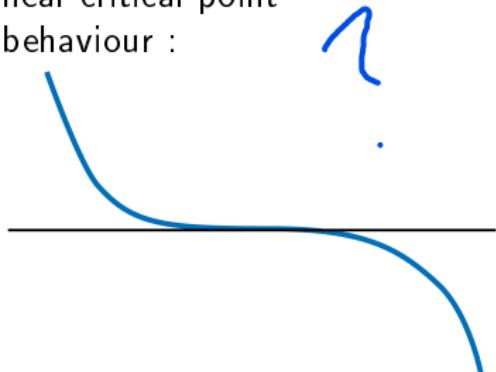
van der Waals loops occur when both terms have similar magnitude

- ▶ 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 :



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

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

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

critical compression factor,

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

Below a critical temperature, T_C , van der Waals isotherms show oscillations

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 the molecules are non-spherical or polar

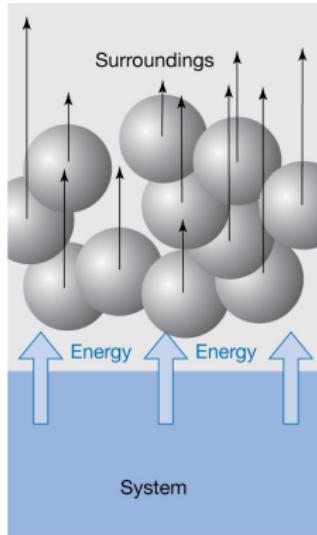
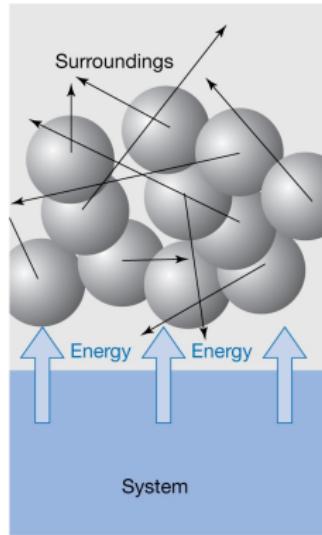
The principle of corresponding states :

Equation	Reduced form*	Critical constants			
		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	$p = \frac{nRT}{V} \left\{ 1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2} + \dots \right\}$				

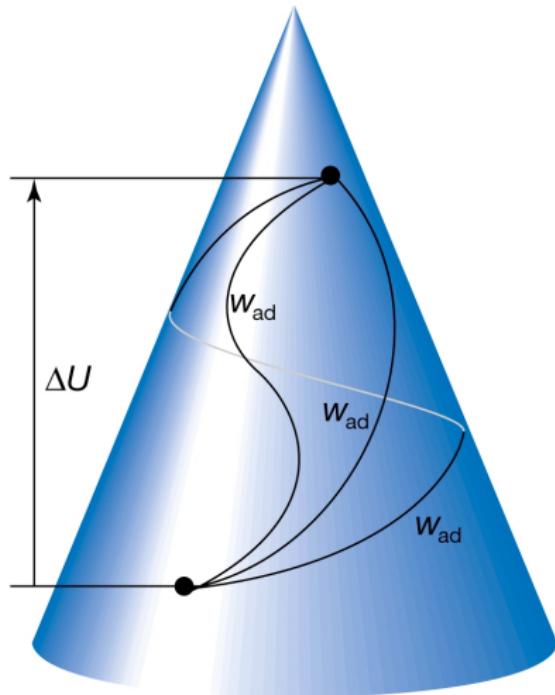
critical constants : typical values

gas	p_c atm	V_c cm^3	T_c K	$Z_c = \frac{\rho V_m}{RT}$	T_B K
Ar	48.0	75.3	150.7	0.292	411.5
CO_2	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O_2	50.14	78.0	154.8	0.308	405.9

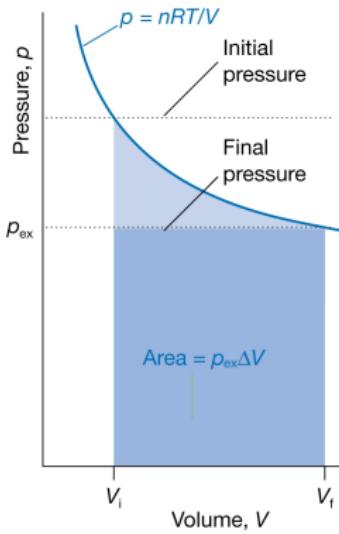
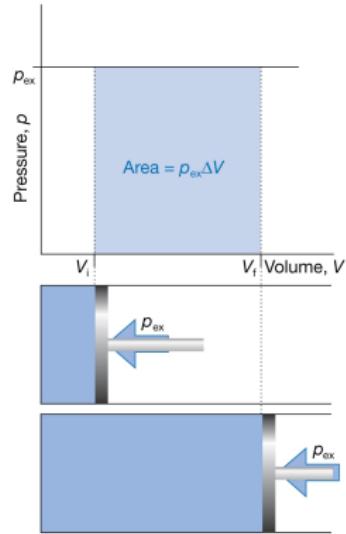
Heat and work :



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



Calculating work :



Heat :

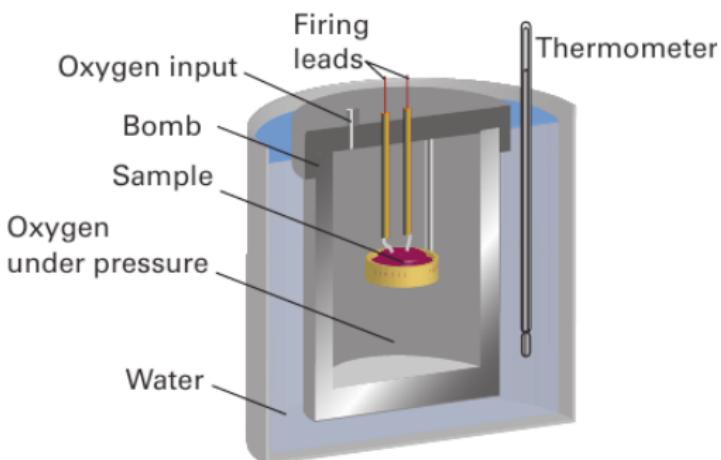
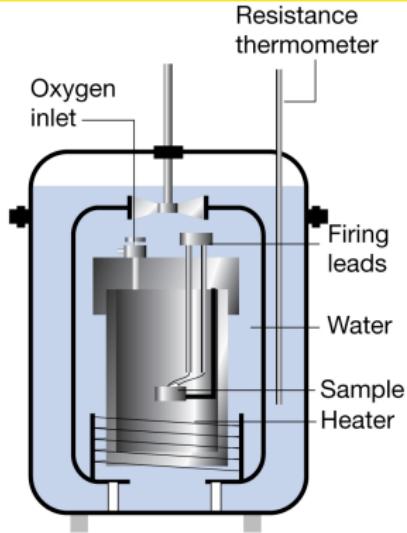
$$dU = dq + dw_{\text{exp}} + dw_{\text{e}}$$

↑ ↑ ↑ ↑
upper case lower case expansion extra

$$dU = dq_V$$

Calorimetry

- Constant volume bomb calorimeter : measurement of q_V



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

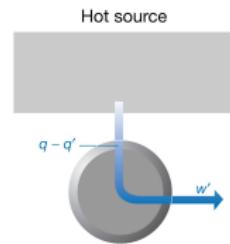
To ensure adiabaticity, calorimeter is immersed in a water bath with temperature continuously readjusted to that of calorimeter at each stage of combustion

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

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

$$q = C\Delta T$$

Thermodynamic engine :



Type of work	dw	Comments	Units [†]
Expansion	$-p_{\text{ex}} dV$	p_{ex} is the external pressure dV is the change in volume	Pa m ³
Surface expansion	$\gamma d\sigma$	γ is the surface tension $d\sigma$ is the change in area	N m ⁻¹ m ²
Extension	$f dl$	f is the tension dl is the change in length	N m
Electrical	ϕdQ	ϕ 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

Suppose a gas is confined by a piston and external pressure, p_{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

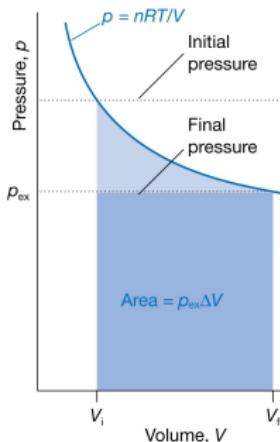
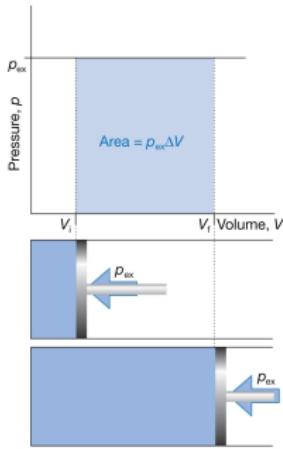
If the external pressure is increased infinitesimally, the gas contracts slightly

In either case the change is reversible in the thermodynamic sense

If, on the other hand, the external pressure differs measurably from the internal pressure, then changing p_{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 :

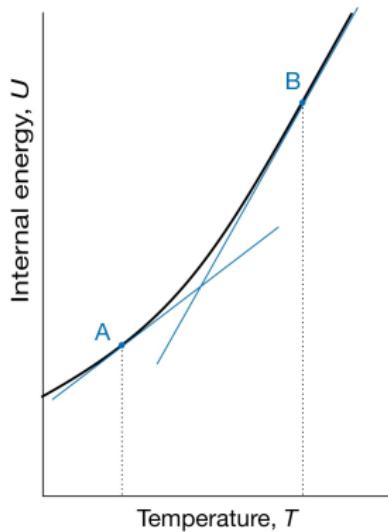


For a perfect gas, reversible work of expansion =

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

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

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

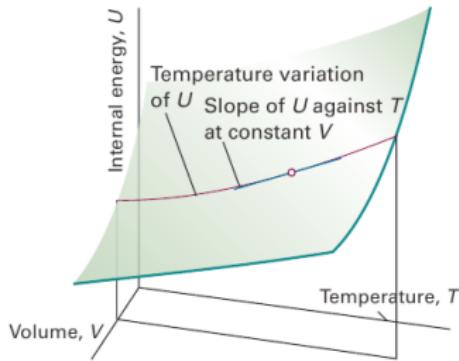


internal energy of a system
increases as temperature is raised
slope of tangent at any
temperature =heat capacity, C

in the Fig.,

C at A < C at B

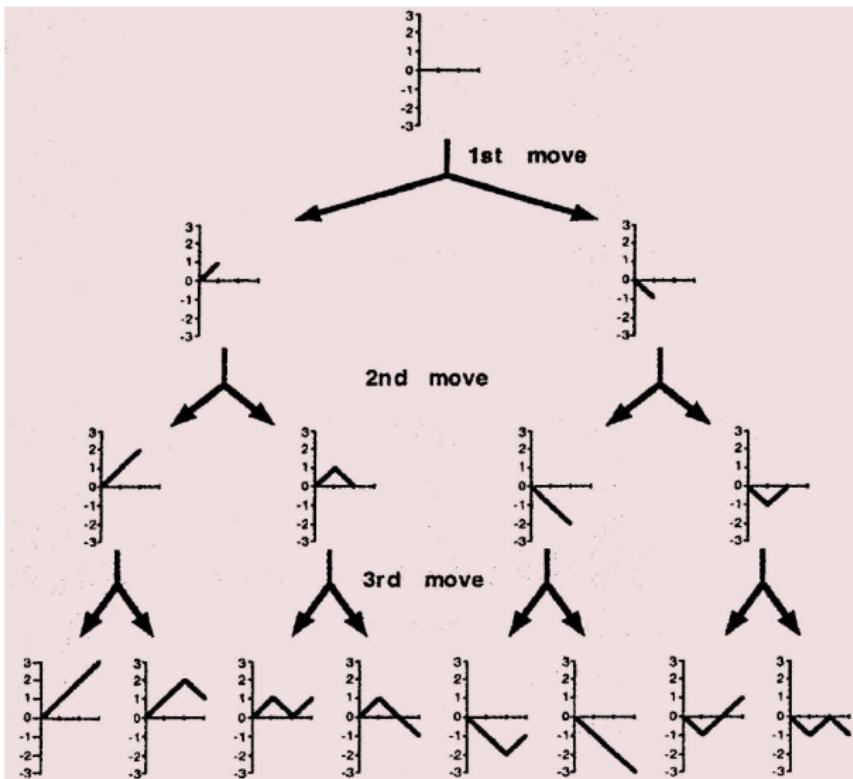
$$U(V, T)$$



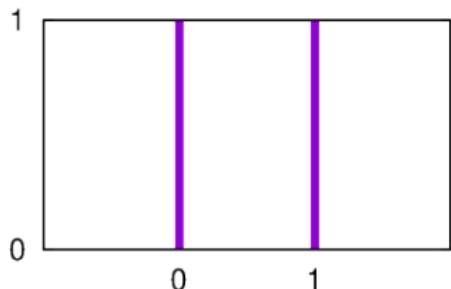
$$C_V = \left(\frac{dq}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$
$$\Rightarrow dU = C_V dT$$

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

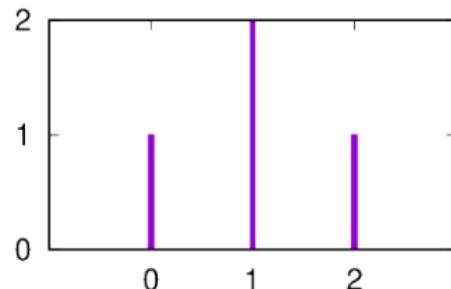
then $\Delta U = C_V \Delta T$



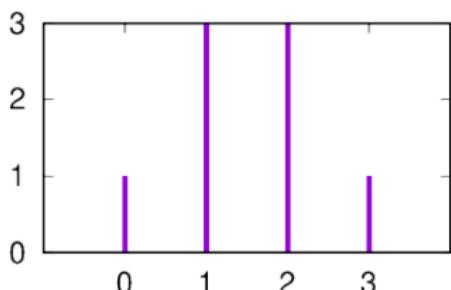
$N=1$



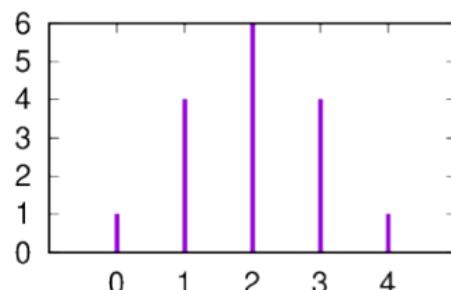
$N=2$



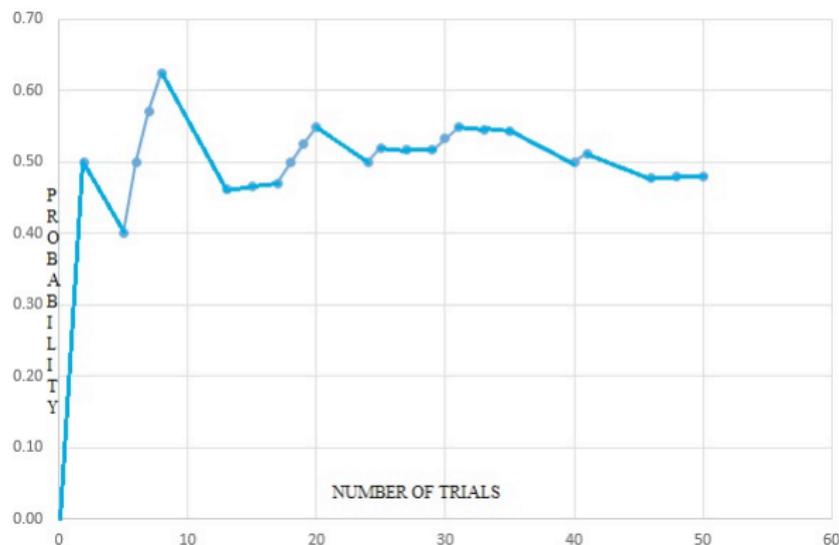
$N=3$

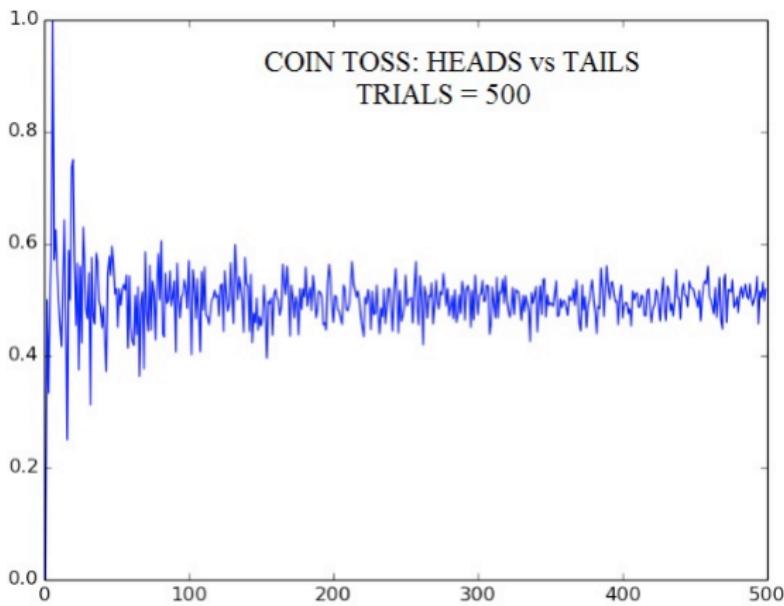


$N=4$



COIN TOSS HEADS VS TAILS RUNNING AVERAGE

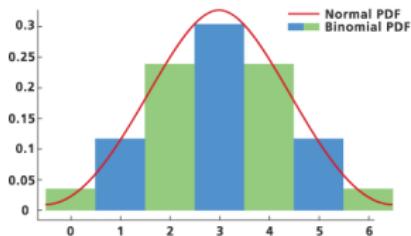




In the limit of large numbers :
Binomial distribution

$$\xrightarrow{N \rightarrow \infty} \text{Gaussian}$$

where one deals with very many identical particles $\mathcal{O}(10^{23})$, statistical arguments become particularly effective



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

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

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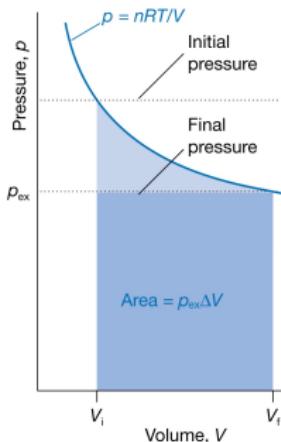
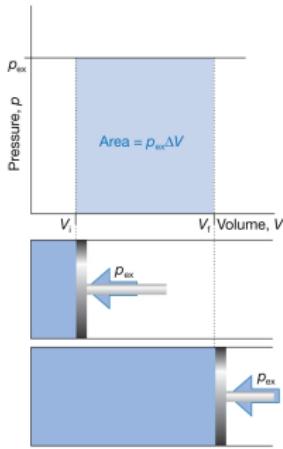
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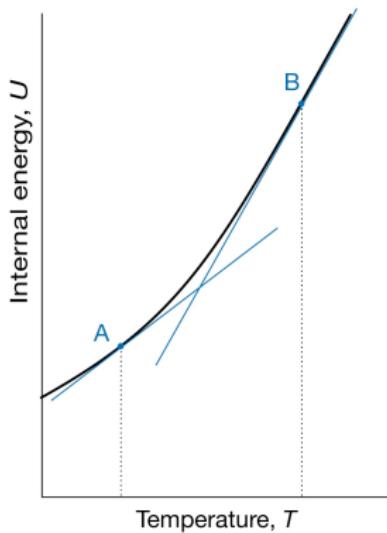


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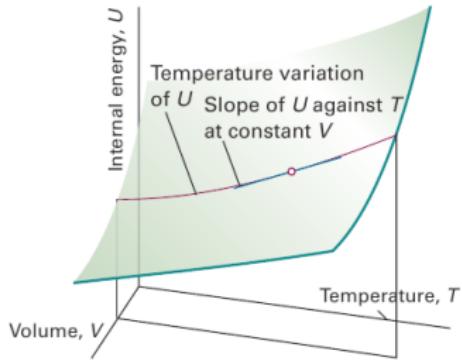


internal energy of a system
increases as temperature is raised
slope of tangent at any
temperature =heat capacity, C

in the Fig.,

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

$U(V, T)$



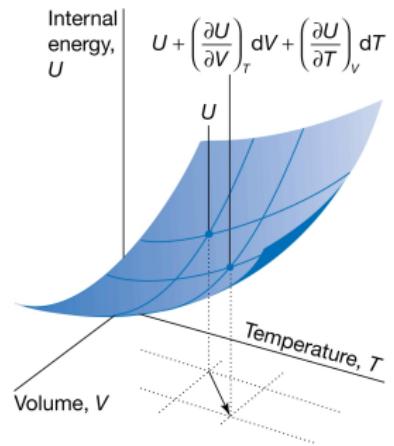
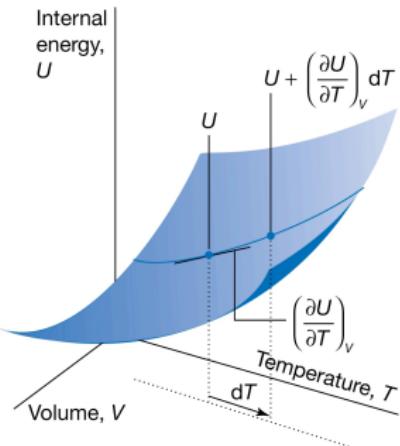
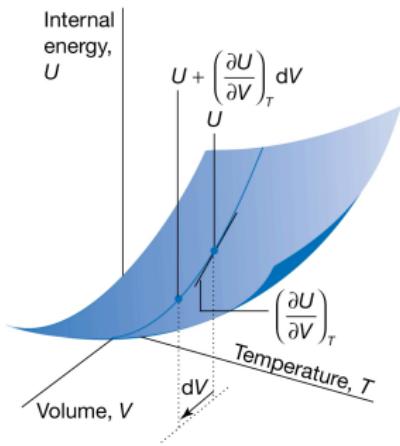
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If heat capacity is independent of temperature over range of temperatures of interest

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

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

\implies 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 :

e.g., for CO_2 , $U_m(T) = U_m(0) + \frac{3}{2}RT + RT + \dots$

Thermodynamic definition of a perfect gas :

no intermolecular interactions in a perfect gas

∴ distance between molecules has no effect on energy

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

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

Heat :

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

↑ ↑ ↗ ↑ ↑
upper case lower case expansion extra

generally, we consider only w_{exp} , $dU = dq_V$

Heat and work are equivalent 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

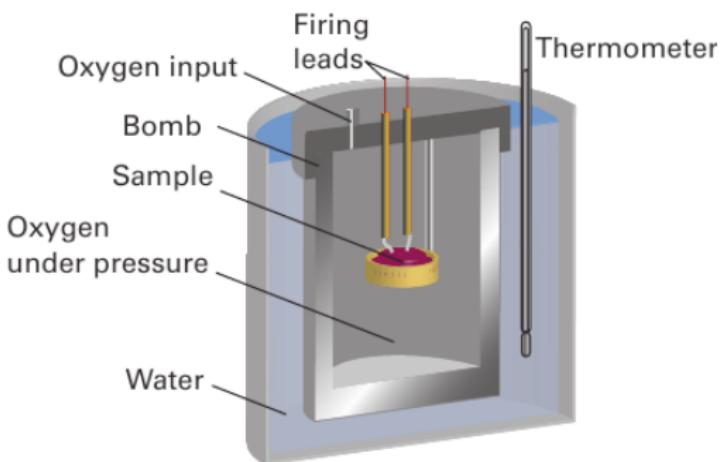
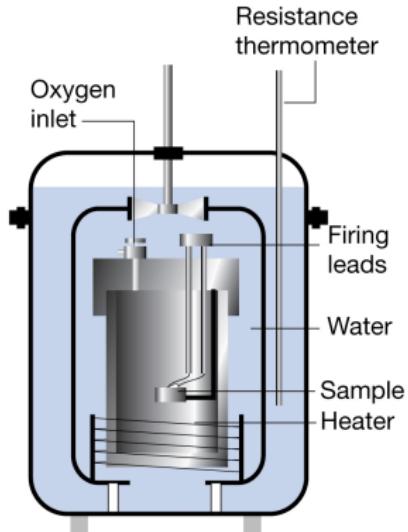
First Law : internal energy of an isolated system is constant

$$\Delta U = q + w$$

$$dU = dq + dw$$

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

measure $\Delta T \implies q_v$ and hence ΔU

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

$$q = C\Delta T$$

Enthalpy

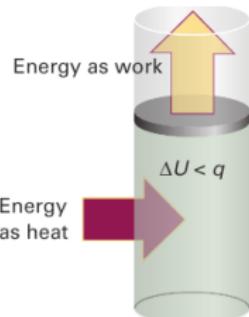
$\Delta U \neq \text{energy transferred as heat}$
when system is free to change its volume

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

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

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



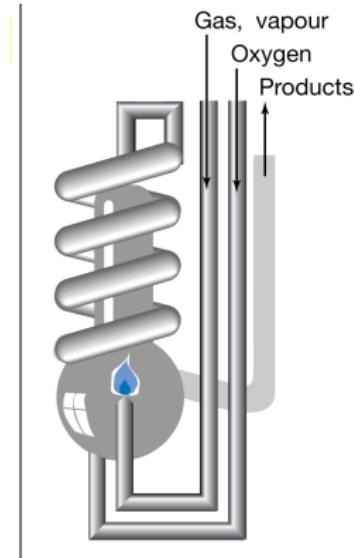
work done at constant pressure

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

$$\underbrace{H_f - H_i}_{f} \quad \underbrace{q_p}_{i}$$
$$\int_i^f dH = \int_i^f dq_p$$

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.

solved problem :

when 1.0 mol 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 g cm^{-3} and 2.93 g cm^{-3} respectively

- ▶
$$\begin{aligned}\Delta[H(\text{aragonite}) - H(\text{calcite})] &= [U + pV](\text{a}) - [U + pV](\text{c}) \\ &= \Delta U + p[V(\text{a}) - V(\text{c})] = \Delta U + p\Delta V\end{aligned}$$
- ▶ V_m for 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 ΔU)
- ▶ usually justifiable to ignore $\Delta H - \Delta U$ for condensed phases, except at very high pressures, when pV is no longer negligible

Ex. Calculate $\Delta H - \Delta U$ when 1.0 mol Sn(s, grey) of density 5.75 g cm⁻³ changes to Sn(s, white) of density 7.31 g cm⁻³ 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) = $\frac{20.65(\text{g})}{16.24(\text{w})} \text{ cm}^3$
- ▶ $\therefore p\Delta V = 10 \times 10^5 \text{ Pa} \times (16.24 - 20.65) \times 10^{-6} \text{ m}^3 = -4.4 \text{ J}$
- ▶ $\therefore \Delta H - \Delta U = -0.44 \text{ J}$ ($\approx 0.2\%$ of ΔU)

enthalpy of a perfect gas:

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

solved problem :

Water is heated to boiling under $p = 1.0$ atm. When an 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 ΔU_m and ΔH_m at the boiling point (373.15 K)

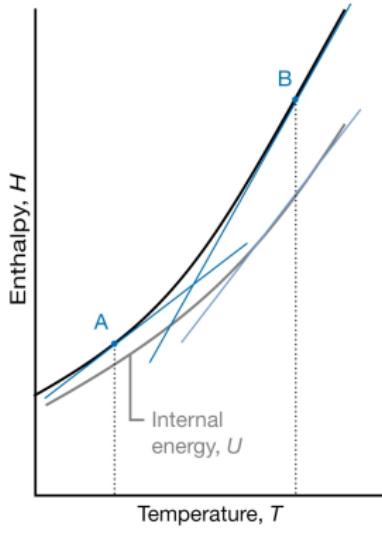
$$\underline{\Delta H = q_p = 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s}}$$

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

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

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

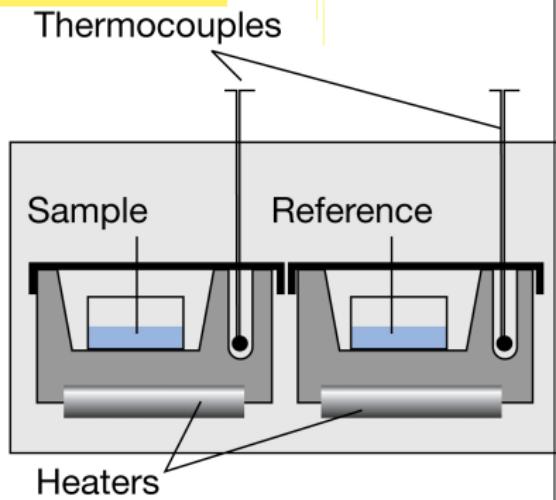
For gases, at a given temperature the slope is steeper than that of internal energy versus temperature

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

Differential scanning calorimeter (DSC) measures energy transferred as heat to or from a sample at constant pressure during a physical or chemical change
'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis

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

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



output : difference in power needed to maintain heat sinks at equal temperatures as temperature rises. $T(t) = T_0 + \alpha t$, where T_0 = initial temperature α = temperature scan rate (in Ks^{-1})

A computer controls electrical power to maintain same temperature in sample and reference compartments

sample temperature changes significantly relative to that of reference material
if transfer of energy as heat occurs in the sample during the 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 and, as a result, the sample must be heated more strongly than reference in order 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 chemical or physical process requires the transfer of $q_p + q_{p, ex}$

where $q_{p, ex}$ = excess energy transferred as heat, to attain same change in temperature of the sample

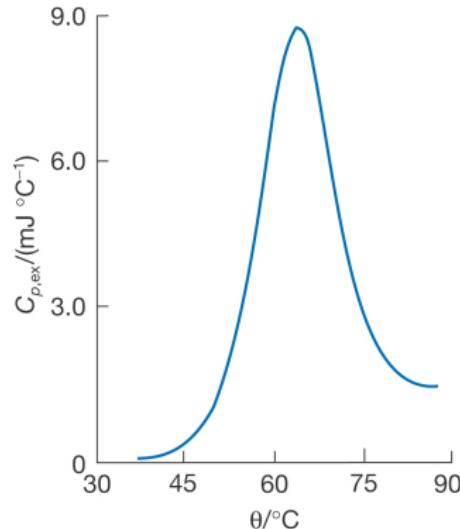
$q_{p, ex}$ = apparent change in heat capacity at constant pressure, C_p during temperature scan

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

thermogram for protein ubiquitin
at pH = 2.45

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

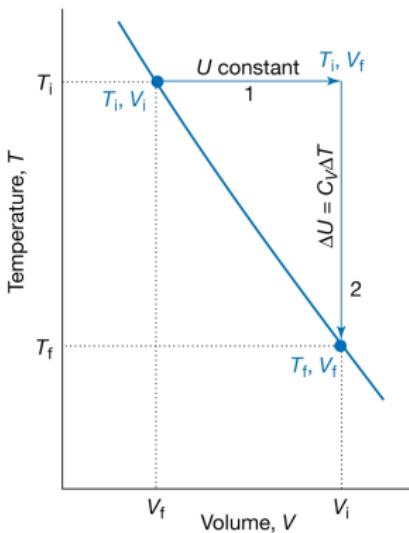


DSC trace - a thermogram : plot
of P_{ex} or C against T

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

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

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
 \therefore temperature falls

ΔU 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 ΔU 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, $C_v \frac{dT}{T} = -\frac{nRdV}{V}$

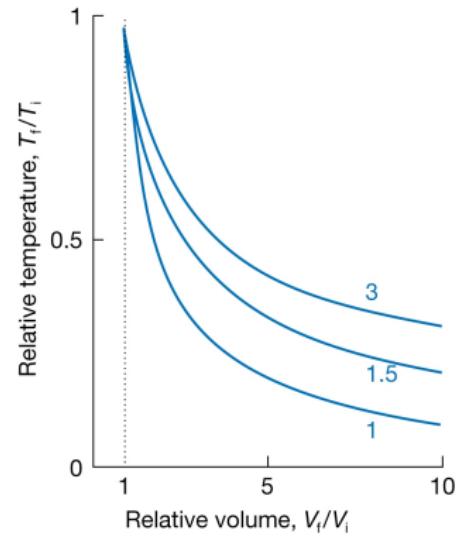
$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{nRdV}{V}$$

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

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

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

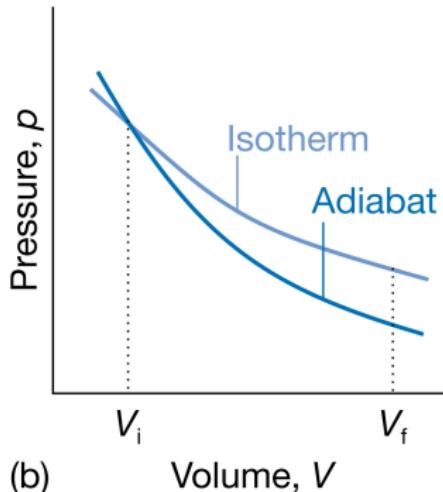
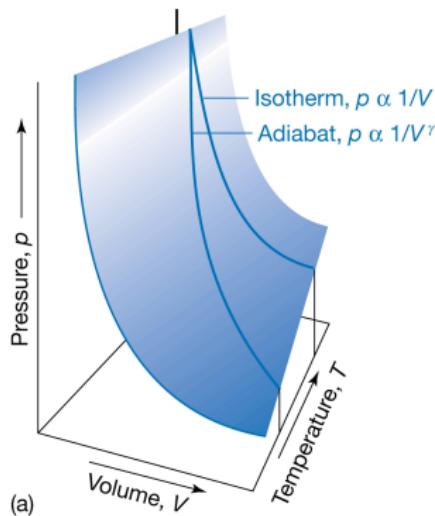
show: $pV^\gamma = \text{const}$



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 dm³ to 1.00 dm³

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

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 : ΔT is independent of the amount of gas but the work is not

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 ΔU or ΔH 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

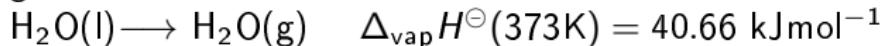
solid iron at 500 K is pure iron at 500 K and 1 bar

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

enthalpy of products_{standard states} — enthalpy of reactants_{standard states}

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



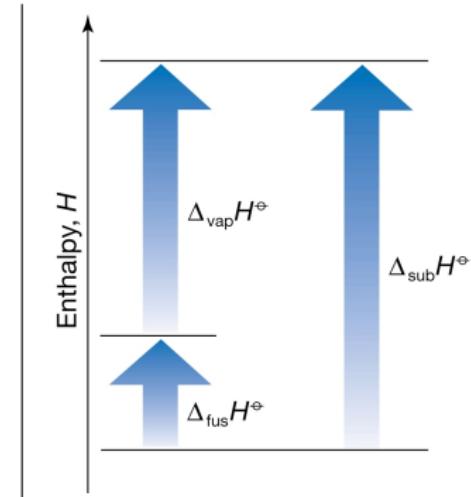
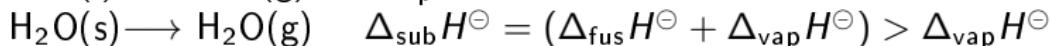
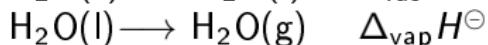
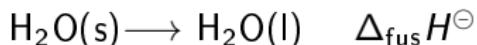
standard enthalpies may be reported for any temperature

enthalpy is a state function

ΔH is independent of path between the two states

same ΔH^\ominus for change brought about between same initial and final states

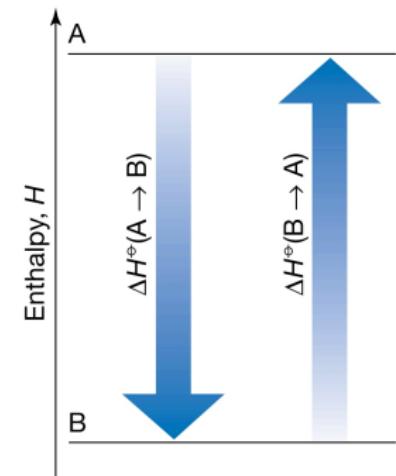
e.g., conversion of a solid to a vapour either as occurring by sublimation



ΔH^\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

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



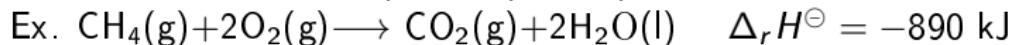
Transition	Process	Symbol
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{trs}H$
Fusion	s \rightarrow l	$\Delta_{fus}H$
Vaporization	l \rightarrow g	$\Delta_{vap}H$
Sublimation	s \rightarrow g	$\Delta_{sub}H$
Mixing	Pure \rightarrow mixture	$\Delta_{mix}H$
Solution	Solute \rightarrow solution	$\Delta_{sol}H$
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	Δ_rH
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	Δ_cH
Formation	Elements \rightarrow compound	Δ_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



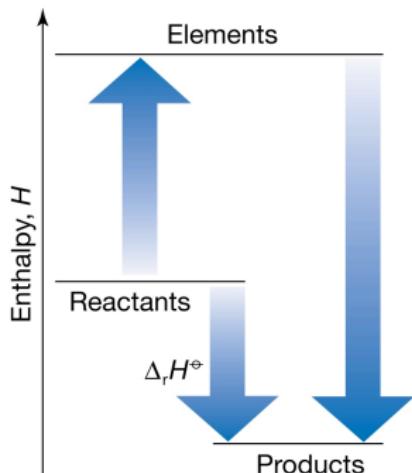
For the reaction $2\text{A} + \text{B} \rightarrow 3\text{C} + \text{D}$

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

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

standard enthalpy of combustion, $\Delta_C H^\ominus$ = standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid water if the compound contains C, H, and O, and to N_2 gas if N is also present

reaction enthalpy in terms of enthalpies of formation

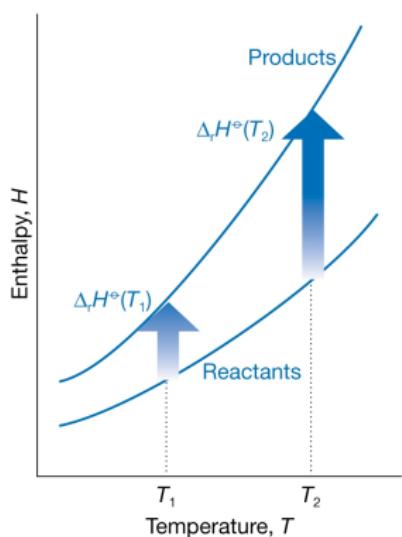


$$\Delta_r H^\ominus = \sum_{\text{products}} \nu \Delta_f H^\ominus - \sum_{\text{reactants}} \nu \Delta_f H^\ominus$$

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

$C_{p,m}(\text{O}_2,\text{g}) = 29.37 \text{ JK}^{-1} \text{ mol}^{-1}$

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

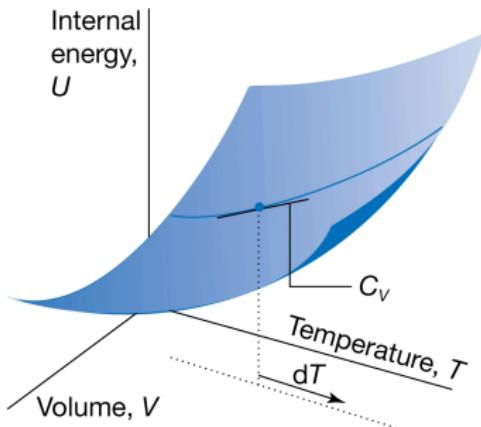
$$\therefore \Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + (T_2 - T_1)\Delta_r C_p^\ominus$$

$$= -241.82 - 75 \times 9.94 \times 10^{-3} = -242.6 \text{ kJ mol}^{-1}$$

Real systems :

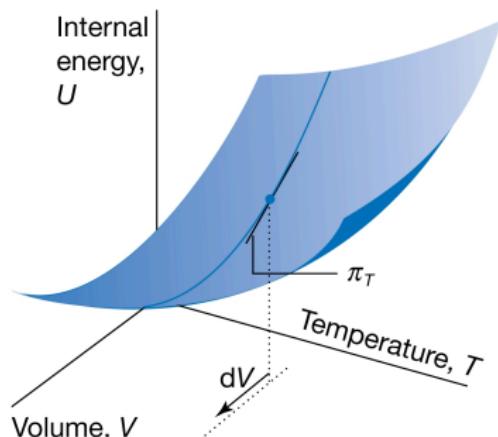
heat capacity at constant volume

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



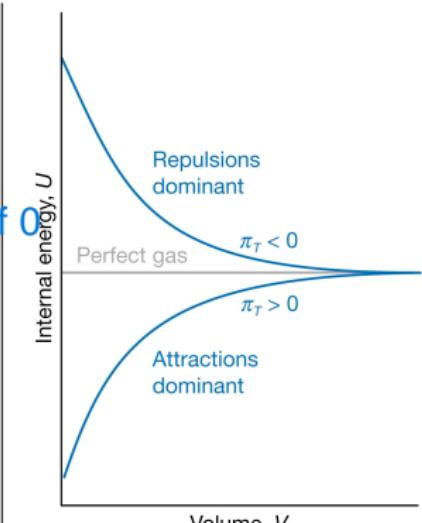
remember this is for real systems only.

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



perfect gas has internal pressure of 0

If $\Delta U > 0$ as $\Delta V > 0$ isothermally when there are attractive forces between the particles then a plot of U against V slopes upwards and $\pi_T > 0$



Joule-experiment

Joule : could we measure π_T by observing the ΔT 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

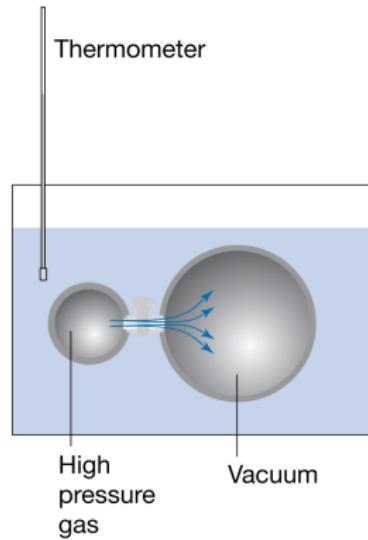
measured ΔT of water when a stopcock was opened and air expanded into a vacuum. He observed $\Delta T = 0$

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, $\Delta U = 0$ and
 $\therefore \pi_T = 0$ (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 $C_p - C_V = \alpha(p + \pi_T)V$

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

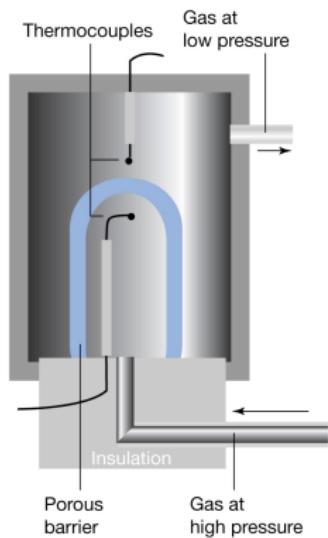
for constant z , $dz = 0$, $\implies \left(\frac{\partial z}{\partial x}\right)_y dx_z = - \left(\frac{\partial z}{\partial y}\right)_x dy_z$

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

$$\begin{aligned} H \equiv H(p, T) \implies dH &= \underbrace{\left(\frac{\partial H}{\partial p}\right)_T}_{\text{blue arrow}} dp + \left(\frac{\partial H}{\partial T}\right)_p dT \\ &\quad - \underbrace{\frac{1}{\left(\frac{\partial p}{\partial T}\right)_H \underbrace{\left(\frac{\partial T}{\partial H}\right)_p}_{\substack{\mu \\ \uparrow \\ \text{J T coefficient}}}} = - \underbrace{\left(\frac{\partial T}{\partial p}\right)_H}_{\substack{\mu \\ \uparrow}} \left(\frac{\partial H}{\partial T}\right)_p = -\mu C_p \end{aligned}$$

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

Joule-Thomson coefficient - apparatus



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

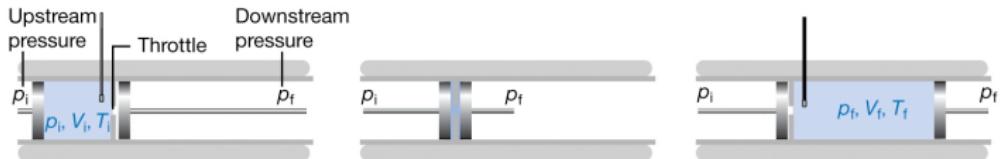
monitor the difference of temperature that arises from expansion

whole apparatus is insulated : adiabatic
 $q = 0 \implies \Delta U = w$

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

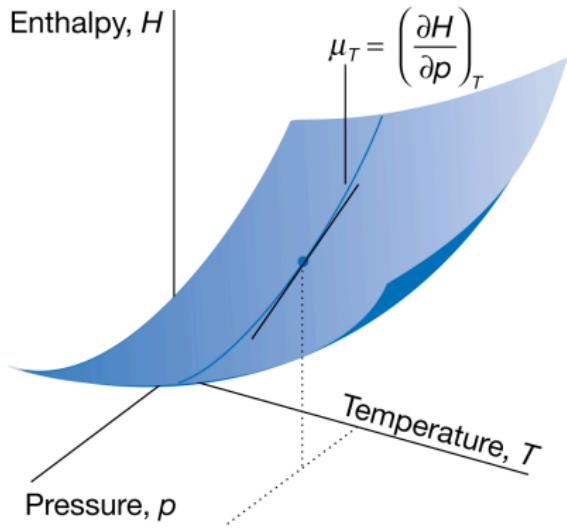
Joule-Thomson effect : cooling by isenthalpic expansion

Joule-Thomson coefficient - thermodynamic basis



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

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



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

Isothermal Joule-Thomson coefficient - measurement

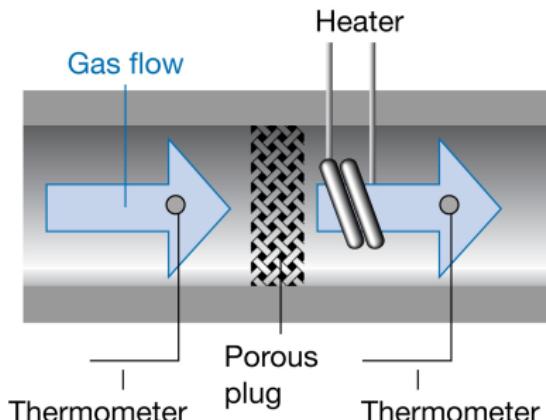
gas pumped continuously at steady pressure through heat exchanger (which brings it to required temperature)

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 = ΔH_p

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

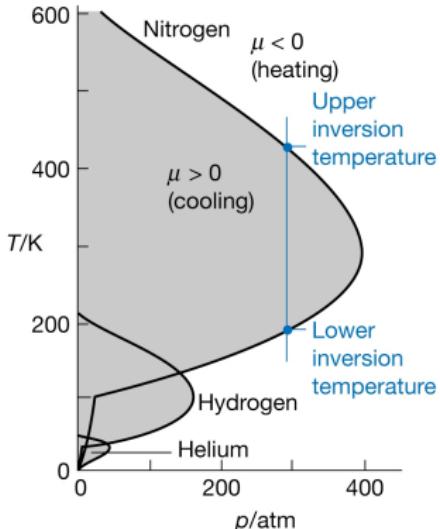
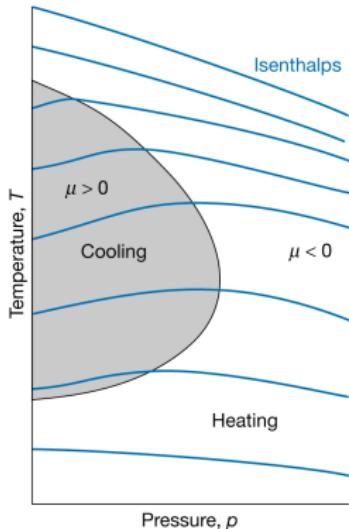


- ▶ Real gases have nonzero J T coefficients
- ▶ speed of molecules $\propto T$
- ▶ reducing average speed is equivalent to cooling
- ▶ If speed is reduced to the point that neighbours can capture each other by intermolecular attractions, then it condenses to a liquid
- ▶ Sign of μ depends on the gas,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

molecular interpretation :

- ▶ As gas expands, molecules move apart to fill the available volume, struggling against attraction of neighbours
- ▶ some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as separation increases
- ▶ This sequence explains the J T effect: the 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 have to climb apart against attractive force in order to travel more slowly
- ▶ when repulsions are dominant, $Z > 1$: heating effect
- ▶ typically there are two inversion temperatures, one at high temperature and other at low : $\mu < 0$ at one temperature
 - ▶ and cooling effect $\mu > 0$ when $T <$ upper inversion temperature

Inversion temperature :



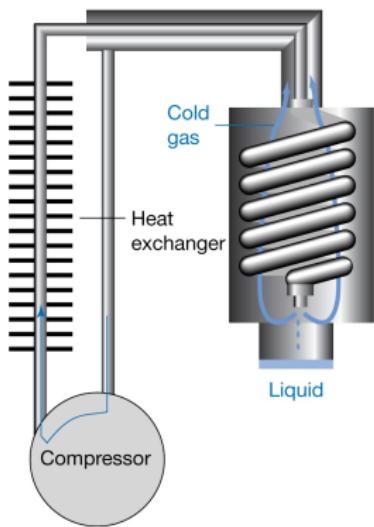
Inversion temperature corresponds to the boundary at a given pressure

For a given pressure, temperature must be below a certain value if cooling is required

but, if it becomes too low, the boundary is crossed again and heating occurs
Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy

inversion temperature curve runs through points of isenthalps where their 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

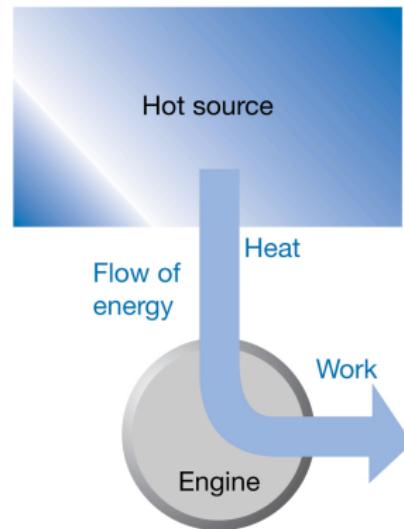
There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

- ▶ For a perfect gas, $\mu = 0$
- ▶ \therefore temperature of perfect gas is unchanged by J T expansion
- ▶ However, μ 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

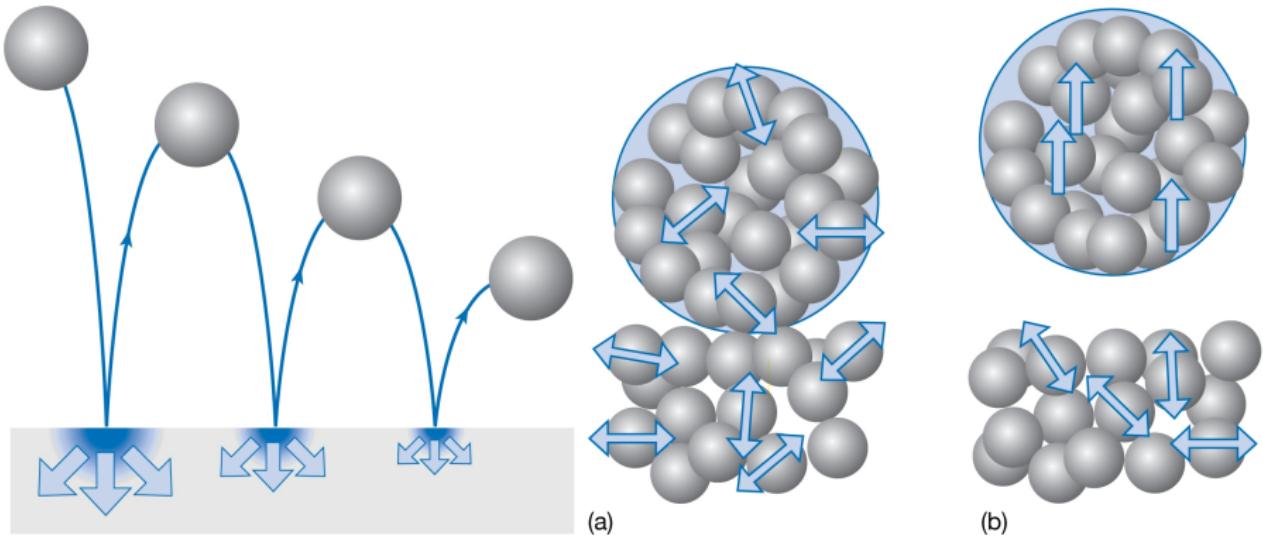
Thermodynamic engine : device that allows a system to draw heat from a source, convert part of it into work and dump unused heat to a sink



Second law : complete conversion
of heat into work impossible

NOT POSSIBLE

Heat and work : molecular understanding



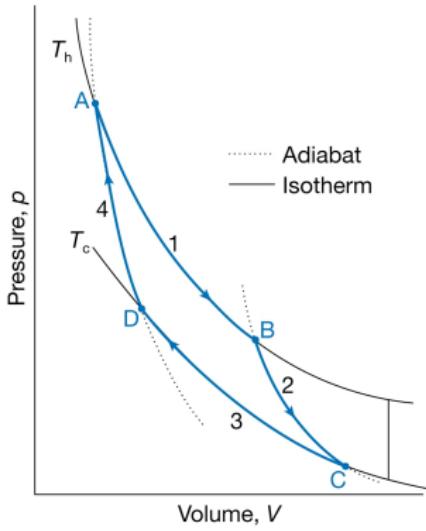
spontaneous change: direction of change leading to dispersal of total energy of isolated systems

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

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

$$\text{adiabatic process : } \Delta S = 0$$

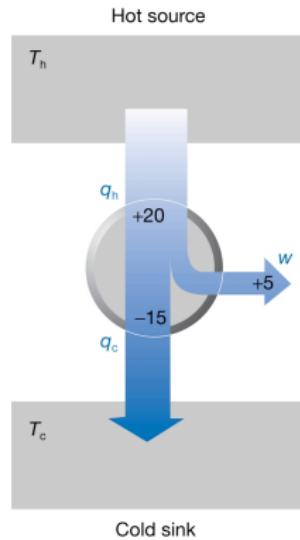
Carnot cycle : a model - perfect gas as fuel for an engine



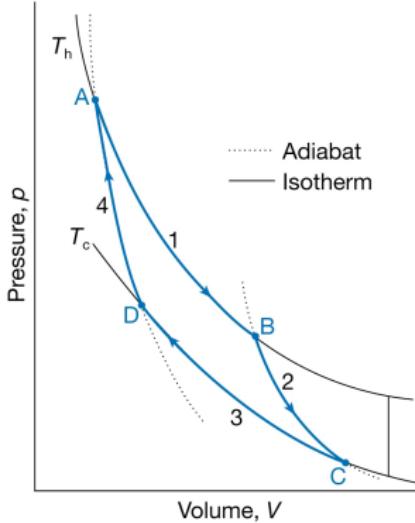
1. Reversible isothermal expansion from A to B at T_h ; $\Delta S = \frac{q_h}{T_h}$;
where q_h = energy supplied from hot source > 0
2. Reversible adiabatic expansion from B to C
 $\Delta S = 0$; $\Delta T = -(T_h - T_c)$
3. Reversible isothermal compression from C to D at T_c ; $\Delta S = \frac{q_c}{T_c}$
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 $\therefore \frac{V_A}{V_B} = \frac{V_D}{V_C} \implies q_c = -nRT_c \ln \frac{V_B}{V_A}$

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

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

- ▶ Equivalent to Kelvin-Planck statement : Proof by contradiction

Let $\eta_A > \eta_B$

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

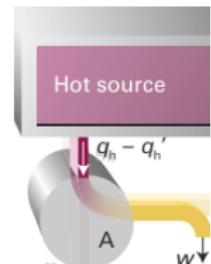
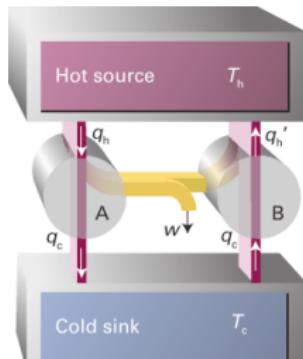
Reverse engine B

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

⇒ violation of Kelvin-Planck statement of second law

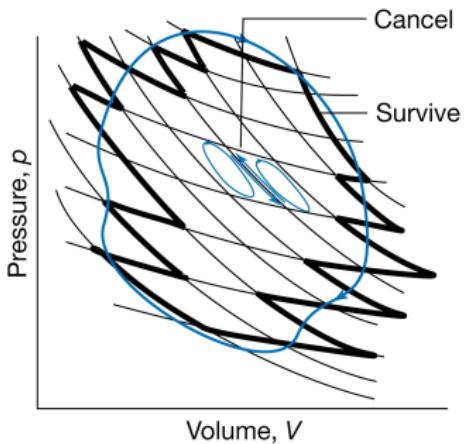


universality of 2nd law :

any reversible cycle \approx
collection of Carnot cycles

\oint (arbitrary path)

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



ΔS along an individual path inside is
cancelled by ΔS 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

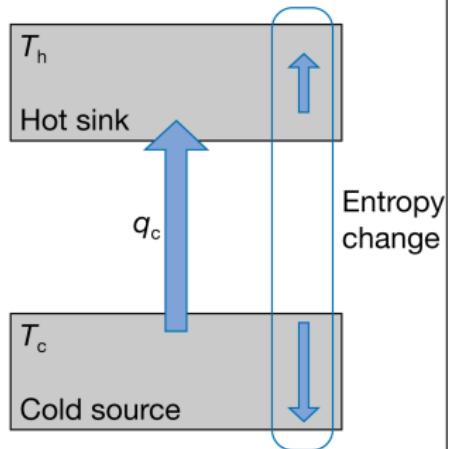
$$\therefore -dw_{\text{rev}} \geq -dw \text{ or, } dw \geq dw_{\text{rev}}$$

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

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

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

thermodynamic refrigerator



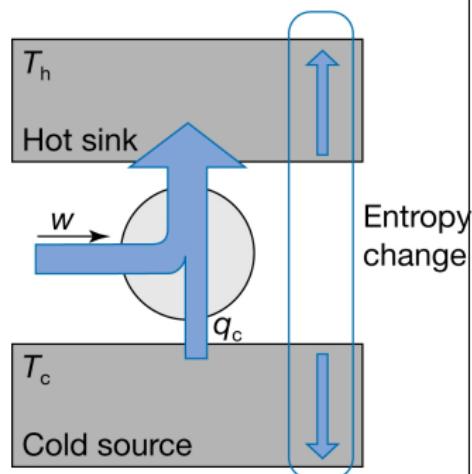
energy removed from cool source at temp. T_c
 $= \frac{|q_c|}{T_c}$

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



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

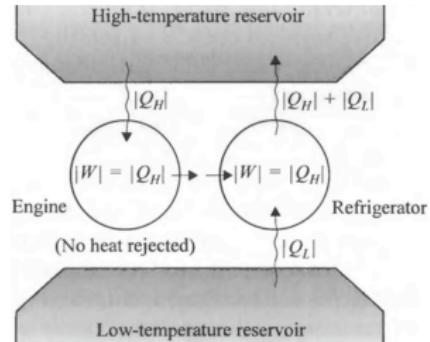
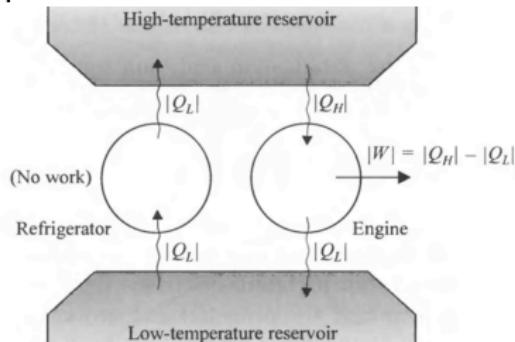
then minimum power, P , required to maintain original ΔT by pumping out energy by heating surroundings

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

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

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

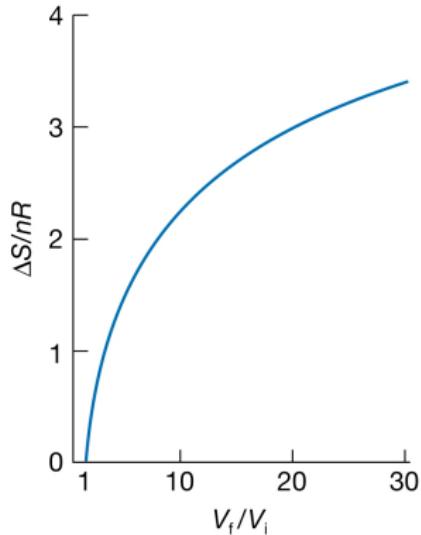
Equivalence of Kelvin-Planck and Clausius statements



$$-C \subset -K$$

$$-K \subset -C$$

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,
 $w_{\text{surr}} = 0$ 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. Br_2 :

- no complexity like hydrogen bonding in liquid Br_2

there is no unusual behaviour in the gas phase

- safe to use Trotton's rule

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

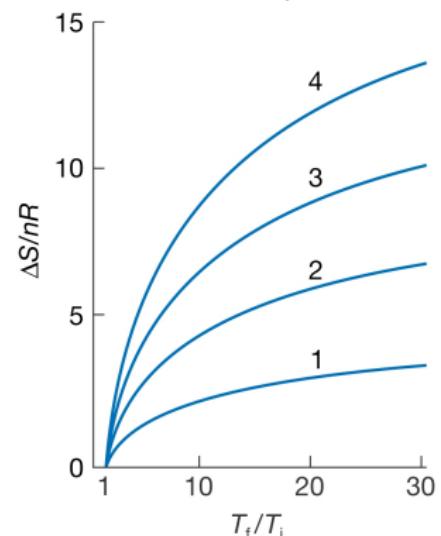
experimental value : $29.45 \text{ kJ mol}^{-1}$

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. $p(V)$: $S(T_f) = S(T_i) + \int_{T_1}^{T_f} \frac{C_{p(V)} dT}{T}$

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



label : heat capacity

solved problem : Calculate ΔS when 0.500 dm³ of Ar at 25°C and 1.00 bar expands to 1.000 dm³ and is simultaneously heated to 100°C

solved problem : Calculate ΔS when 0.500 dm³ of Ar at 25°C and 1.00 bar expands to 1.000 dm³ and is simultaneously heated to 100°C

S is a state function

∴ choose a convenient path from initial state

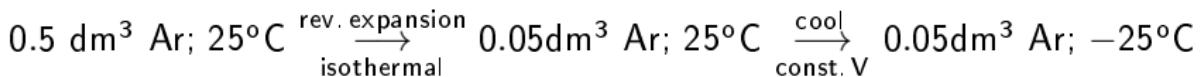


$$\Delta S_{\text{I}} = nR \ln \frac{V_f}{V_i} = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i}; \quad \Delta S_{\text{II}} = C_V \ln \frac{T_f}{T_i}$$

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

solved problem : Calculate ΔS when 0.5 dm^3 of Ar at 25°C and 1.00 bar is compressed to 0.05 dm^3 and is simultaneously cooled to -25°C

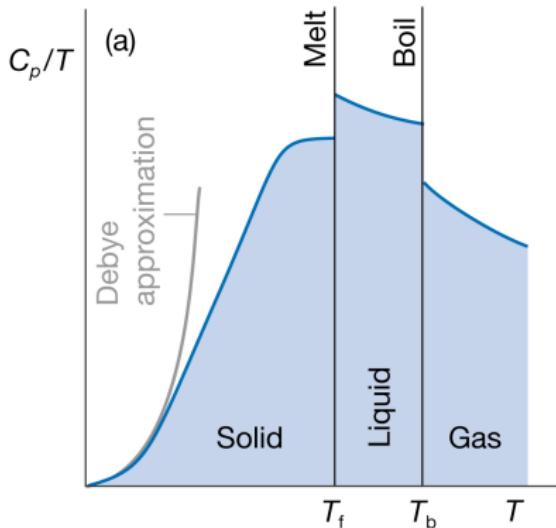
solved problem : Calculate ΔS when 0.5 dm³ of Ar at 25°C and 1.00 bar is compressed to 0.05 dm³ and is simultaneously cooled to -25°C



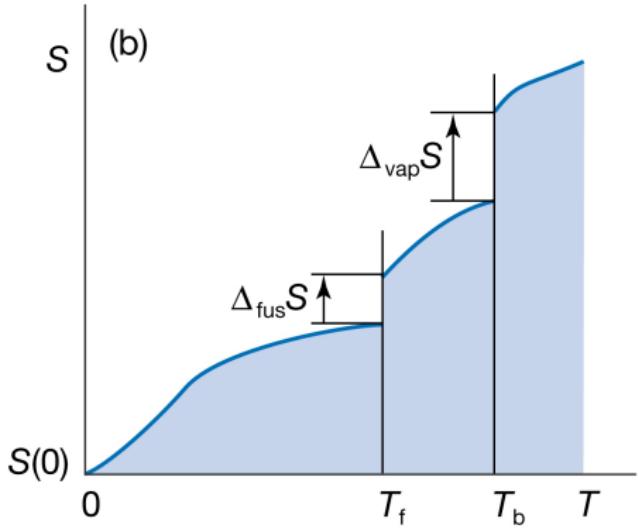
$$\Delta S_I = nR \ln \frac{V_f}{V_i} = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i}; \quad \Delta S_{II} = C_V \ln \frac{T_f}{T_i}$$

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

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

$\therefore \frac{dT}{T} = d \ln T$, 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°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 : 35.61K	6.43
$\int_{35.61}^{63.14}$	23.38
Fusion : 63.14K	11.42
$\int_{63.14}^{77.32}$	11.41
Vaporization : 77.32K	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 : $S = k_B \ln \Omega$

Ω = #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

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

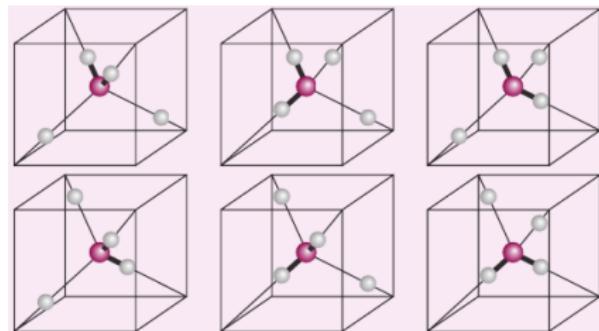
H_2O molecules with $2N$ H atoms = 2^{2N}

consider a single central O atom.

total number of arrangements of locations of H atoms around central O atom of one H_2O 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



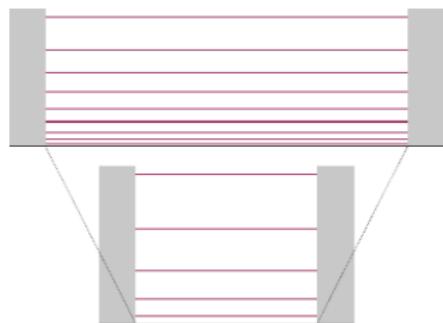
\therefore for N water molecules
of possible configurations
 $= 2^{2N}(3/8)^N = (\frac{3}{2})^N$

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

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 (Ω) 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

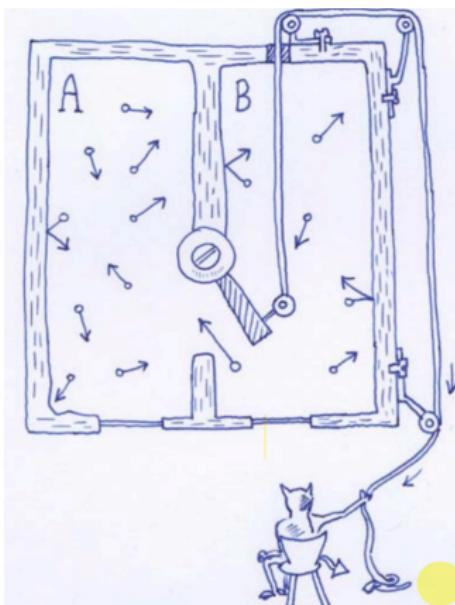
Equilibrium established and pressure in each

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 and the demon is no exception
- ▶ Modern explanation : demon needs to have a memory to operate, this act of storing information (actually it is 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 in the system
- ▶ The 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
- ▶ Erasing information has an associated increase in entropy
- ▶ Maxwell's demon can operate reversibly therefore, but only if it has a large enough hard disc that it doesn't ever need to clear space to continue operating.

The Landauer principle : “information is physical” and it has an energy equivalent

quantifies the thermodynamic cost of the recording/erasure of one bit of information,

- ▶ Erasure of one bit of information requires a minimum energy cost equal to $k_B T \ln 2 \approx 0.018 \text{ eV}$, where T is the temperature of a thermal reservoir used in the process.

- ▶ 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 it is transmitted by physical devices exploiting electrical or optical signals.
- ▶ ∴ it must obey the laws of physics and, first and foremost, the laws of thermodynamics.

- (1) any logically irreversible process must result in an entropy increase in the non-information-bearing degrees of freedom of the information-processing system or its environment
 - (2) any logically reversible process can be implemented thermodynamically reversibly.
- an amount of energy equal to $k_B T \ln 2$ ($k_B T$ = thermal noise per unit bandwidth) is needed to transmit a bit of information, and more if quantized channels are used with photon energies $h\nu > kT$

Thermodynamics

Reversible Change – Change that can be easily undone by making a tiny adjustment.

Specific Heat Capacity – Amount of heat required to raise temperature of one mass unit of substance by 1°C .

Enthalpy – Total heat content of the system at constant pressure.

convert to P and T equation and then do partial differentiation.

Internal Energy – Total energy contained within the system.

Entropy – Degree of randomness of the system.

Internal Pressure – Measure of how the internal energy of a system changes when it expands/contracts at constant temperature.

for a real system only, ideal gas has zero internal pressure

Calorimetry – Science Of measuring change in heat associated with a chemical reaction.

Relations in Linear Partial Differential Equations -

$$1. \ dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

$$2. \left(\frac{\partial z}{\partial x} \right)_y = \frac{1}{\left(\frac{\partial x}{\partial z} \right)_y}$$

convert to P and T equation and then do partial differentiation.

$$3. \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

for a real system only, ideal gas has zero internal pressure

Adiabatic Process

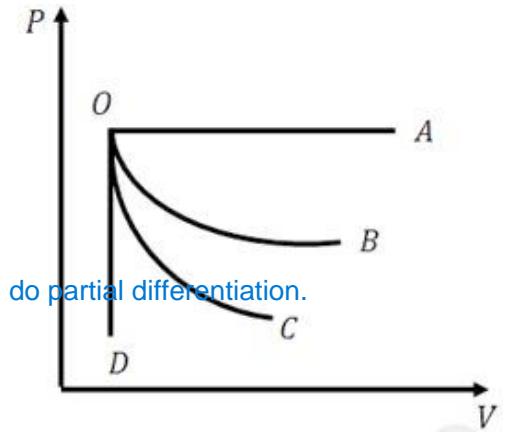
Adiabatic Process - No heat is transferred into or out of the system.

$$dQ = 0$$

In adiabatic process – $p v^\gamma = \text{Constant}$

Work done in adiabatic process – $w = \frac{1}{\gamma-1} (p_i v_i - p_f v_f)$

convert to P and T equation and then do partial differentiation.



What is the ratio of slopes of P-V graphs of adiabatic and isothermal process?

Identify thermodynamic process of each curve shown in the figure.

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Adiabatic Lapse Rate

Find the rate of change of temperature with altitude in a column of air that undergoes adiabatic process.

$$pv^\gamma = K$$

convert to P and T equation and then do partial differentiation.

$$P^{1-\gamma}T^\gamma = K$$

$$(1 - \gamma) \frac{dp}{p} + \gamma \frac{dT}{T} = 0$$

for a real system only, ideal gas has zero internal pressure

Adiabatic Lapse Rate

Find the rate of change of temperature with altitude in a column of air that undergoes adiabatic process.

$$dp = -\rho g dh$$

convert to P and T equation and then do partial differentiation.

$$\frac{dp}{p} = -\frac{\rho g dh}{\frac{nRT}{V}}$$

$$\frac{dp}{p} = -\frac{mg dh}{nRT}$$

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convert to P and T equation and then do partial differentiation.

$$\frac{dT}{dh} = \left(\frac{1-\gamma}{\gamma}\right) \frac{gm}{nR}$$

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Maxwell's Relations

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

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

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

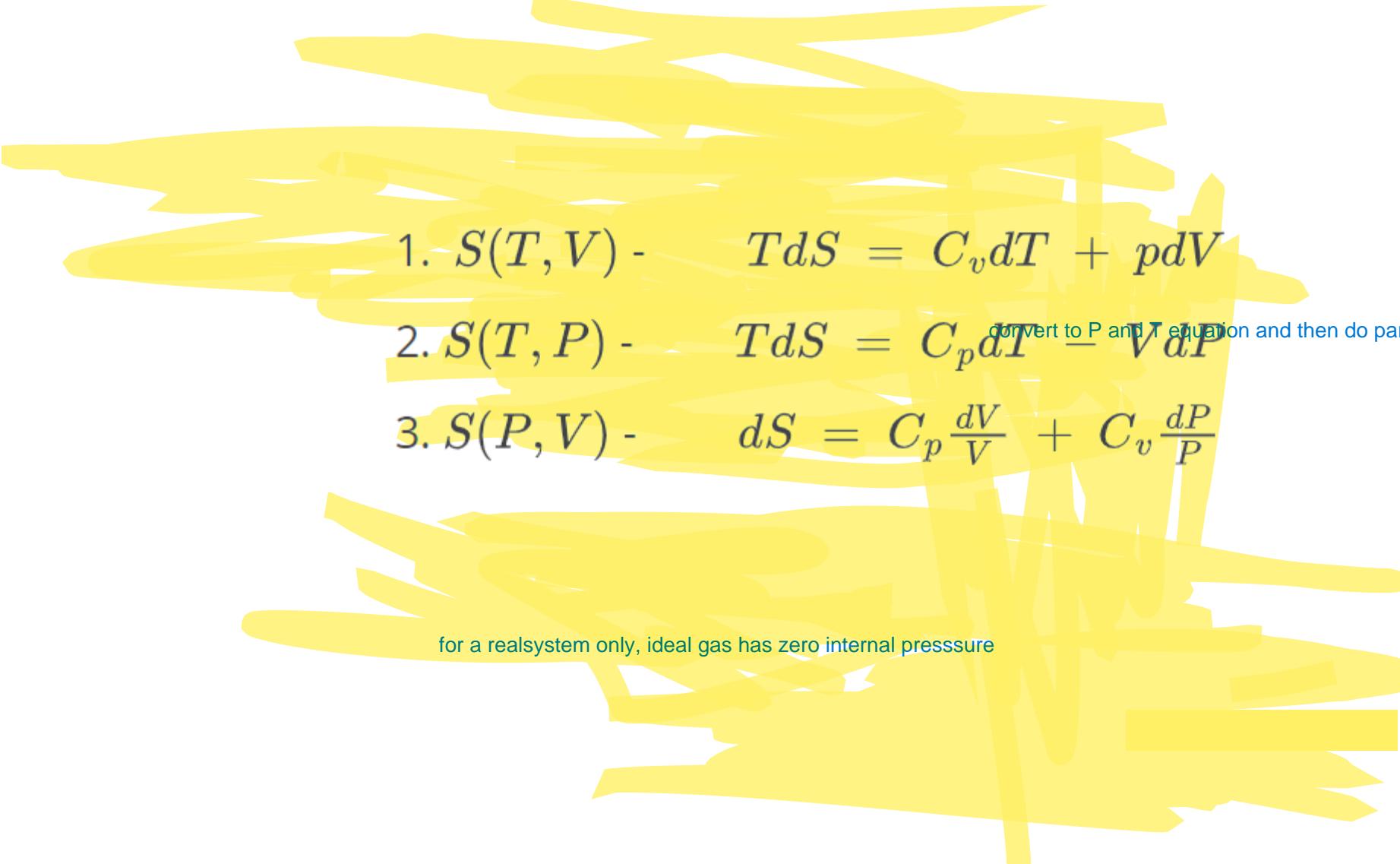
$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

convert to P and T equation and then do partial differentiation.

for a real system only, ideal gas has zero internal pressure

Not taught in class. These will be used in later parts of derivations.

T-dS Relations For Ideal Gases

- 
1. $S(T, V)$ - $TdS = C_v dT + pdV$
 2. $S(T, P)$ - $TdS = C_p dT - VdP$
convert to P and T equation and then do partial differentiation.
 3. $S(P, V)$ - $dS = C_p \frac{dV}{V} + C_v \frac{dP}{P}$

for a real system only, ideal gas has zero internal pressure

Enthalpy

Enthalpy is a state function. It is independent of path between the two states.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

In endothermic reaction, heat is absorbed from the surroundings.

$$H = U + PV$$

convert to P and T equation and then do partial differentiation.

$$dH = dU + PdV + VdP$$

$$dH = dq + VdP$$

$$dq_P = dH$$

for a real system only, ideal gas has zero internal pressure

$$dH = C_PdT$$

Internal Pressure

Internal Pressure – Measure of how the internal energy of a system changes when it expands/contracts at constant temperature.

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

$$U(V, T)$$

convert to P and T equation and then do partial differentiation.

$$dU = TdS - PdV$$

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

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

$$\pi_T = \frac{an^2}{V^2}$$

for a real system only, ideal gas has zero internal pressure

If $\pi_T > 0$, Attractive forces are dominant

If $\pi_T < 0$, repulsive forces are dominant

Internal Pressure

Internal Pressure – Measure of how the internal energy of a system changes when it expands/contracts at constant temperature.

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

convert to P and T equation and then do partial differentiation.

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 $C_p - C_V = \alpha (p + \pi_T) V$

for a real system only, ideal gas has zero internal pressure

Internal Pressure

Internal Pressure – Measure of how the internal energy of a system changes when it expands/contracts at constant temperature.

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

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

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

convert to P and T equation and then do partial differentiation.

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

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

for a real system only, ideal gas has zero internal pressure

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

Joule Thompson Effect

The Joule-Thomson effect is a significant phenomenon in thermodynamics that describes the cooling or heating of a gas as it undergoes adiabatic expansion or compression. This effect is particularly relevant when gases deviate from ideal behavior due to intermolecular forces.

JT Effect describes about change in fluid's temperature as it flows from a higher pressure to lower pressure through a porous plug. Such expansion is called throttling process.

JT Effect is especially pronounced in real gases due to their non-ideal behavior and intermolecular forces.

convert to P and T equation and then do partial differentiation.

JT Coefficient - The Joule-Thomson coefficient measures the temperature change per unit pressure change during a Joule-Thomson process.

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H$$

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$$H = U + PV$$

$$dH = TdS + VdP$$

convert to P and T equation and then do partial differentiation.

$$\text{By TdS relations, } TdS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$dH = 0$$

$$C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP + VdP = 0$$

$$dT = \frac{1}{C_P} \left(T \left(\frac{\partial V}{\partial T} \right)_P - V \right) dP$$

for a real system only, ideal gas has zero internal pressure

$$\mu = \frac{1}{C_P} \left(T \left(\frac{\partial V}{\partial T} \right)_P - V \right)$$

Inversion Temperature

Inversion Temperature refers to the temperature at which the behavior of a gas undergoing Joule-Thomson expansion transitions from cooling to heating, or vice versa.

$\mu > 0 \implies dT < 0$ when $dp < 0 \implies$ gas cools on expansion, attractive interactions dominant - molecules have to climb apart against attractive force in order to travel more slowly

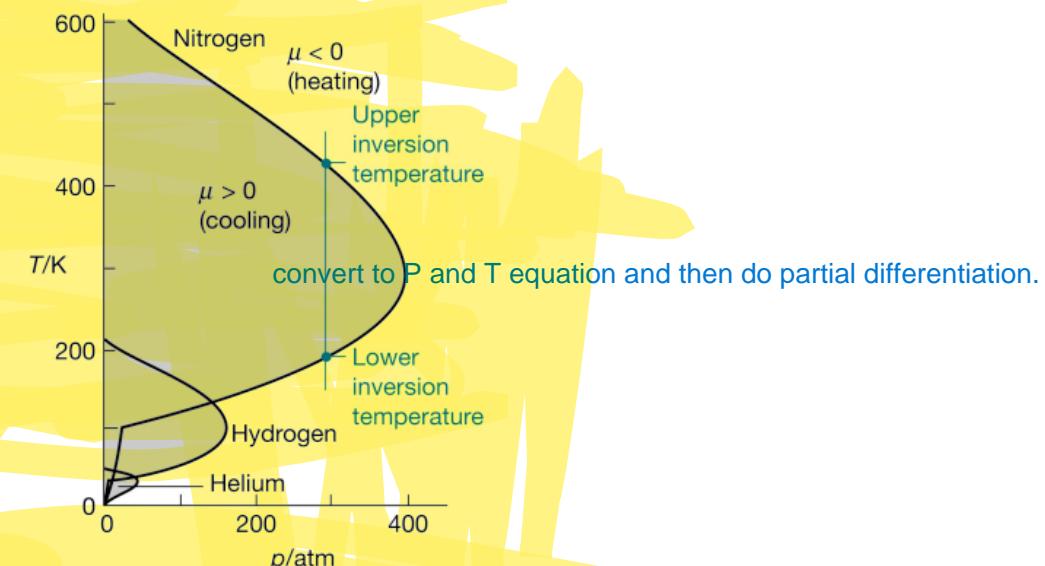
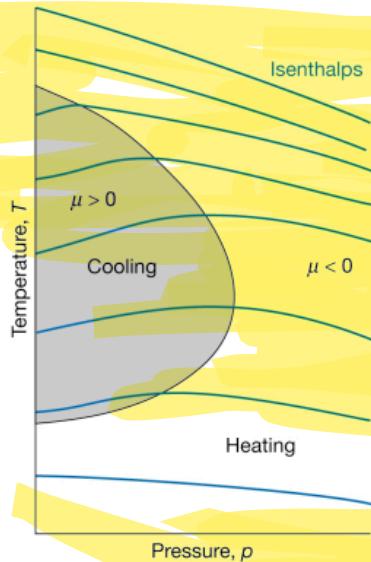
During an adiabatic expansion, two factors can cause a fluid's temperature to change: a change in internal energy or the conversion of potential to kinetic internal energy. Because temperature is a measure of thermal kinetic energy (the energy associated with molecular motion), any change in temperature indicates a change in thermal kinetic energy. The sum of thermal kinetic energy and thermal potential energy is internal energy.

for a real system only, ideal gas has zero internal pressure

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Inversion temperature :



Inversion temperature corresponds to the boundary at a given pressure

For a given ^{or real system only} pressure, temperature must be below a certain value if cooling is required

but, if it becomes too low, the boundary is crossed again and heating occurs

Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy

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

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

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Ex. $S_m^\ominus \text{ Cl}^-$ (aq) is $57 \text{ JK}^{-1} \text{ mol}^{-1}$ and that of Mg^{+2} (aq) is $-138 \text{ JK}^{-1} \text{ mol}^{-1}$

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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

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

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and ignoring extra non-mechanical work

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Legendre transform : changing the natural variables :

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

$\boxed{\text{Information from } (x, y) \equiv \text{Information from } (m, c)}$

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

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

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call it A

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

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Maximum work :

$$dU \leq TdS + dw \quad ;$$

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

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

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

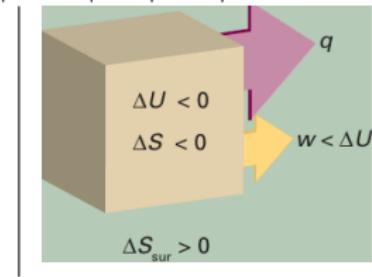
$$\text{At const. } T, \quad dw_{\max} = dA; \quad \Delta A = \Delta U - T\Delta S$$

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

some energy must escape as heat

to generate enough entropy in surroundings

to overcome reduction in entropy in the system



For spontaneity,

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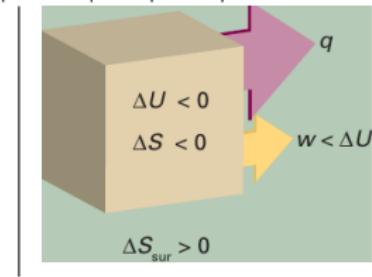
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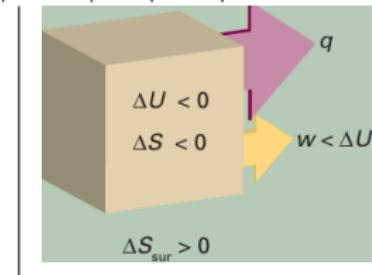
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$A = \text{part of } U \text{ that is free to use as work}; TS = \text{unavailable energy}$

Maximum work :

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

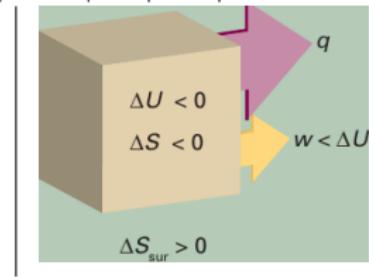
the most negative value of dw , and therefore the max. energy that can be obtained from system as work, is

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

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

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

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 ΔU is converted into work

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

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

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

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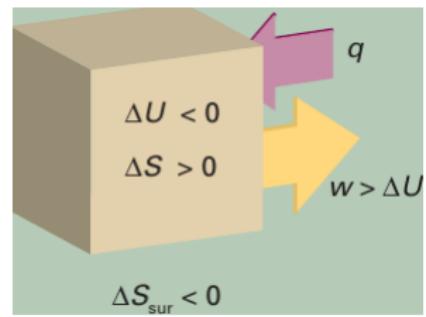
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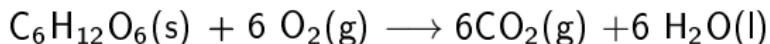
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Nature is providing a tax refund



Ex. 1.0 mol C₆H₁₂O₆ (glucose) is oxidized to CO₂ and water at 25°C

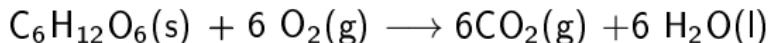


$$\Delta_r U^\ominus = -2808 \text{ kJ mol}^{-1} \text{ and } \Delta_r S^\ominus = 259.1 \text{ J K}^{-1}\text{mol}^{-1}$$

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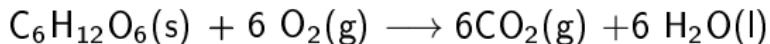
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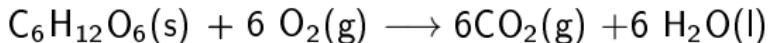
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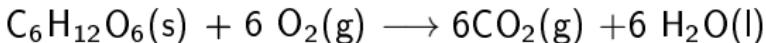
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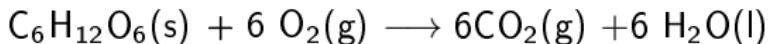
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system can draw in energy from the surroundings (reducing their entropy) and make it available for work

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

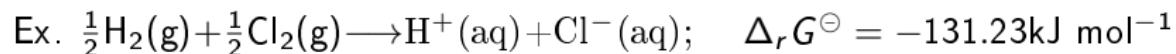
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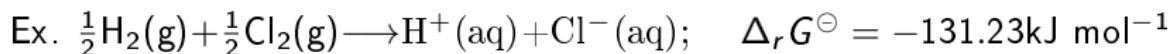
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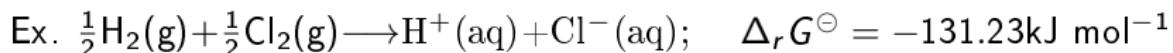
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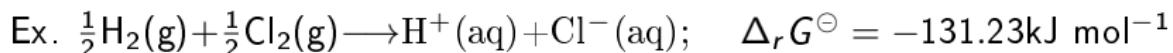


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With $\therefore \Delta_f G^\ominus(Cl^-, \text{aq})$ known, we can find $\Delta_f G^\ominus$ for other ions

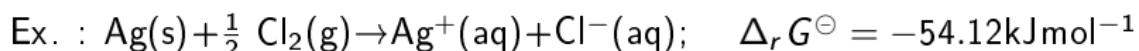
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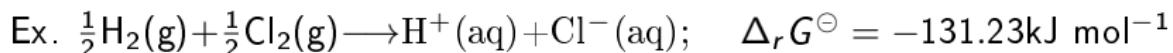
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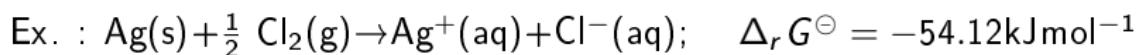
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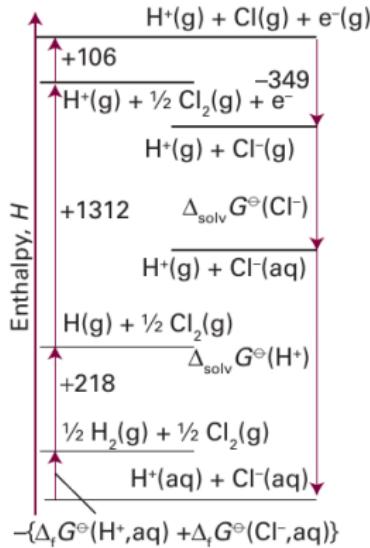
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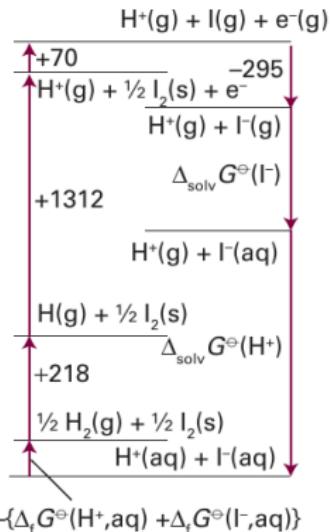


$$\Delta_f G^\ominus(Ag^+, \text{aq}) = -54.12 + 131.23 = 77.11 \text{ kJ mol}^{-1}$$

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

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

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

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

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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

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2. total volume, V
3. total mass of the one component, N (no. of moles)

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and

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

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 $p^{(1)} = p^{(2)}$

impermeable, rigid, diathermal wall \implies $dV^{(1)} = dV^{(2)} = 0$
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$$\therefore dU^{(1)} + dU^{(2)} = 0 \implies dU^{(1)} = -dU^{(2)} = dU \text{ (say)}$$

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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), $dS = 0$

thermal and mechanical equilibrium, flexible, permeable, diathermal wall

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A general property of exact differentials :

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

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

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

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for reversible changes in systems with no non-mechanical work

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Thermodynamic equation of state :

$$dU = TdS - pdV$$

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

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

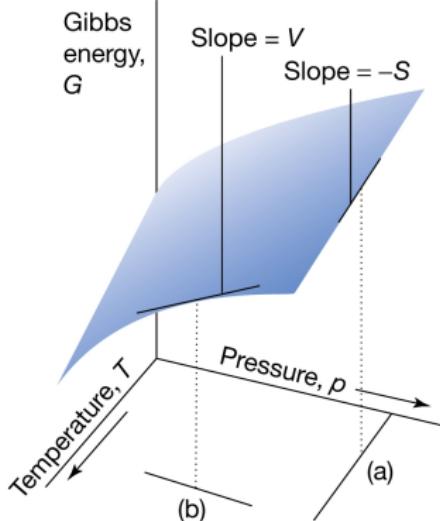
Gibbs' Free energy and entropy

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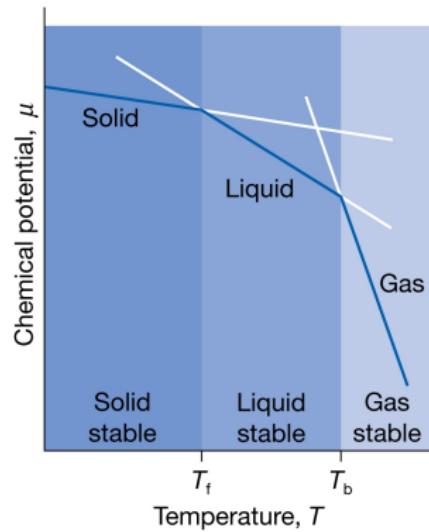
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Gibbs' Free energy and entropy

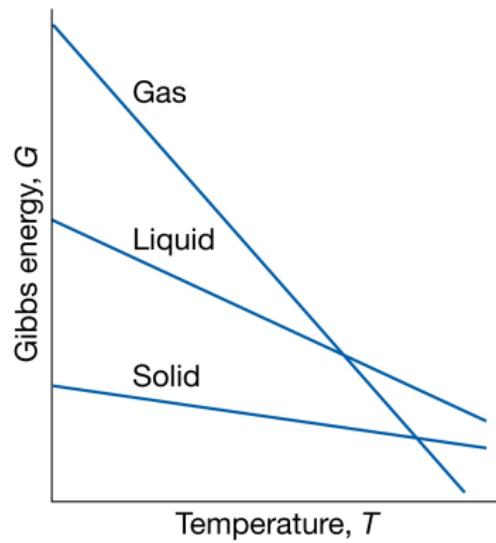
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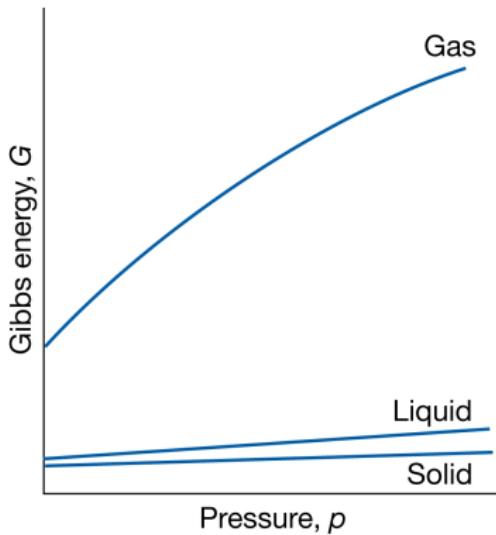
chemical potential and phase equilibrium : $\left(\frac{\partial\mu}{\partial T}\right)_p = -S_m$



sublimation before melting



$$\left(\frac{\partial G}{\partial p}\right)_T = V > 0$$



Gibbs-Helmholtz equation :

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

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

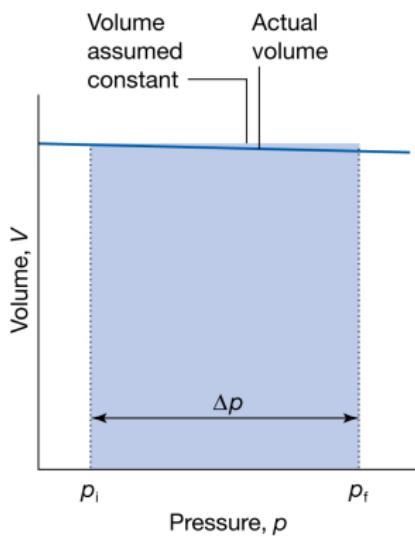
$$\boxed{\left(\frac{\partial \left[\frac{\Delta G}{T}\right]}{\partial T}\right)_p = -\frac{\Delta H}{T^2}}$$

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

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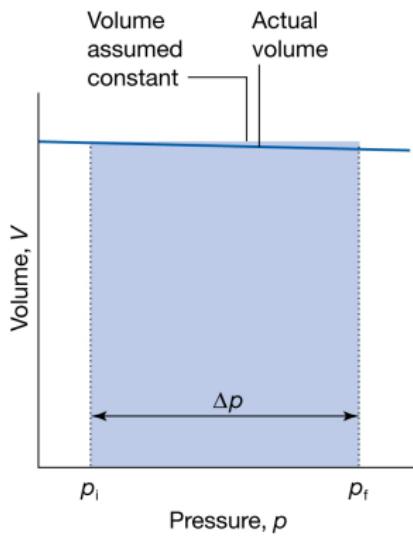
for condensed phases

gases

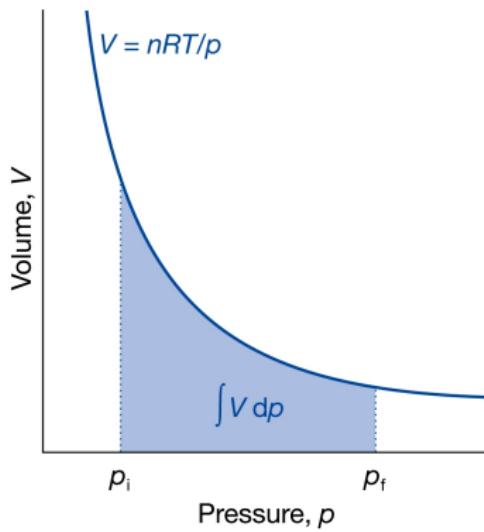


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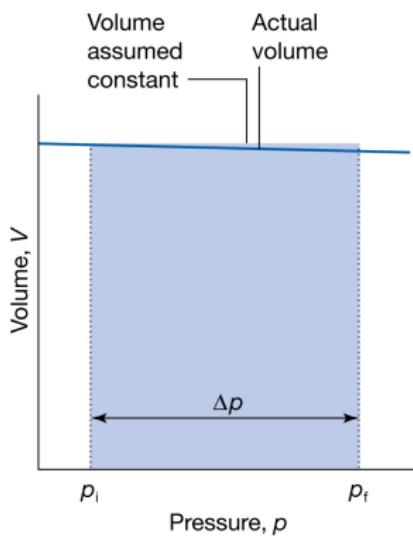


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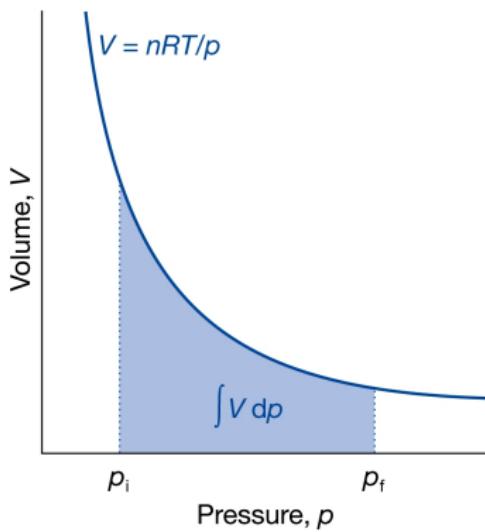


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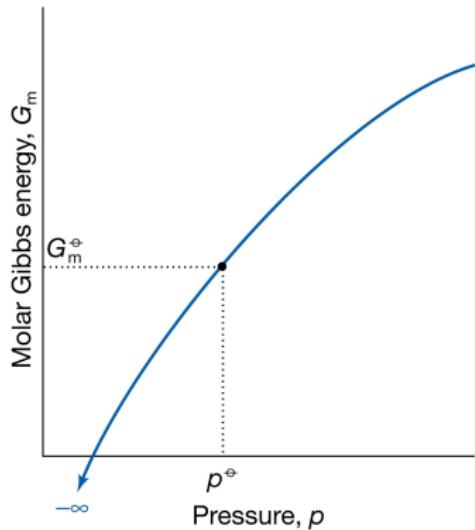
gases



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

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

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



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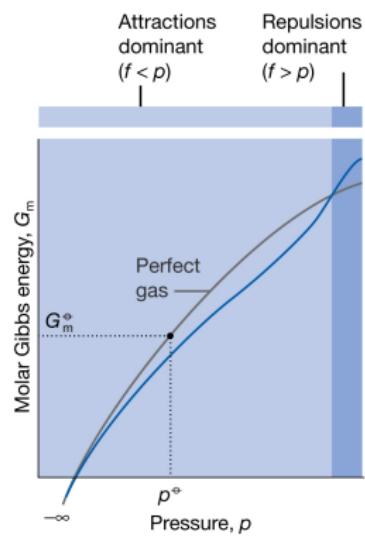
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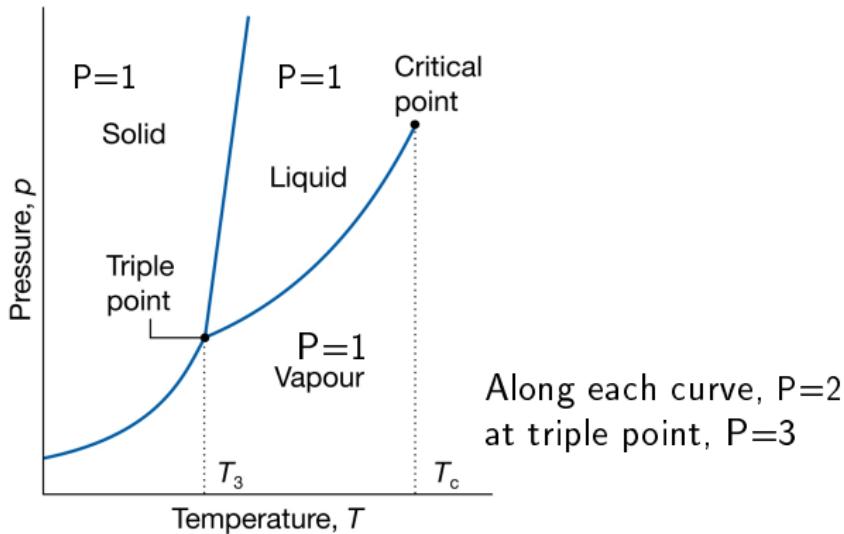
$$\text{or, } \ln \phi = \int_0^p \frac{V_m - V_{\text{perfect, } m}}{p} dp$$



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

$P = \#$ phases in a system

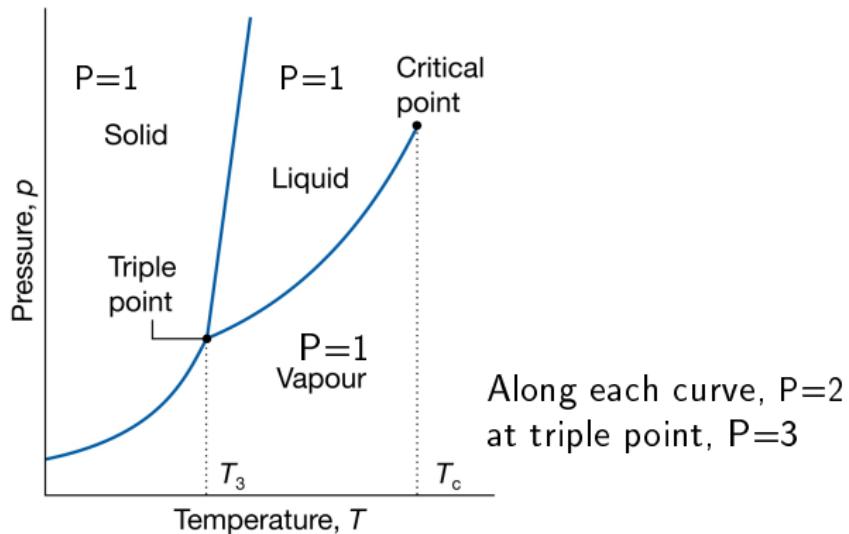
Phase equilibria - triple point (T_3) and critical point (T_c)



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



For water : $T_3 = 273.16$ K and 611 Pa (6.11 mbar)

- ▶ 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

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F = #degrees of freedom, C = #components, P = #phases

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

eqn. relates p and T ,

so only one variable is independent

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single-component
three-phases

single-component, single-phase

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phases α and β 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

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

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

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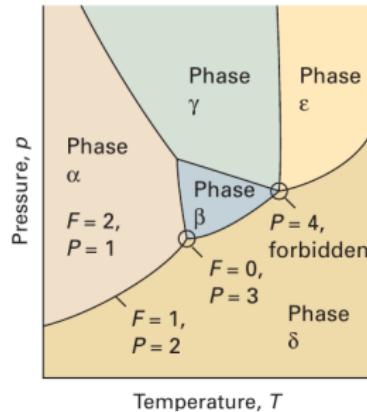
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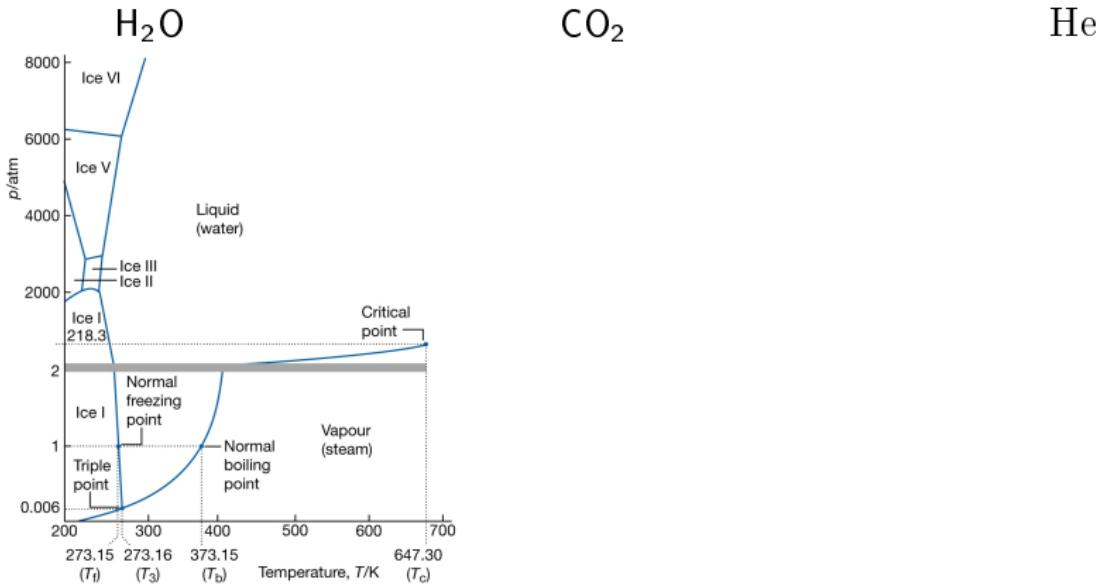
fixed soln.

so no variation possible

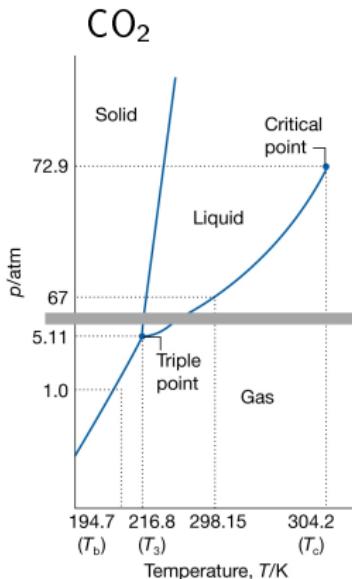
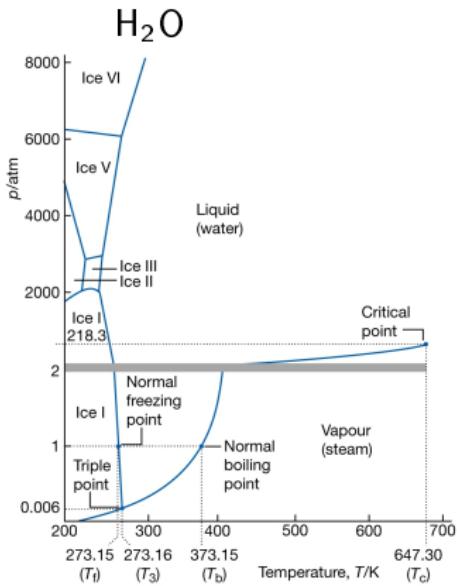
Typical phase diagram



Experimental phase diagrams

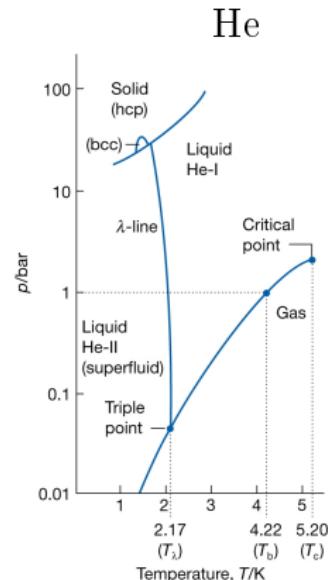
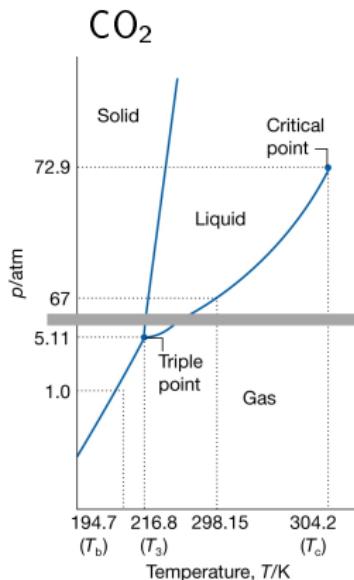
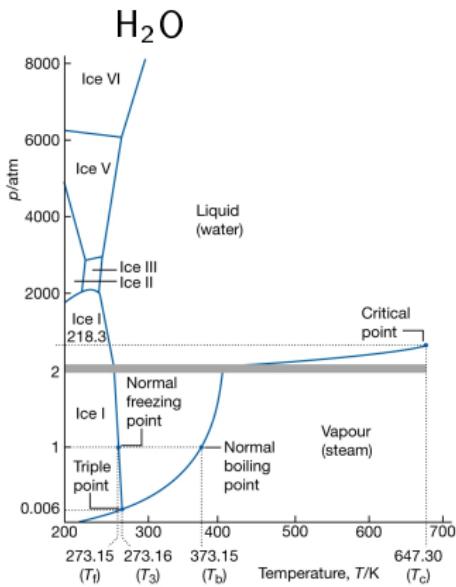


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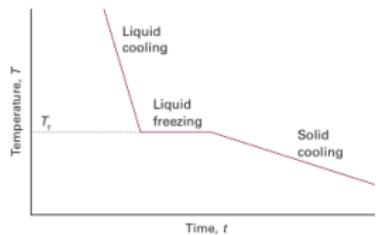


He

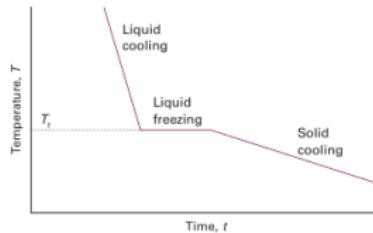
Experimental phase diagrams



Phase transition : Thermal analysis and Cooling curve



Phase transition : Thermal analysis and Cooling curve



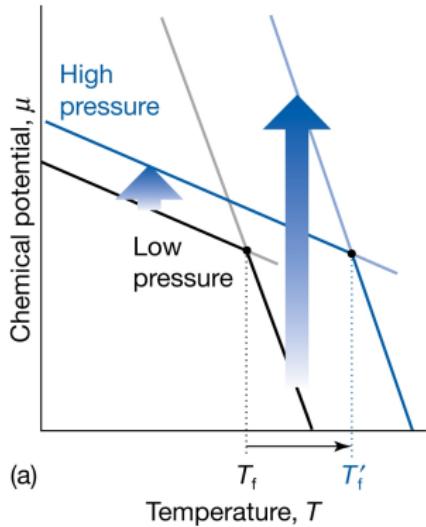
metastable phases : Kinetic barriers

Response of melting to applied pressure

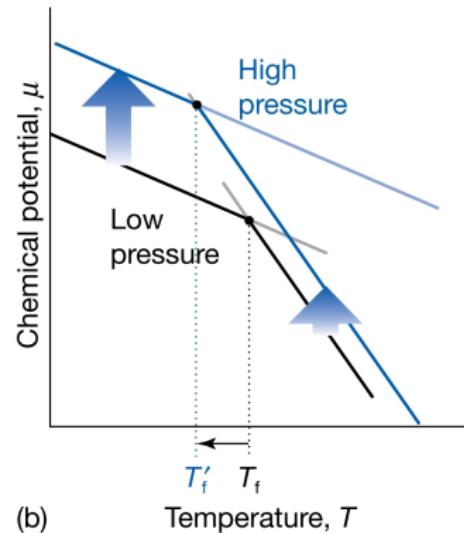
Response of melting to applied pressure

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

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



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



$$G_m(p) = G_m^\ominus + RT \ln \frac{p}{p^\ominus}$$

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

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

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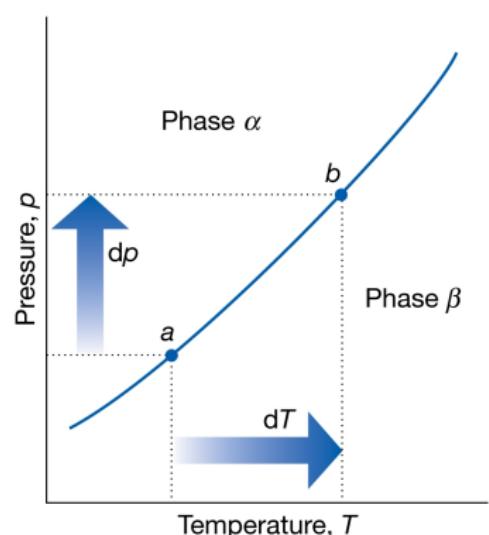
When pressure is applied to a system with two phases in equilibrium (at a), the equilibrium is disturbed
It can be restored by changing T , moving state of system to b

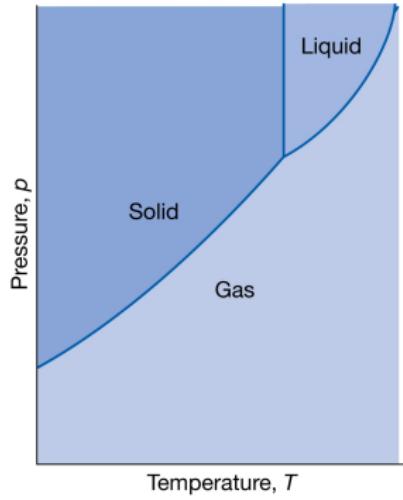
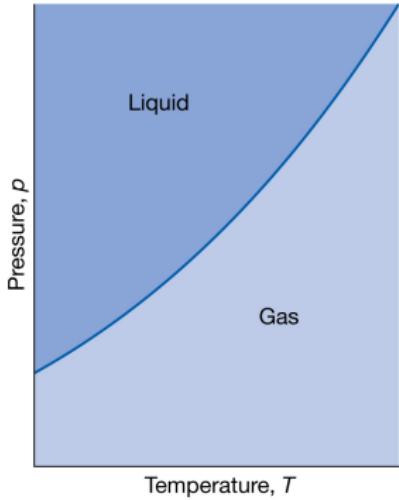
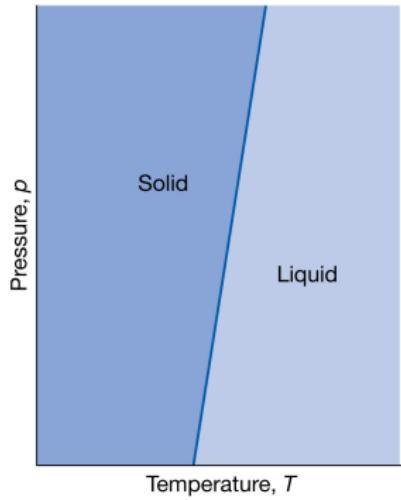
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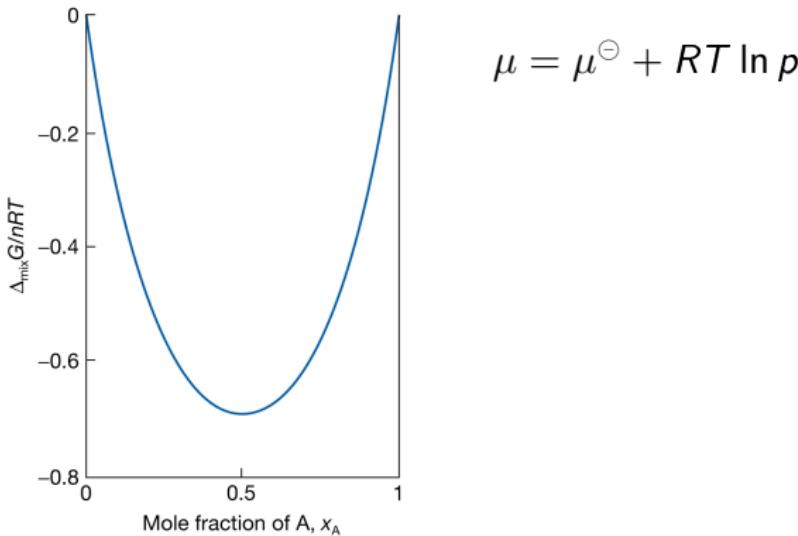
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relation between dp and dT ensures that system remains in equilibrium as either variable is changed

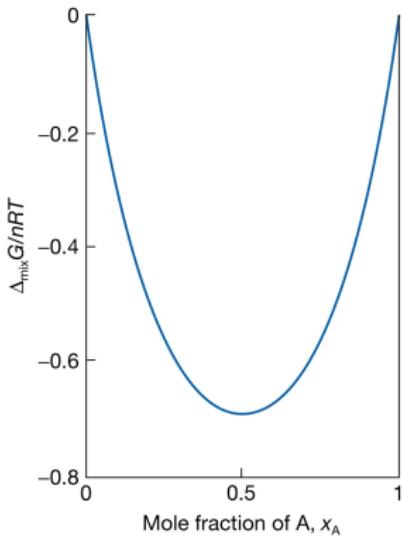




Gibbs energy of mixing of perfect gases



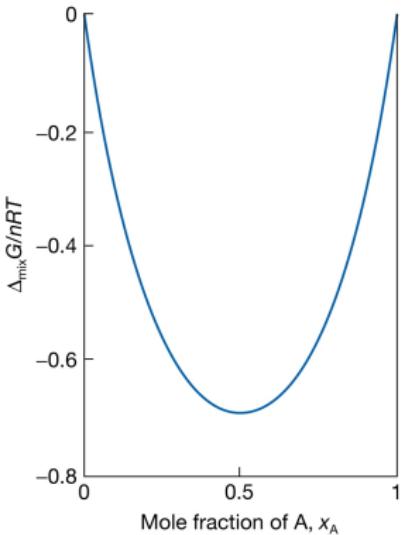
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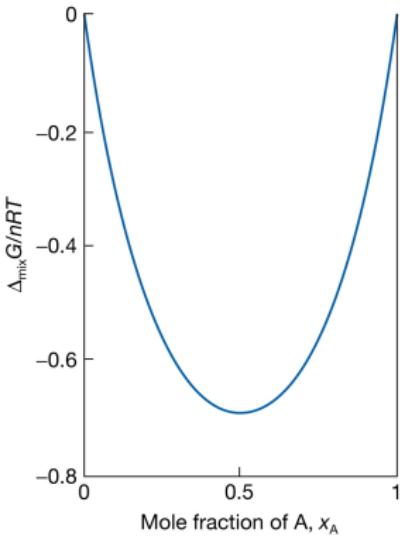


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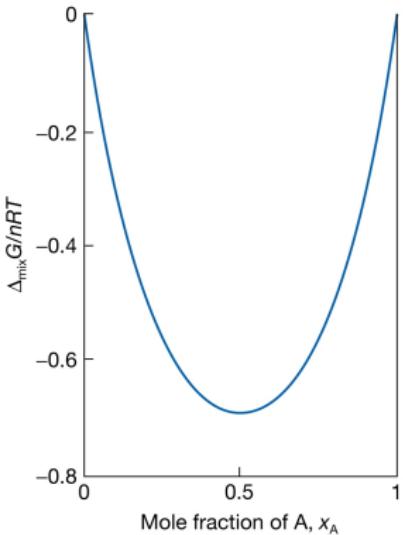
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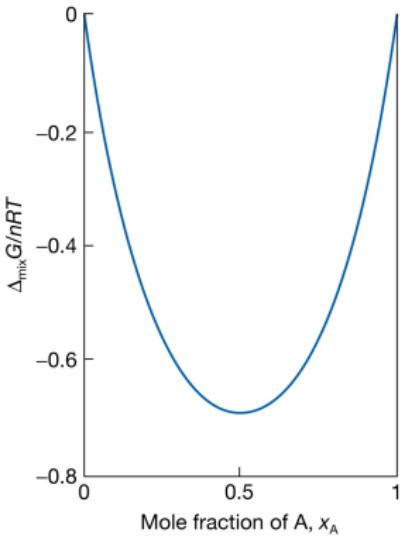
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$$\therefore \Delta_{\text{mix}} G = G_f - G_i$$

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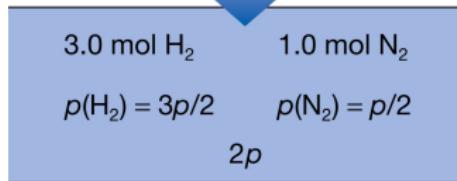
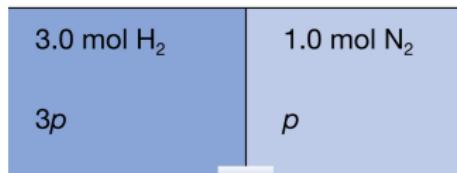
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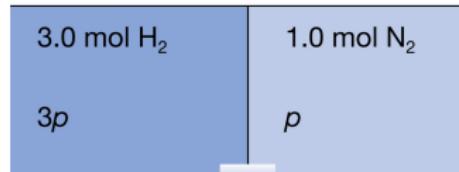
$$= n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

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

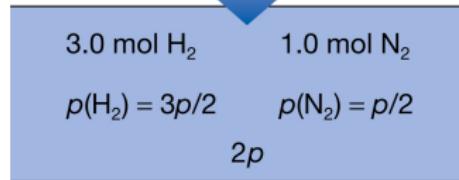
Ex. : initial pressures not the same :



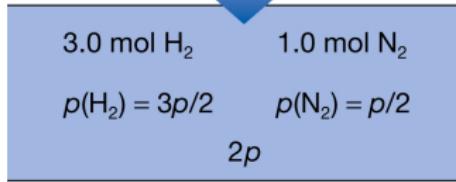
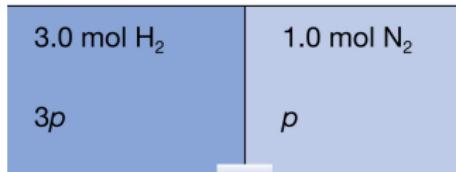
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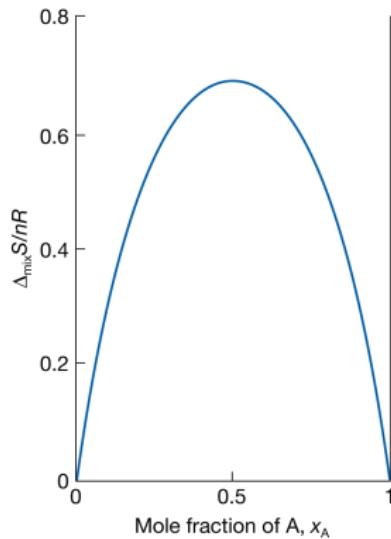
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$$G_f = 3 (\mu_{\text{H}_2}^\ominus + RT \ln \frac{3}{2}p) + n_B (\mu_{\text{N}_2}^\ominus + RT \ln \frac{p}{2})$$

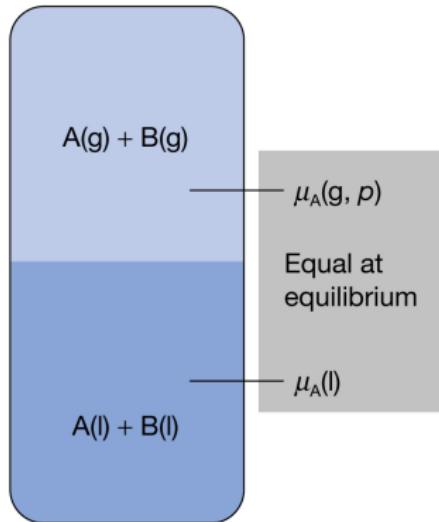
$$\begin{aligned}\therefore \Delta_{\text{mix}} G &= G_f - G_i \\ &= -4RT \ln 2 \quad T = 298 \quad -6.9 \text{ kJ}\end{aligned}$$

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

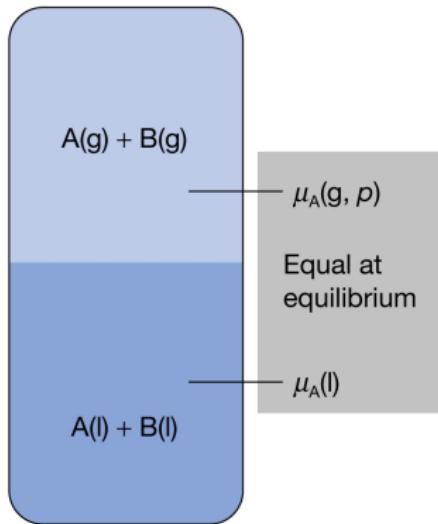
$$\Delta_{\text{mix}}S = - \left(\frac{\partial \Delta_{\text{mix}}G}{\partial T} \right)_{p, n_A, n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$



Ideal solutions



Ideal solutions

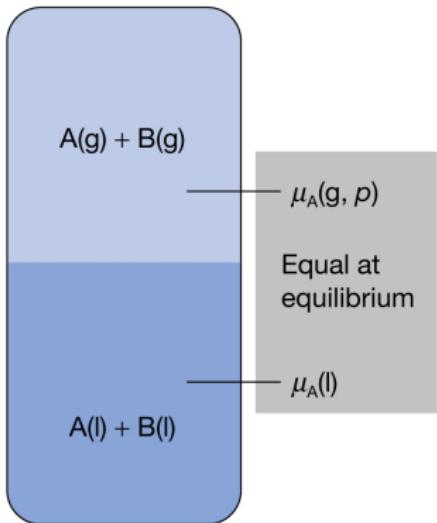


* \equiv pure substance

μ_A^* = chemical potential of pure A

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

Ideal solutions



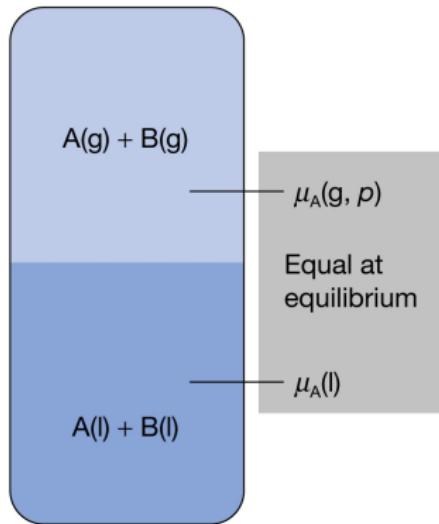
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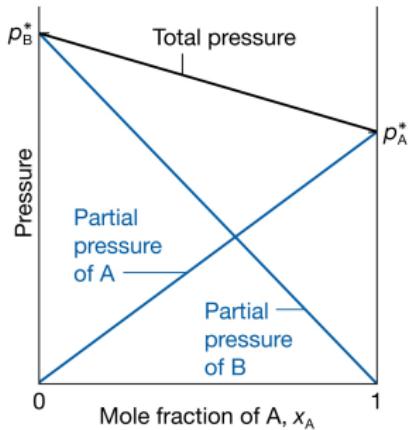
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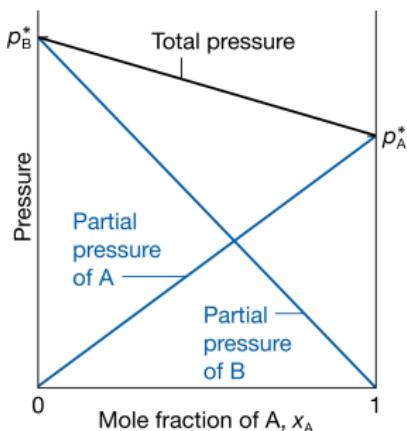
$$\text{soln. : } \mu_A = \mu_A^\ominus + RT \ln p_A$$

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

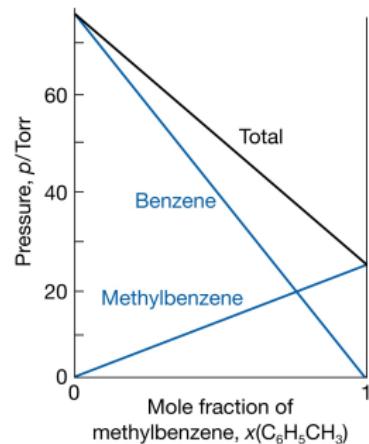
Ideal solutions - Raoult's law: $p_A = x_A p_A^* \implies \mu_A = \mu_A^* + RT \ln x_A$



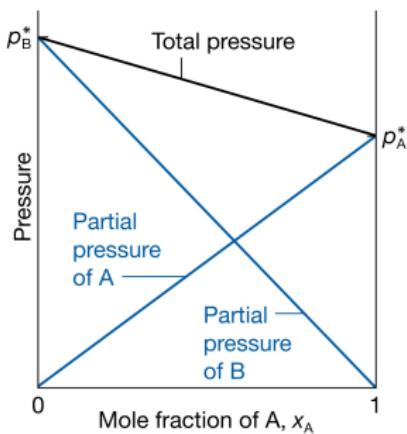
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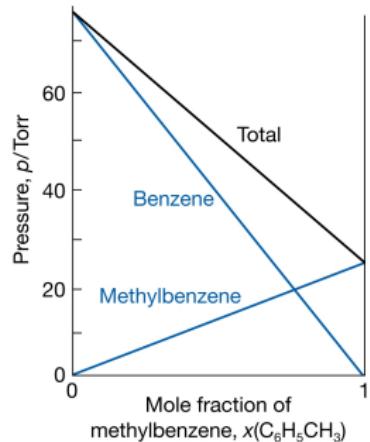
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Mixtures that obey the law throughout from pure A to pure B are called **ideal solutions**

molecular origin of Raoult's law :

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- ▶ \therefore vapour pressure of solvent in solution $<$ that of pure solvent

Ideal-dilute solutions

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although vapour pressure of solute
 \propto mole fraction
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 \neq vapour pressure of pure substance

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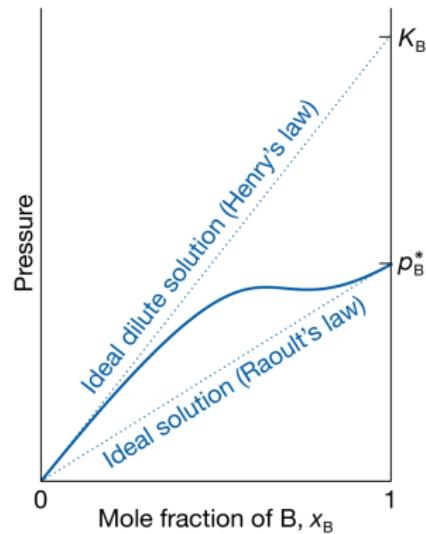
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Henry's law : $p_B = x_B K_B$

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

$$p_B = b_B K_B$$



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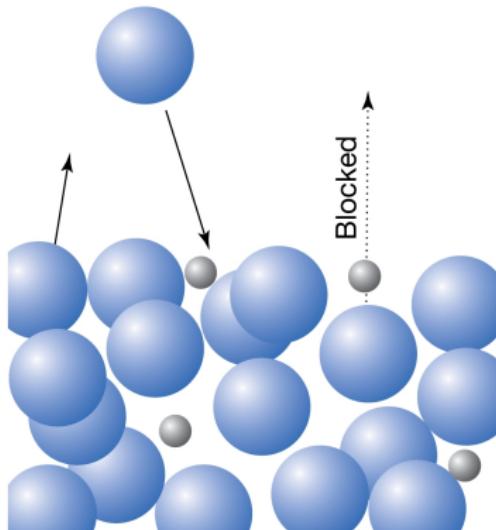
solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure

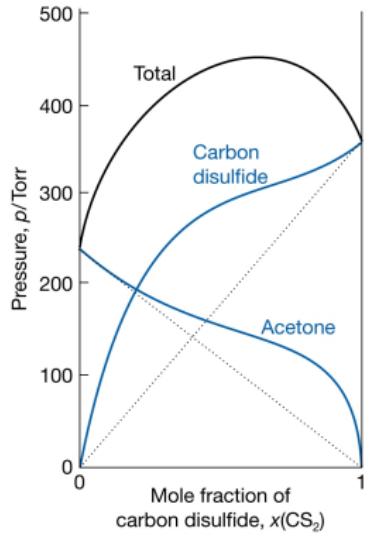
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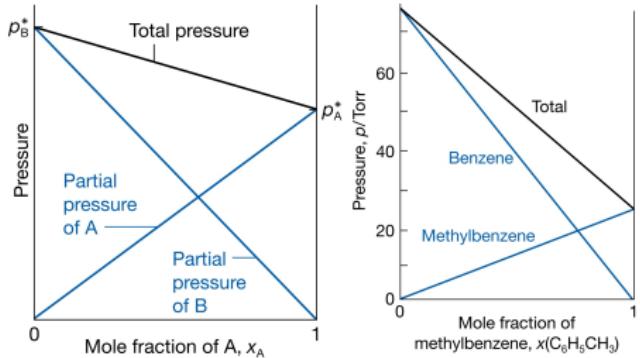
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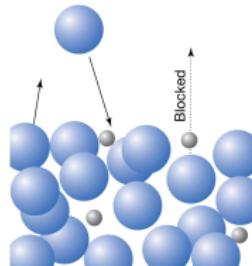
solvent behaves like a slightly modified pure liquid, but the solute behaves entirely differently from its pure state unless the solvent and solute molecules happen to be very similar

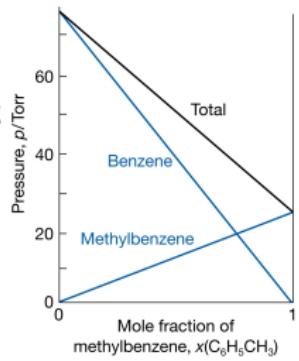
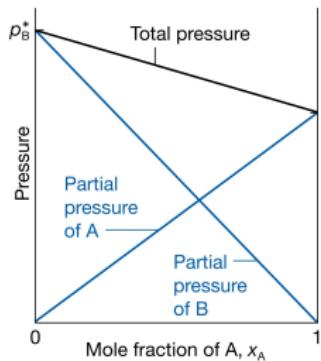




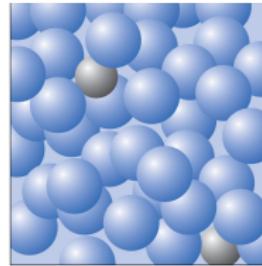
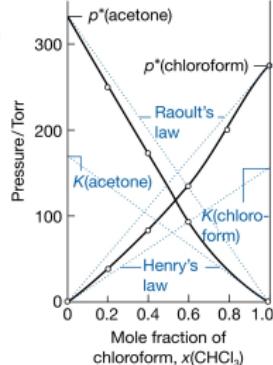
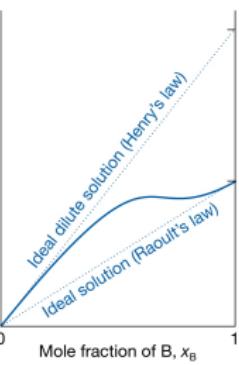
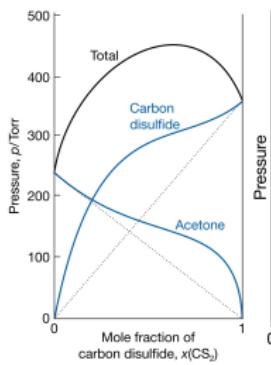
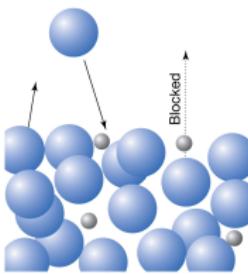


vaporisation (blocked by solute)
& condensation (not hindered)





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

chemical potential of an ideal solvent :

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} = \mu_A^* + RT \ln x_A = \mu_{A,\text{modified}}^* + RT \ln b_A$$

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$$\begin{aligned} \mu_A &= \mu_A^* + RT \ln a_A; \quad a_A = \frac{p_A}{p_A^*} \\ \text{activity coefficient, } \gamma &: \quad a_A = \gamma_A x_A \end{aligned} \quad \left\{ \begin{array}{l} \text{as } x_A \rightarrow 1 \\ \gamma_A \rightarrow 1 \\ a_A \rightarrow x_A \end{array} \right.$$

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activity coefficient, γ : $a_A = \gamma_A x_A$

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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^e	$a = \gamma b/b^e$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

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General expression: $\boxed{\mu = \mu^\ominus + RT \ln a = \mu^{\text{ideal}} + RT \ln \gamma}$

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two standard values differ by about 40 kJ mol^{-1}

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- ▶ reaction Gibbs energy : $\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p, T}$; ξ measures extent of reaction
 - ▶ $\Delta_r G$ is a derivative

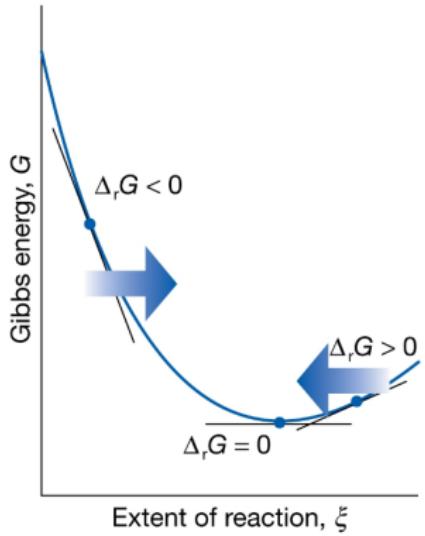
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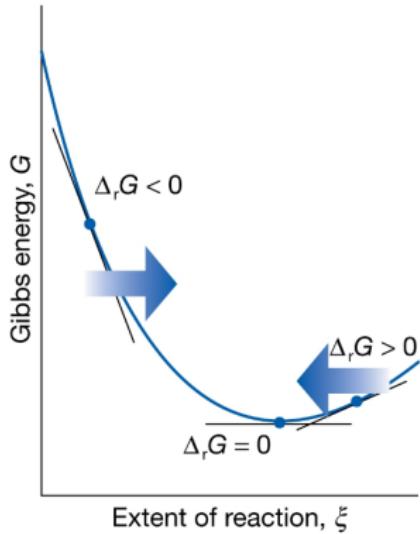
$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

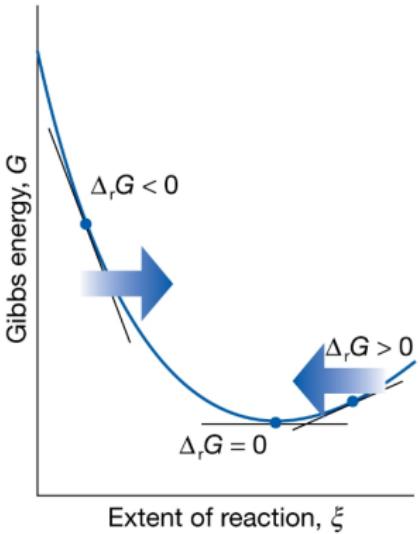
$$\text{or, } \Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p, T} = \mu_B - \mu_A$$

= difference between chemical potentials of reactants and products
at the composition of the reaction mixture

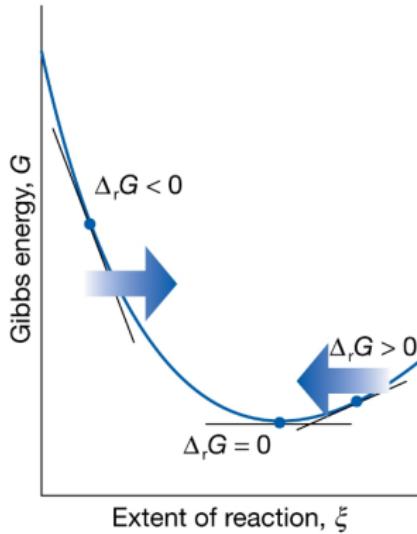


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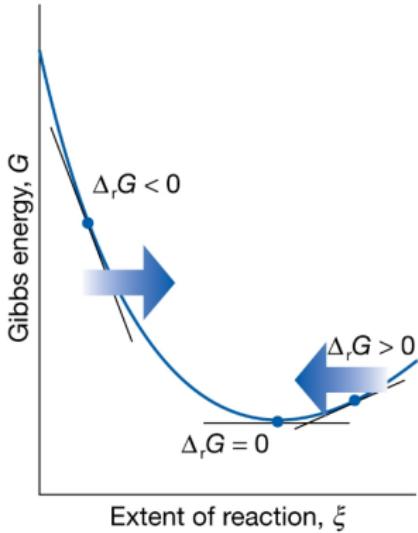




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- ▶ Equilibrium corresponds to zero slope
 $\Delta_r G = 0 \implies$ foot of the valley
: reaction at equilibrium

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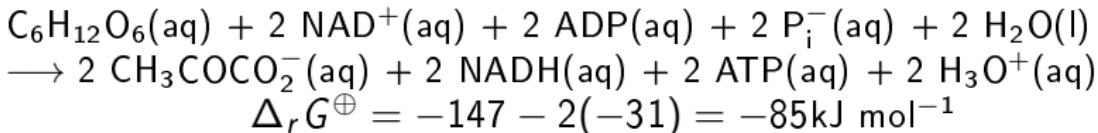
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- ▶ but biosynthesis occurs indirectly and is equivalent to consumption of 3 ATP molecules for each link

In moderately small protein like myoglobin, with about 150 peptide links, construction alone requires 450 ATP molecules

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and $\Delta_r G^\ominus = \Delta_f G_m^\ominus(B) - \Delta_f G_m^\ominus(A)$ = standard reaction Gibbs energy

At equilibrium, $\Delta_r G = 0$

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At equilibrium, $\Delta_r G = 0 \implies \Delta_r G^\ominus + RT \ln K$ with $K = \left(\frac{p_B}{p_A}\right)_{\text{equilibr}}$

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$\Delta_r G^\ominus = \nu_C \mu_C^\ominus + \nu_D \mu_D^\ominus - \nu_A \mu_A^\ominus - \nu_B \mu_{AB}^\ominus$ 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

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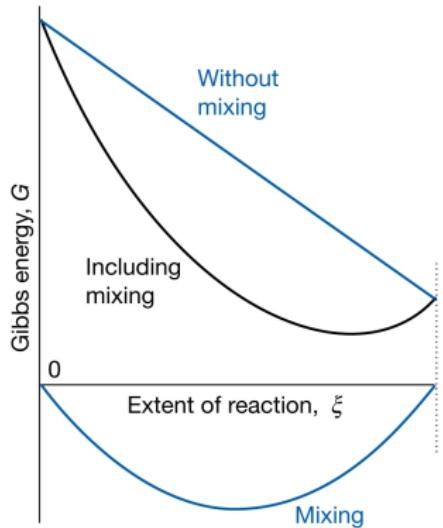
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$$Q = \frac{\text{activities of products raised to powers of stoichiometric coefficients}}{\text{activities of reactants raised to powers of stoichiometric coefficients}}$$

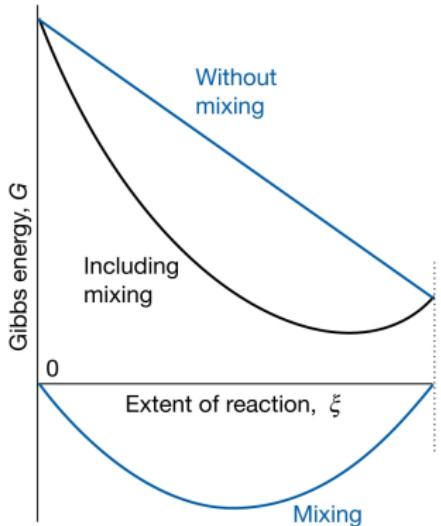
Writing ν_s for reactants as negative integers, $Q = \prod_j a_j^{\nu_j}$

In molecular terms, the minimum at $\Delta_r G^\ominus = 0$ stems from $\Delta_{\text{mix}} G$



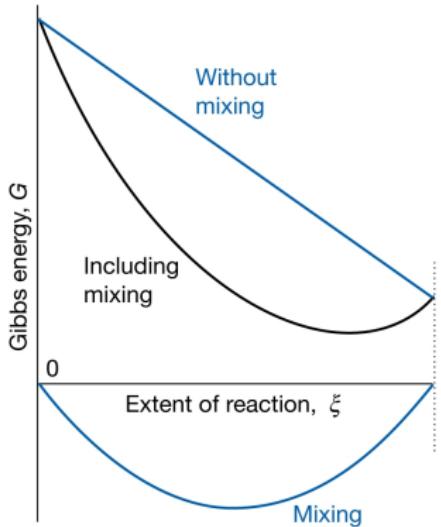
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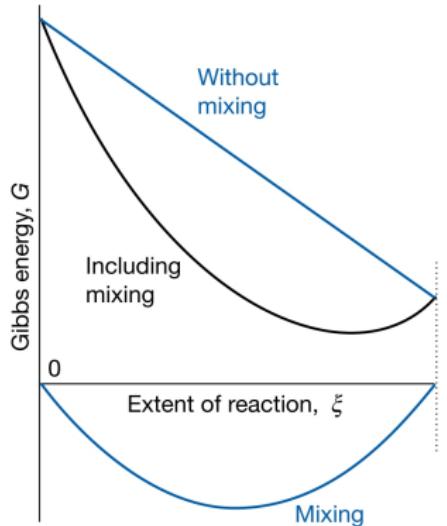


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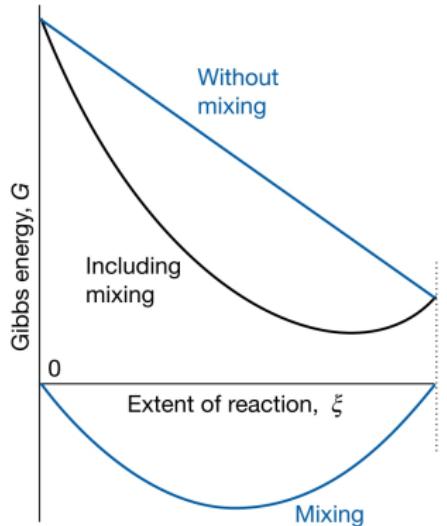


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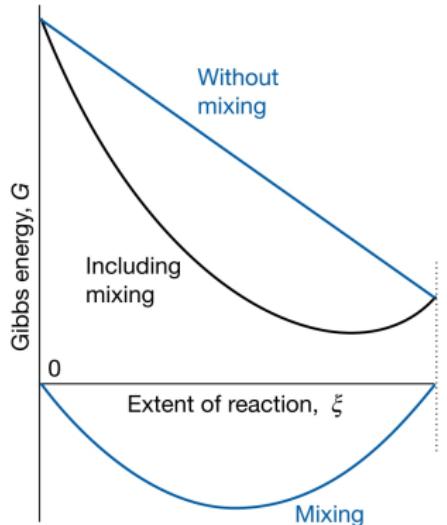
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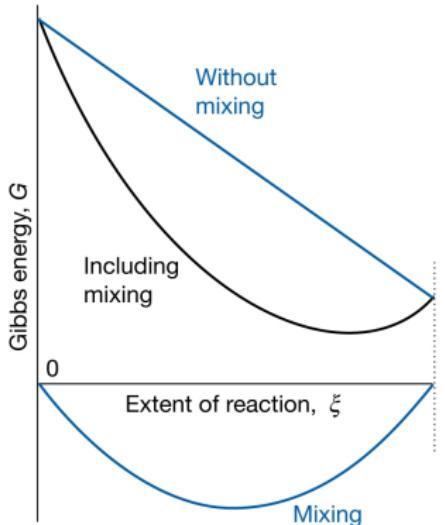
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 - ▶ corresponds to equilibrium composition

dependence of $\Delta_r G$ on Q : $dG = \sum_j \mu_j d\eta_j = \sum_j \nu_j \mu_j d\xi$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p, T} = \sum_j \nu_j \mu_j = \underbrace{\sum_j \nu_j \mu_j^\ominus}_{\Delta_r G^\ominus} + RT \sum_j \nu_j \ln a_j = \Delta_r G^\ominus + RT \ln \overbrace{\prod_j a_j^{\nu_j}}^Q$$

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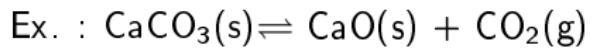
- ▶ molalities, by replacing a_j by $\frac{b_j}{b^\ominus}$ where $b^\ominus = 1 \text{ mol kg}^{-1}$

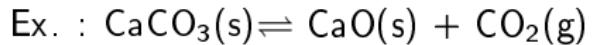
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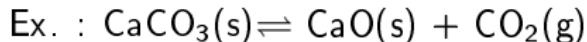
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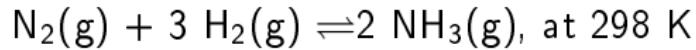
$$K = a_{\text{CaCO}_3(s)}^{-1} \cdot a_{\text{CaO}(s)} \cdot a_{\text{CO}_2(g)} = \frac{\overbrace{a_{\text{CaO}(s)} \cdot a_{\text{CO}_2(g)}}^{=1}}{\underbrace{a_{\text{CaCO}_3(s)}}_{=1}} = a_{\text{CO}_2(g)}$$



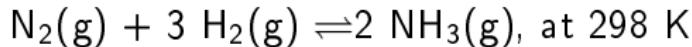
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Provided CO_2 can be treated as a perfect gas, $K = \frac{p_{\text{CO}_2(\text{g})}}{p^\ominus} = p_{\text{CO}_2(\text{g})}$

=numerical value of decomposition vapour pressure of calcium carbonate



$$\Delta_r G^\ominus = 2\Delta_f G^\ominus(\text{NH}_3, g) - [\Delta_f G^\ominus(\text{N}_2, g) + 3\Delta_f G^\ominus(\text{H}_2, g)]$$



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$$\therefore \ln K = -\frac{2 \times (-16.5 \times 10^3)}{8.3145 \times 298} = 6.1 \times 10^5$$

$$K=\tfrac{a_D^{\nu_D}a_C^{\nu_C}}{a_A^{\nu_A}a_B^{\nu_B}}$$

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with $pH = 7$, $\Delta_r G^\oplus = \Delta_r G^\ominus + 7\nu RT \ln 10$

response of equilibria to the conditions

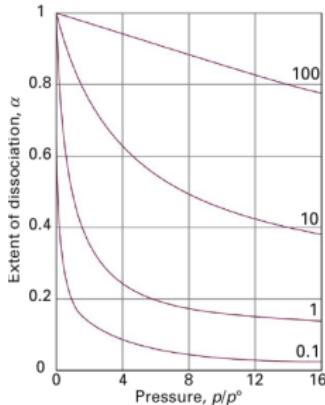
Le Chatelier's principle :

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 $A \rightleftharpoons 2B$

$$\alpha = \sqrt{\frac{1}{1 + \frac{4p}{K_p^\ominus}}}$$

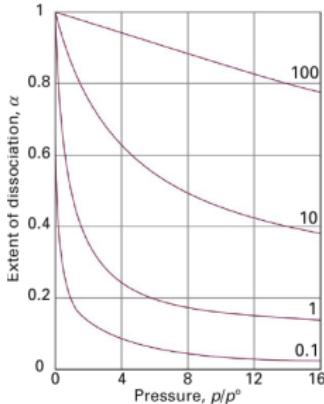


label : K

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$$\alpha = \sqrt{\frac{1}{1 + \frac{4p}{K_p^\ominus}}}$$



even though K is independent of pressure
amounts of A and B do depend on pressure
as p is increased, α decreases

in accord with Le Chatelier's principle

label : K

effect of increase in pressure on ammonia synthesis

$$K = \frac{p_{\text{NH}_3}^2 p^\ominus^2}{p_{\text{N}_2} p_{\text{H}_2}^3} = \frac{x_{\text{NH}_3}^2 p^2 p^\ominus^2}{x_{\text{N}_2} x_{\text{H}_2}^3 p^4} = \frac{K_x p^\ominus^2}{p^2}$$

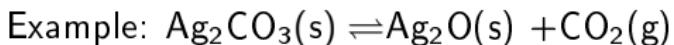
response of equilibria to changes of temperature

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$$

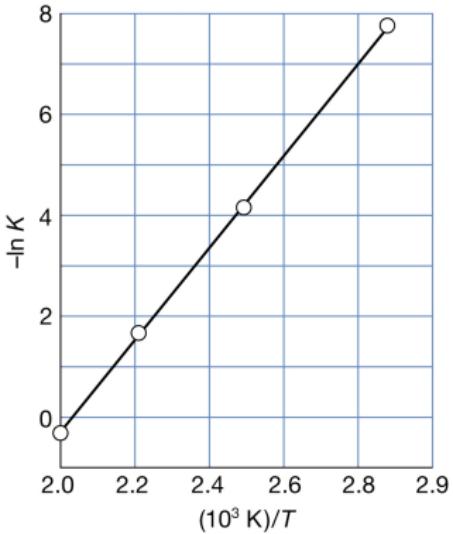
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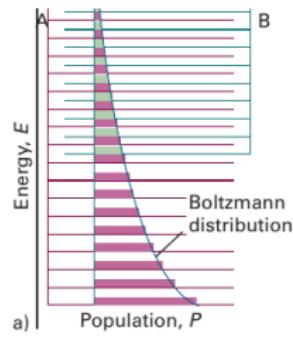
or, $\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_r H^\ominus}{R}$



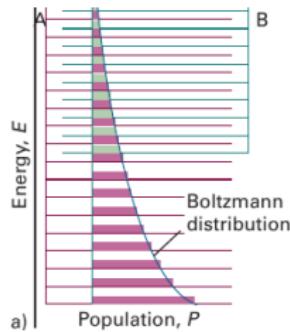
K vs. T(K)



At a given temperature, there is a specific distribution of populations, and hence specific composition of reaction mixture

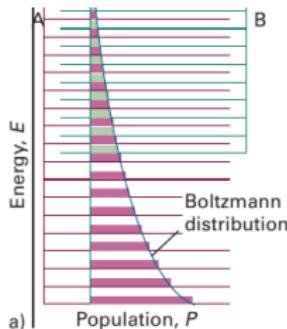


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usually dominant species in a mixture at equilibrium is the one with lower set of energy levels

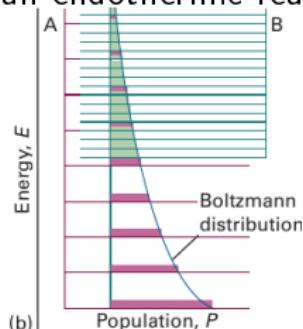
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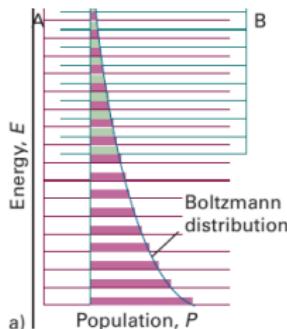
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In a reaction, entropy plays a role as well as energy

an endothermic reaction



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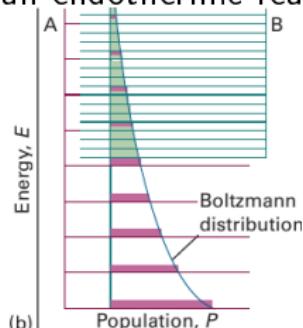


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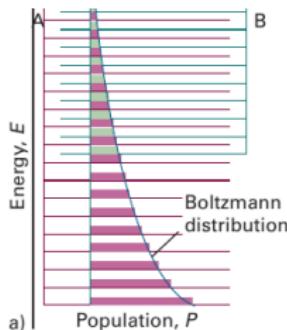
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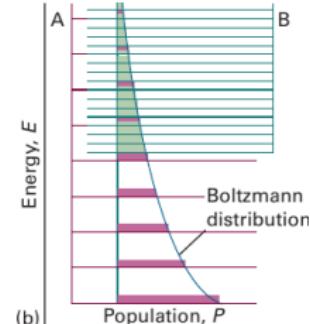


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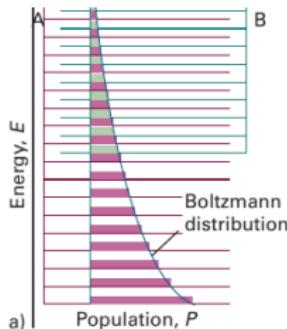
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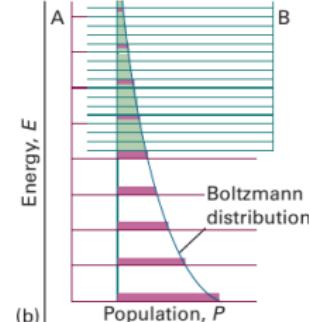
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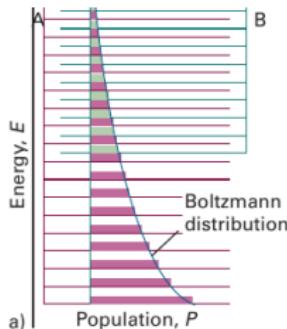


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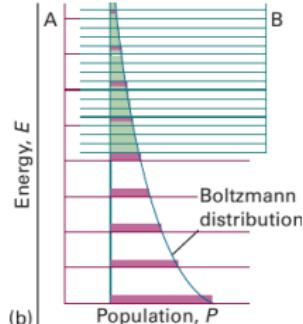
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