

Introduction

PHYS 224 Prof. Heron (pheron@uw.edu) PAC 208

2 midterm + 1 final (Scantron + Cheat Sheet)
HW due Wednesdays 5 p.m. -> box (Starts from 4/10)
Poll 10% + HW 15% + Exams 75%

An Introduction to Thermal Physics Ch 1-6 (Daniel V. Schroder)

3 Models

- Ideal gas
- Ideal paramagnet
- Einstein solid

Apply the 1st law of thermodynamics

$$\Delta U = Q + W \quad \text{Energy is conservative}$$

~ the 2nd law of thermodynamics

$$S \geq \int \frac{dq}{T} \quad \text{Entropy is not conservative}$$

Ch 1 Energy in Thermal Physics

Definition of Temperature

- Operational: what you measure with a thermometer.
- Theoretical: the thing that is the same for two systems after they have been in contact long enough
direct contact with no insulation Larger than the relaxation time

Equilibrium

Type	Quantity
Thermal	$T_1 = T_2$
Mechanical	no large-scale motion (e.g. balloon expansion)
Diffusive	no net particle exchange

Intensive: not depend on the total amount (temperature, pressure, density)
Extensive: depend on the total amount (energy)

Ideal gas: model of real gas provided that variables P, T are not too extreme.

Ideal gas law

(Chemistry) $PV=nRT$

(Physics) $\boxed{PV=NkT}$ <- related to # of particles

Variable Unit

Pressure "P" Pascals $P_a = N/m^2$

Temperature "T" Kelvin (same degree as Celsius, no degree kelvin, S.I. units not capitalize)

Volume "V" m^3

K: Boltzmann's constant $1.38 \times 10^{-23} J/K$

Room temperature: $300 K$ ($?K = T(^{\circ}C) + 273.1$)

Standard atmospheric pressure: $101 kPa$

Control conditions

- Pressure: we can use a container with a piston on top. The total mass of the piston controls the pressure.
- Volume: fix the position AND make sure the container is RIGID
- Temperature: use a thermal reservoir e.g. a big tank of water at the temperature I want to maintain, make sure the container is thermal conducting.

Assumptions of $PV=NkT$

Microscopically:

- The gas is "dilute" (not extremes of pressure, density, temperature.)
- The gas is at equilibrium: a single well-defined value of P and T that describe the entire sample.

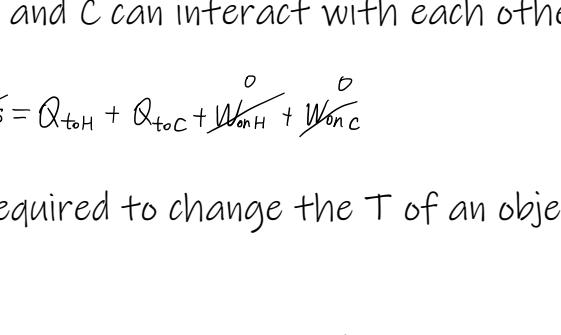
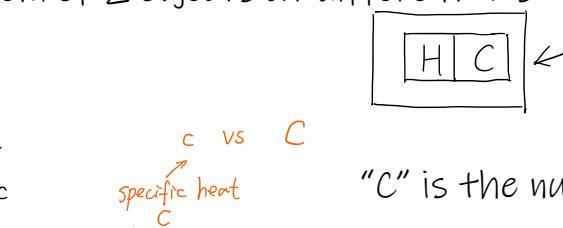
Macroscopically:

- The gas particles are VERY small compared to the distances between them.

- The gas particles do not interact except when they collide; collisions are elastic.

Quiz: Two ideal, monatomic gas particles move toward one another, collide and move apart. The total kinetic energy of the system stays the same; but each particle will typically change speed. (Average would not change.)

Picture a large number of particles with random directions and speeds confined to a rigid container, and they collide with the walls of container.



A monatomic ideal gas particle of mass m traveling with speed v collides with the wall of a container and rebounds with speed v. Taking the positive x-direction to the right, the particle's change in momentum is $-2mv_x$.

$$\overline{P} = \frac{F}{A} = \frac{\Delta p}{\Delta t} = \frac{-2mv_x}{\Delta t}$$

time average

$$\overline{P} = \frac{\overline{F}_{\text{on piston}}}{A} = \frac{-\overline{F}_{\text{on particle}}}{A}$$

(Newton's 3rd Law) $= -m \left(\frac{\Delta v_x}{\Delta t} \right)$ (Newton's 2nd Law)

$\Delta t = \text{time of one round trip} = \frac{2L}{v_x}$

time-average pressure due to a SINGLE particle

$$= -\frac{m}{A} \frac{\Delta v_x}{2L} v_x$$

We also know $\Delta v_x = -2v_x$

$$= \frac{mv_x^2}{A} = \frac{mv_x^2}{V}$$

\overline{P} depends on m, change in momentum of each collision $\propto v_x$, frequency of collisions $\propto v_x$.

$$\begin{cases} \text{for } N \text{ particles, } \overline{P} = \frac{Nmv_x^2}{V} \\ \text{PV} = NkT \end{cases} \Rightarrow \frac{1}{2} Nv_x^2 = \frac{1}{2} kT$$

(translational/kinetic energy only)

$$\overline{k} = \overline{k}_x + \overline{k}_y + \overline{k}_z = \frac{3}{2} kT$$

average kinetic energy of a particle

$$\Rightarrow \frac{1}{2} m V^2 = \frac{3}{2} kT \Rightarrow V_{rms} = \sqrt{\frac{3kT}{m}}$$

(root-mean-square velocity) NOTE: $\overline{v^2} \neq \overline{v}^2$

At temperature T, the average energy associated with each "quadratic degree of freedom" is $\frac{1}{2} kT$

$$x, y, z \Rightarrow v_x, v_y, v_z \text{ (3df)}$$

If the molecule is not monatomic

=> rotational degrees of freedom

=> vibrational - depends on temperature and shape of molecule

$$\text{In General } \boxed{U_{\text{internal}} = Nf \frac{1}{2} kT}$$

f depends on shape = 3 monatomic

of quadratic df = 5* diatomic \Rightarrow at moderate temp

Quiz: A rigid thermally insulating box contains 10 moles of helium gas (monatomic) and 10 moles of oxygen gas (diatomic). The box is divided into two parts by a thermally conducting partition that can move without friction but that does not allow any particles to escape. In equilibrium, the partition should be at the middle. Same T, P, N, so according to $PV=NkT$, V should be the same.

$$\text{But total mass different } V_{rms} = \sqrt{\frac{3kT}{m}} \quad U \text{ is different } \frac{3}{2} NkT \text{ for He} \\ \frac{3}{2} NkT \text{ for O}_2$$

To exert the same pressure with less mass, lighter particles have to move faster.

average change in momentum of each collision \Rightarrow particle flux = # of collisions with container wall / (unit time * unit area) $\Rightarrow \overline{P} = \frac{1}{2} \overline{F} \overline{A}$

Quiz: Two identical thermally insulating containers are filled with the same number of molecules of the same type of ideal gas. The containers are sealed with pistons of mass M that can move without friction but that don't allow any gas to enter or escape.

$$\begin{array}{c} \text{Same } P, V \\ \text{TB} > TA \Rightarrow V_{rmsB} > V_{rmsA} \Rightarrow |\overline{p_B}| > |\overline{p_A}| \end{array}$$

Heat & Work

$$\text{1st law of thermodynamics} \quad \Delta U = Q_{\text{to s}} + W_{\text{on s}} \quad \begin{array}{l} \uparrow \text{heat transfer to system} \\ \downarrow \text{heat done on system} \end{array} \quad U = \text{total + potential} \\ = \frac{1}{2} NkT + 0 \quad (\text{for ideal gas})$$

Energy is conserved.

Q: "Heat" spontaneous flow of energy from higher T to lower T, measured in Joules in the S.I. system.

Consider a system of 2 objects at different T's insulation \Rightarrow H and C can interact with each other but nothing else

$$\Rightarrow Q_{\text{to H}} = -Q_{\text{to C}}$$

c vs C

specific heat = $\frac{C}{M}$

heat capacity

$$1^{\text{st Law}} \Rightarrow \Delta U_{\text{sys}} = Q_{\text{to H}} + Q_{\text{to C}} + W_{\text{on H}} + W_{\text{on C}}$$

"C" is the number of Joules required to change the T of an object by 1 K

$$= \dots$$

Quiz: $C_H = C_C \Rightarrow \frac{T_H - T_{\text{initial}}}{T_C - T_{\text{initial}}} = -1$

$$\Rightarrow T_F = \frac{C_H T_H + C_C T_C}{C_H + C_C}$$

Special Cases

$$\text{① } C_H = C_C \Rightarrow \frac{T_H - T_{\text{initial}}}{2} = 0$$

$$\text{② } C_H > C_C \Rightarrow T_F = \frac{C_H T_H + C_C T_C}{C_H + C_C} \approx T_H \quad (\text{reservoir})$$

Quiz: A beaker of water contain a copper cube (200 J/K) and an aluminum cube (100 J/K). The water and the cubes are in thermal equilibrium at 80°C . The cubes are then placed in a singer beaker of water that is initially at 20°C . The heat transfer from the copper is greater. $\Delta T_{\text{cu}} > \Delta T_{\text{Al}}$

A related concept in "Latent Heat": number of Joules required to change the phase of 1 kg of a substance.

e.g. 1 kg ice \leftrightarrow water

Quiz: Consider mixing 1 kg of water at 50°C and 1 kg of ice at 0°C . Water is 4.2 kJ/kg K. Ice is 2.2 kJ/kg K. Latent heat (ice \rightarrow water) = 333 kJ/kg. After the mixture reaches equilibrium, water is between 1 kg and 2 kg.

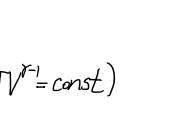
Work $dW_{\text{sys}} = \vec{F}_{\text{sys}} \cdot d\vec{x}$ \Rightarrow $W = \int \vec{F}_{\text{sys}} \cdot d\vec{x}$ \Rightarrow $W = -\int \vec{F}_{\text{ext}} \cdot d\vec{x}$ \Rightarrow $W = -\int F \cos \theta dx$

small displacement of point of application of the force

Application of gas

o container has x-sectional area A

o piston exerts a force on the gas = Force exerted by gas on piston



$F_{\text{gas}} = PA$ \leftarrow to left

if piston moves to left on amount dx

$$dW_{\text{gas}} = PAdx \quad \text{+ve} \quad dW_{\text{ext}} = -PAdx \quad dV = -Adx \quad (V \text{ decreases})$$

If the process is quasistatic, a series of steps between equilibrium states.

For an ideal gas $PV=NkT$ is valid at my interest.

$$\boxed{W = -\int p dV}$$

If an ideal gas process is quasistatic we can present it with a solid line on a PV-diagram

$\Rightarrow \Delta U = Q_{\text{to s}} + W_{\text{on s}}$

heat transfer to system work done on system

$U = \text{total + potential} = \frac{1}{2} NkT + 0 \quad (\text{for ideal gas})$

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Special Cases

o isothermal \Rightarrow constant T \Rightarrow constant U \Rightarrow Q+W=0 \Rightarrow Q=-W

o isobaric \Rightarrow constant P \Rightarrow W=PΔV

o isochoric \Rightarrow constant V \Rightarrow W=0 \Rightarrow ΔU=Q

o adiabatic \Rightarrow no Q (fast and/or insulated) \Rightarrow ΔU=W

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Ch 2 The Second Law

The second law of thermal physics exploits why heat flows from hot to cold and not the other way around, and why the gas expands to fill the container instead of occupying only part.

Review the 2-state system. For example, a coin can have 1 of 2 states: Heads or Tails.

Imagine 3 coins: Penny(H/T) Nickel(H/T) Dime(H/T) $2^3=8$ possibilities => microstates μ states

E.g. HTH is a μ state 2H is a macrostate.

If the coins are fair, all μ states are equally probable; all macrostates are NOT => Most probable has the most μ states

Number of μ states associated with a macrostate is "multiplicity" denoted Ω e.g. $\Omega(2H, 1T)=3$

Probability of obtaining 2H is $P(2H)=\frac{\Omega(2H)}{\Omega(2H)+\Omega(1H)+\Omega(2H)+\Omega(3H)}=\frac{3}{8}$

$$\Omega(nH \text{ out of } N \text{ coins}) = \binom{N}{n} = \frac{N!}{n!(N-n)!}$$

Quiz: A section of a classroom has three seats occupied by 2 Sophomores and 1 Junior. 3 ways this can happen. (Assume all Sophomores are interchangeable and all Juniors are interchangeable.)

A section of a classroom has three seats. A total of 2 Easter eggs are hidden under these three seats. 6 ways this can happen. (Assume all Easter eggs are interchangeable.) (2 armrests=3 seats-1)+2 eggs => 4 objects

$$\begin{array}{c} 3 \\ 2 \quad 0 \quad 0 \rightarrow 0 \quad 0 \quad 1 \\ 1 \quad 1 \quad 0 \quad 0 \quad 0 \quad 1 \\ 1 \quad 0 \quad 1 \quad 0 \quad 0 \quad 1 \\ 0 \quad 1 \quad 1 \quad 0 \quad 0 \quad 1 \\ 0 \quad 2 \quad 0 \quad 0 \quad 1 \quad 1 \\ 0 \quad 0 \quad 2 \quad 0 \quad 1 \quad 1 \end{array} \quad \frac{4!}{2!2!} = \frac{(2+3-1)!}{2!(3-1)!} = 6$$

Einstein model for a solid

$$\text{an atom has } K = \frac{1}{2} m (V_x^2 + V_y^2 + V_z^2) \quad \text{Einstein model: } \text{atoms are } \text{small } \text{and } \text{far} \text{ apart}$$

$$P.E. = \frac{1}{2} K (x^2 + y^2 + z^2)$$

For N atoms => $6N$ numbers to calculate energy

Einstein suggests treating atoms as quantum mechanical harmonic oscillators. One oscillator has an integer number of units $\hbar\omega$

$$\hbar\omega = \frac{\hbar}{2\pi} \omega \quad (\hbar = \text{Planck's constant } 6.63 \times 10^{-34} \text{ Js} \quad \omega = \text{angular frequency})$$

$$E = \hbar\omega(n_x + \frac{1}{2}) + \hbar\omega(n_y + \frac{1}{2}) + \hbar\omega(n_z + \frac{1}{2})$$

$$= \sum_i \hbar\omega(n_i + \frac{1}{2}) \Rightarrow 3N \text{ integers}$$

"an integer associate with one oscillator"

Ex. 1 atom + 4 energy units => 3 "oscillators" + 4 energy units => 15 unique arrangements

3 oscillators -> 2 "armrests" $\frac{(4+3-1)!}{4!(3-1)!} = 15$

4 energy units -> 4 "Easter eggs" $\frac{(4+3-1)!}{4!(3-1)!} = 15$

For N oscillators ($N/3$ atoms) and q energy units $\Omega(N, q) = \frac{(q+N-1)!}{q!(N-1)!}$

Interacting systems: put Einstein solids in contact => can exchange energy

$$\boxed{A} \quad \boxed{B} \quad U_{\text{total}} = (q_A + q_B) \text{ energy units}$$

$$N_A q_A \quad N_B q_B \quad \text{fixed}$$

$$\Omega_{AB} = \Omega_A + \Omega_B \quad P(U_A, U_B) = \frac{\Omega_A(U_A) \Omega_B(U_B)}{\sum \Omega_{AB}}$$

"macropartition" specifies q_A and q_B

Fundamental assumption of statistical mechanics: in an isolated system, in thermal equilibrium, all accessible μ states are equally probable.

$$\text{Ex. } N_A = N_B = 3 \quad U_{\text{total}} = 6E$$

$$\Omega_{AB}(2,4) = \Omega_A(2) \Omega_B(4) = \frac{(2+3-1)!}{2!(3-1)!} \frac{(4+3-1)!}{4!(3-1)!} = 90$$

$$\sum \Omega_{AB} = \Omega_{AB}(0,6) + \dots + \Omega_{AB}(6,0) \text{ or } \frac{(q_{\text{total}}+1)(q_{\text{total}}-1)!}{q_{\text{total}}!(q_{\text{total}}-1)!} = 462$$

$$P(2,4) = \frac{90}{462}$$

Irreversibility: if a large system is not in the most probable macrostate it will rapidly and inevitably move there and then stay there.

Quiz: Assume two systems are in thermal contact. System A has twice as many particles as System B. Initially each one has the same amount of thermal energy. Eventually, the two systems will have the same amount of energy per particle. highest probability macropartition $q_A/N_A = q_B/N_B$

e.g. same temperature

ex. 2 Einstein solids $N_A = N_B = 750 \quad U = 1000E$

if we start in a low-probability macrostate $U_A = 12E \quad U_B = 98E$

bring them into contact and exchange 1 energy unit

$$\frac{P(A \rightarrow B)}{P(B \rightarrow A)} = \frac{\Omega_{AB}(11,98)}{\Omega_{AB}(13,78)} = 0.75 \times 10^{-3}$$

energy flows from hotter to colder because that's where the μ states are.

Large and extra large numbers

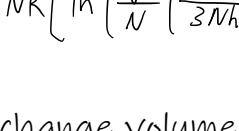
large number $\sim 10^{23}$

extra large number

if N is extra large AND

\rightarrow We can write Ω as $\Omega_{\text{max}} e^{-N(\frac{U}{kT})^2}$

\rightarrow Gaussian function with a sharp peak at $x=0$



if we have 2 Einstein solids of N oscillators each
(i.e. $q_A = q_B$)

Ideal gas

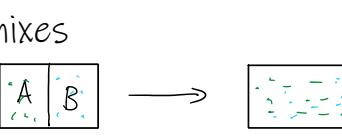
μ states: we know $x \propto z$ and $p_x p_y p_z$ for each and every molecule.

more volume => more μ states $\Omega \propto V$

more momentum => more volume in momentum-space $\Omega \propto V_p$



Imagine a SPHERE in p-space:



We also know that $p_x^2 + p_y^2 + p_z^2 = 2mU \Rightarrow \text{radius} = \sqrt{2mU}$

$$K = \frac{p^2}{2m}$$

Heisenberg's uncertainty principle gives us a constant bound on $\Delta x \Delta p_x \approx \hbar$

6-D hypersphere

$$2 \text{ molecules: } \frac{p_x^2 + p_y^2}{2m} = 2mU \Rightarrow \Omega \propto \frac{V^2}{2! \hbar^6} \text{ indistinguishable}$$

$$N \text{ molecules: } \Omega_N = \frac{1}{N!} \frac{V^N}{\hbar^N} \times \text{volume of a } 3N\text{-dimensional spherical shell of radius } \sqrt{2mU}$$

$$= \frac{1}{N!} \frac{V^N}{\hbar^N} \frac{4\pi^{3N/2}}{(3N/2)!} \text{ mass of one particle}$$

$$= f(N) V^N U^{3N/2} \text{ number of molecules} \text{ volume} \text{ total energy} \leftrightarrow \text{temperature}$$

Ideal paramagnet $\Omega = \frac{N!}{N_A! N_B!}$

Entropy

2 statements of the 2nd Law of Thermodynamics

Any large system will be found in the macrostate with the greatest multiplicity

Multiplicity tends to increase

Define entropy "S" $S = k \ln \Omega$ ($k = \text{Boltzmann const } 1.38 \times 10^{-23} \text{ J/K}$)

Unit: J/K

$$\Omega_{AB} = \Omega_A \Omega_B$$

$$S_{AB} = S_A + S_B$$

reversible process: no net change in entropy

irreversible process: net increase in entropy

adiabatic free expansion -> irreversible -> $\Delta S > 0$

Entropy of ideal gas (Sackur-Tetrode equation)

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nk} \right)^{3/2} \right) + \frac{\Sigma}{2} \right] \quad U = \frac{1}{2} NkT$$

If we change volume at fixed N, U

$$\Delta S = S_f - S_i = Nk \left[\ln \left(\frac{V_f}{V_i} \right) \right] - Nk \left[\ln \left(\frac{V_i}{V_f} \right) \right]$$

stay the same

$$= Nk \ln \left(\frac{V_f}{V_i} \right)$$

e.g. adiabatic free expansion example $\Delta S = Nk \ln 2$

isothermal expansion $\Delta U = 0$ ($Q = W$)

Entropy of mixes

$$V_A = V_B$$

$$N_A = N_B$$

entropy increases $\Delta S = \Delta S_A + \Delta S_B$

$$= Nk \ln \left(\frac{V_f}{V_i} \right) + Nk \ln \left(\frac{V_f}{V_i} \right)$$

$$= 2Nk \ln 2$$

Same gas on both sides!

No change in entropy

$$\text{Initially: } S = S_L + S_R = 2Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nk} \right)^{3/2} \right) + \frac{\Sigma}{2} \right]$$

$$= 2Nk \left[\ln \left(\frac{V}{2N} \left(\frac{4\pi m U}{3Nk} \right)^{3/2} \right) + \frac{\Sigma}{2} \right]$$

$$2N, 2U, V: S = 2Nk \left[\ln \left(\frac{V}{2N} \left(\frac{4\pi m U}{3Nk} \right)^{3/2} \right) + \frac{\Sigma}{2} \right]$$

$$= 2Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nk} \right)^{3/2} \right) + \frac{\Sigma}{2} \right] - 2Nk \ln 2$$

Same as entropy when the particles were on either sides of partition.

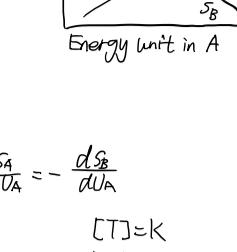
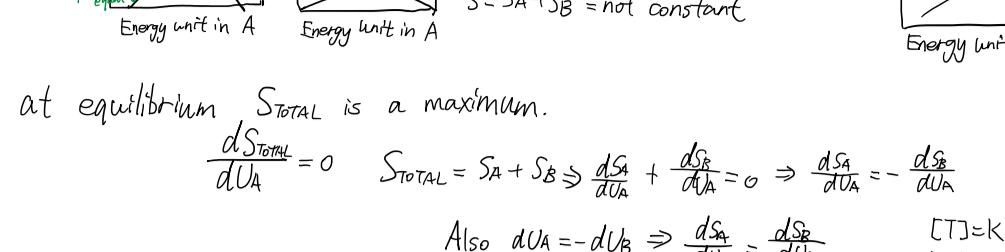
Reversible & irreversible processes

Processes that create entropy are irreversible => there is no process that can completely remove the new entropy from the universe.

Processes that don't create entropy are reversible but in reality we can only approximate these processes.

Ch.3 Interactions and Implications

Temperature



at equilibrium S_{TOTAL} is a maximum.

$$\frac{dS_{TOTAL}}{dU_A} = 0 \quad S_{TOTAL} = S_A + S_B \Rightarrow \frac{dS_A}{dU_A} + \frac{dS_B}{dU_A} = 0 \Rightarrow \frac{dS_A}{dU_A} = -\frac{dS_B}{dU_A}$$

Also $\frac{\partial U_A}{\partial T} = -\frac{\partial S_A}{\partial T} \Rightarrow \frac{dS_A}{dU_A} = \frac{dS_B}{dU_B}$

If we define $T \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$ $\Rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$

Greater slope \Rightarrow lower temperature

Function of time: reaches equilibrium

Measuring Entropy

$$dS = \frac{dU}{T} \quad \text{small change in energy}$$

change in entropy $\Delta S = \frac{\alpha}{T}$ \leftarrow temp of the system

$= \frac{\alpha}{C_V \frac{dT}{T}}$ (no change in $V \Rightarrow$ no W)

$= \frac{\alpha}{C_V \frac{dT}{T}}$ heat capacity at constant V

$$\Rightarrow \Delta S = \int_0^{T_f} \frac{C_V dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right)$$

$$\text{Let } T_i=0, S(T_f) - S(0) = C_V \ln T_f - C_V \ln 0$$

\uparrow 0 at absolute 0, not entropy

$$\text{ex. } \boxed{H} \xrightarrow{Q} \boxed{C} \quad \Delta S_H = \frac{Q_H}{T_H} \quad \Delta S_C = \frac{Q_C}{T_C}$$

$$Q_H = Q_C$$

$$T_H > T_C$$

$$\Rightarrow |\Delta S_H| < |\Delta S_C|$$

\Rightarrow the cold object gains more entropy than the hot object loses.

$$\Rightarrow \Delta S_{\text{universe}} = \Delta S_H + \Delta S_C > 0$$

in limit that $T_H = T_C$, $|\Delta S_H| = |\Delta S_C|$ & $\Delta S_{\text{universe}} \rightarrow 0$

if two things exchange heat but they are at different temperatures then the changes in entropy will not be the same.

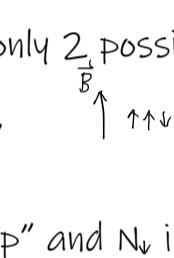
Quiz:

Process 1: N molecules of an ideal gas at room temperature expands into a vacuum in a container that is thermally insulated.

Process 2: N molecules of an ideal gas is in a cylinder sealed with a frictionless piston that has a pile of sand on it. The cylinder is at room temperature and is not insulated. Grains of sand are removed one at a time until the volume has doubled.



(adiabatic free expansion)



(isothermal expansion)

For both, $T_f = T_i$

$$V_f = 2V_i$$

$$P_f = \frac{1}{2} P_i$$

① Process 2 is reversible \Leftarrow same temperature

② $\Delta S_1 = \Delta S_2 \Leftarrow S$ is a state function

adiabatic free expansion

$$Q_{to} = 0$$

$$W_{av} = 0$$

$$\Delta U = 0$$

$$\left\{ \begin{array}{l} \Delta S_{\text{gas}} \\ \Delta S_{\text{env}} \\ \Delta S_{\text{universe}} \end{array} \right\} \begin{array}{l} \textcircled{+} > \alpha \\ 0 \\ + \end{array}$$

Reversible? NO

Quasistatic adiabatic expansion (isentropic)

$$0$$

$$-$$

$$-$$

$$0$$

YES

Quasistatic isothermal expansion

$$+$$

$$-$$

$$0$$

YES

$$\text{In general, } \Delta S_{\text{system}} \geq \int \frac{dQ_{to}}{T} \Rightarrow \text{adiabatic free expansion } \int \frac{dQ_{to}}{T} = 0$$

The ideal paramagnet

a system of independent magnetic dipoles \Rightarrow they don't interact with each other

Spin 1/2 particles: magnetic dipoles have only 2 possible (because quantum) orientations:

\sim parallel to applied field \uparrow "up" \uparrow "down"

If we have N dipoles, N_u is the number "up" and N_d is the number "down" $\Rightarrow N_u + N_d = N$

Microstate: $\Omega = \frac{N!}{N_u! N_d!}$ we know the orientation of every dipole.

Macrostate: we know how many are up and how many are down.

Energy $U = -\vec{\mu} \cdot \vec{B} \Rightarrow U_{\uparrow} = -\mu B$ and $U_{\downarrow} = \mu B \Rightarrow U_{\uparrow}$ is lowest

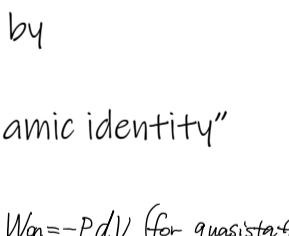
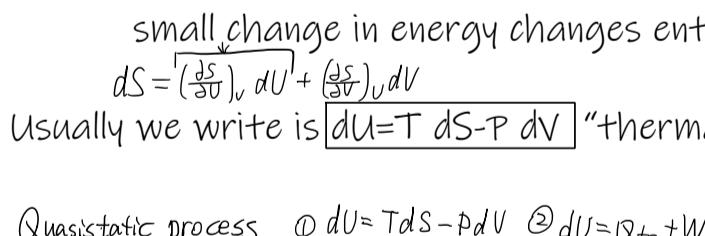
Lowest energy macrostate is $U_{\uparrow}=N$, and the highest energy is making all down.

$U = -\mu B(N-2N_{\uparrow})$

"magnetization" $M = \mu(N_{\uparrow} - N_{\downarrow})$

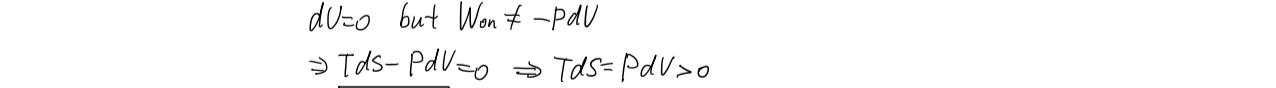
When they are all up or all down, $S=0$.

when $N_{\uparrow} = N_{\downarrow} = N/2 \Rightarrow U=0 \Rightarrow S \text{ max}$



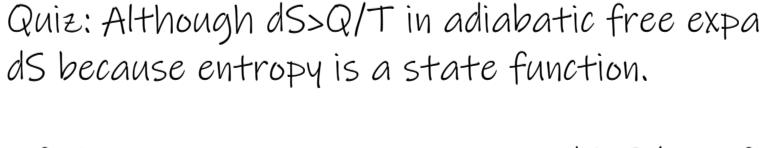
as $T \rightarrow \infty$ the paramagnet will give energy to basically any other system because the other system will gain entropy and the paramagnet's entropy won't change much (S is a max)

when $T < 0$, if the paramagnet gains energy it loses entropy, so it can't gain energy from a system that will also lose entropy in this transaction.



At $T < 0$, the ideal paramagnet will give energy to any normal substance regardless of $|T_p|$ and $|T_{\text{normal}}|$.

Two paramagnet systems



Quiz S

T is positive, $|T|$ is decreases (decreases)

Mechanical equilibrium and pressure (thermal equilibrium and temperature)

Thermal conducting partition that can move without friction but doesn't allow particle to move from side to side. System can exchange volume and energy but not particles.

We know $V_A + V_B = \text{const}$, $U_A + U_B = \text{const}$, N_A and N_B is fixed.

Also know at equilibrium S_{TOTAL} is a maximum, at equilibrium: $P_A = P_B$ and $T_A = T_B$

$$\frac{\partial S_{TOTAL}}{\partial U_A} = 0 \quad \frac{\partial S_{TOTAL}}{\partial V_A} = 0 \Rightarrow \frac{\partial S_{TOTAL}}{\partial U_A} = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 \Rightarrow \frac{\partial S_A}{\partial U_A} = -\frac{\partial S_B}{\partial U_A}$$

$$\text{but } dV_A = -dV_B$$

$$\Rightarrow \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

$$\frac{\partial S}{\partial U} = \frac{\partial S}{\partial U_A} + \frac{\partial S}{\partial U_B}$$

e.g. A short but violent force on piston: $W_{on} = FA > -PdV$

$$\text{In general } dS \geq \frac{Q}{T}$$

Quiz: Although $dS > Q/T$ in adiabatic free expansion and $dS = Q/T$ in isothermal expansion, at the end same $P, V, T \Rightarrow$ same dS because entropy is a state function.

If the process is quasistatic use $dS = Q/T$. If it is not quasistatic, find an equivalent process that is quasistatic, calculate $dS = Q/T$ for that process.

Diffusive equilibrium and chemical potential

Allow them to exchange energy and particles. If they are in diffusive equilibrium (i.e., no net flow of particles from one side to the other), what quantity is the same for both sides?

At equilibrium S_{TOTAL} is a maximum, $\frac{\partial S_{TOTAL}}{\partial N_A, V_A} = 0 \Rightarrow \frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_A} = 0 \Rightarrow dN_A = -dN_B$

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

$$\Rightarrow -T \frac{\partial S_A}{\partial N_A} = T \frac{\partial S_B}{\partial N_B} \quad \text{for thermal and diffusive equilibrium}$$

$$\Rightarrow T \frac{\partial S}{\partial N} = 0$$

e.g. A short but violent force on piston: $W_{on} = FA > -PdV$

$$\text{In general } dS \geq \frac{Q}{T}$$

$$-T_A \frac{\partial S_A}{\partial N_A} > -T_B \frac{\partial S_B}{\partial N_B}$$

$$\frac{\partial S_A}{\partial N_A} < \frac{\partial S_B}{\partial N_B}$$

\Rightarrow spontaneous transfer from "high" to "low" μ system will occur

When two samples interact:

The sample with higher μ will lose N . $\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$

The sample with higher P will gain V . $P = T \left(\frac{\partial S}{\partial V}\right)_{U,N}$

The sample with higher T will lose U . $T = -\frac{1}{S} \left(\frac{\partial S}{\partial U}\right)_{N,V}$

$$\Rightarrow dU = T dS - P dV + \mu dN \quad \text{Quasistatic identity}$$

$$\Rightarrow dU = T dS - P dV + \mu dN \quad \text{Thermal identity}$$

Quiz: If the number of particles in a sample of ideal gas increases but its volume and entropy are constant, the energy must decrease. (μ is negative)

□ Chapter 4 Heat Engines

- a heat engine is a device that operates in a CYCLE in which a "working substance" absorbs heat and convert PART OF that heat to work
- W_{out} will be negative $\Rightarrow W_{\text{in}}$ will be positive

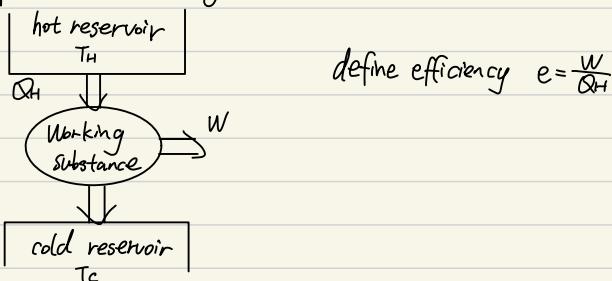
$$1^{\text{st}} \text{ Law} \Rightarrow \text{in a cycle } \Delta U = Q_{\text{in}} + W_{\text{out}} = 0$$

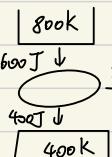
Q_H heat transformed to working substance from a HOTTER system

Q_C heat transformed ... from a COLDER system

$$Q_H - Q_C - W = 0$$

○ A hypothetical heat engine

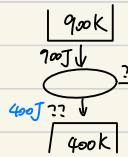


Quiz: 

$$\Delta S = 0 \leftarrow \Delta U = 0 \quad (\text{U and S are state functions})$$

$$\frac{Q_H}{T_H} - \frac{Q_C}{T_C} = -0.25 \text{ J/K} < 0 \quad \Delta S \geq \frac{Q}{T}$$

$$\Delta S = \frac{Q_H}{T_H} + S_{\text{produce}} - \frac{Q_C}{T_C} = 0$$

Quiz: 

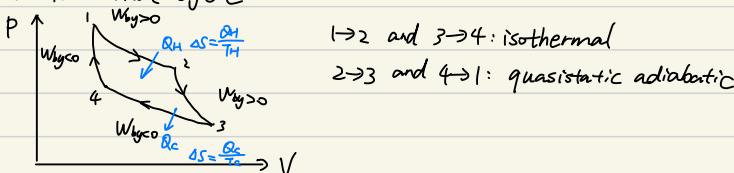
Loss at least 1 J/K.

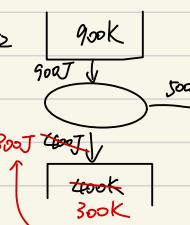
if there are no irreversible processes, then $\frac{Q_H}{T_H} = \frac{Q_C}{T_C} \Rightarrow e = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$

if there are irreversible processes, then $\frac{Q_H}{T_H} < \frac{Q_C}{T_C}$ and $e < 1 - \frac{Q_C}{Q_H}$

$$\Rightarrow e \leq 1 - \frac{T_C}{T_H}$$

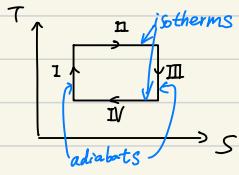
○ Applied to Carnot Cycle



Quiz: 

$$-\frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0$$

$$\epsilon_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$$



Quiz: 800K

900J \downarrow



400J \downarrow

400K

It could not work.

$$\textcircled{1} \text{ 1st law: } 900 - 400 = 500 \text{ J} \quad \checkmark$$

$$\textcircled{2} \text{ } e = \frac{W}{Q_H} = \frac{5}{9} > e_{\text{Carnot}} \times$$

$$1 - \frac{T_C}{T_H} = 0.5$$

$$S_{\text{out}} < S_{\text{in}}$$

o Summary of how to calculate ΔS :

Do you know the equation for S as a function of N, T, V, \dots ?

\checkmark no

\downarrow yes

Is the process reversible?

\checkmark yes

$$\text{Use } \Delta S = \int \frac{dQ}{T} = \int \frac{C dT}{T}$$

Do you know N, T, V for both initial and final states?

\checkmark yes

no

Find a REVERSIBLE process that has the same initial and final states and use $\Delta S = \int \frac{dQ}{T}$

$$\text{Use the equation } \Delta S = S_f - S_i$$

Q, dQ are the same.

If N is fixed, suppose monatomic ideal gas, $S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nk} \right)^{3/2} \right) + \frac{5}{2} \right] = Nk \ln \left(\frac{V_f}{V_i} \frac{N \sqrt{U_f}}{U_i^{3/2}} \right)$

- Isothermal quasistatic expansion

$$\textcircled{1} \text{ } U \uparrow \text{ } V \uparrow \text{ } \Delta S = Nk \ln \left(\frac{V_f}{V_i} \right)$$

\textcircled{2} Since quasistatic and reversible

$$\begin{aligned} \Delta S &= \int \frac{dQ}{T} \text{ but } \Delta U = Q + W \Rightarrow Q = -W \text{ and } W = -PV \\ &\therefore \\ &= \int \frac{P dV}{T} \\ &= Nk \int \frac{dV}{V} \\ &= Nk \ln \left(\frac{V_f}{V_i} \right) \end{aligned}$$

- quasistatic adiabatic expansion

$$\textcircled{1} \text{ } U \uparrow \text{ } V \uparrow$$

$$\Delta S = Nk \ln \left(\frac{V_f U_f^{3/2}}{V_i U_i^{3/2}} \right) = 0$$

because

$$\left(\frac{V_f}{V_i} \right)^{3/2} \rightarrow \left(\frac{T_f}{T_i} \right)^{3/2}$$

$VT^{3/2}$ is constant for an adiabatic quasistatic process (from chapter 1).

$$\textcircled{2} \Delta S = \int \frac{dQ}{T} = 0$$

- quasistatic isochoric (aka constant volume) heating

$$\textcircled{1} \text{ } U \uparrow \text{ } V \uparrow$$

$$\Delta S = Nk \ln \left(\frac{V_f}{V_i} \right)^{3/2} = Nk \ln \left(\frac{T_f}{T_i} \right)^{3/2} = \frac{3}{2} Nk \ln \left(\frac{T_f}{T_i} \right)$$

$$\textcircled{2} \Delta S = \int \frac{dQ}{T} = \int \frac{C_v dT}{T} = \frac{3}{2} Nk \ln \left(\frac{T_f}{T_i} \right) \text{ since } C_v = \frac{3}{2} Nk \text{ for an ideal monatomic gas.}$$

- quasistatic isobaric (aka constant pressure) expansion.

$$\textcircled{1} \text{ } U \uparrow \text{ } V \uparrow$$

$$\Delta S = Nk \ln \left(\frac{V_f U_f^{3/2}}{V_i U_i^{3/2}} \right) = Nk \ln \left(\frac{V_f T_f^{3/2}}{V_i T_i^{3/2}} \right) = Nk \ln \left(\frac{T_f^{5/2}}{T_i^{5/2}} \right) = \frac{5}{2} Nk \ln \left(\frac{T_f}{T_i} \right)$$

$$PV = nRT: \text{constant } P \rightarrow \text{constant } \frac{1}{V} \Rightarrow VT^{3/2} = \frac{V}{T} T^{5/2} = \text{const. } T^{5/2}$$

$$\textcircled{2} \Delta S = \int \frac{dQ}{T} = \int \frac{C_p dT}{T} = \frac{5}{2} Nk \ln \left(\frac{T_f}{T_i} \right) \text{ since } C_p = \frac{5}{2} Nk \text{ for a monatomic ideal gas.}$$

Quiz: System 1

System 2

$$\begin{array}{|c|c|} \hline T_H & T_C \\ \hline \end{array}$$

$N_{\text{left}} = N_{\text{right}} = N$

insulating

$$(T_H + T_C)/2$$

\uparrow

$2N$

$$\left\{ \begin{array}{l} U_1 = U_2 \\ S_1 < S_2 \end{array} \right.$$

$$\Delta S = \int \frac{dQ}{T} \uparrow$$

□ Chapter 5 Free energy and chemical dynamics

$$\boxed{T_H \quad T_C} \leftarrow \text{more "free energy"}$$

"Free energy" energy available to do work

H "enthalpy" $\equiv U + PV$: total energy used to create a system of energy U out of nothing in a constant pressure environment.

F "Helmholtz free energy" $\equiv U - TS$: total energy needed to create a system of energy U out of nothing in a constant T .

G "Gibbs free energy" $\equiv H - TS = F + PV$

$$\begin{array}{|c|c|} \hline U & F \\ \hline H & G \\ \hline \end{array} \xrightarrow{+PV} \xrightarrow{-TS}$$

U, F, H, G are called "thermal/dynamic potential."

- Enthalpy & changes at constant P

$$\begin{aligned} H &\equiv U + PV \rightarrow dH = dU + PdV + VdP \\ &= dU + PdV \\ &= dQ - PdV + W_{\text{other}} + PdV \\ &= dQ + W_{\text{other}} \end{aligned}$$

if $W_{\text{other}} = 0$ (e.g. no electrical work)

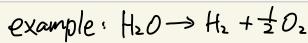
$$\begin{aligned} dH &= dQ \\ \Rightarrow G_p &= \frac{dQ}{dT} = \left(\frac{dH}{dT}\right)_P \end{aligned}$$

- Gibbs free energy & constant T , constant P process

$$\begin{aligned} G &\equiv U + PV - TS \\ dG &= dU + PdV + VdP - TdS - SdT \\ &= dU + PdV - TdS \\ &= dQ + W_{\text{other}} - PdV + PdV - TdS \end{aligned}$$

we know that $dQ - TdS \leq 0$

$$dG \leq W_{\text{other}}$$



$$\begin{array}{lcl} \Delta G = \Delta H - T\Delta S & | & \Delta H = 286 \text{ kJ for one mole at room } T \text{ and } 1 \text{ atm} \\ = 286 \text{ kJ} - 298 \text{ K} \times (131 + \frac{1}{2}205 - 70) \text{ J/K} & | & S(H_2) = 131 \text{ J/K} \\ = 237 \text{ kJ} & | & S(O_2) = 205 \text{ J/K} \end{array}$$

\Rightarrow We need to supply 237 kJ of W_{other} to make this happen (by electrodes)

$$\begin{array}{ccc} \uparrow P\Delta V = 4 \text{ kJ} & \leftarrow \text{calculate using } V \text{ of 1.5 mol of ideal gas at } P = 1 \text{ atm} \\ 237 \text{ kJ} \rightarrow \boxed{\Delta U = 282 \text{ kJ}} & \leftarrow T\Delta S = 49 \text{ kJ} \end{array}$$

○ More thermal dynamic identities

$$dU = TdS - PdV + \mu dN \quad \textcircled{1}$$

$$\left\{ \begin{array}{l} H = U + PV \end{array} \right.$$

$$\left\{ \begin{array}{l} dH = dU + PdV + VdP = TdS - PdV + \mu dN + PdV + VdP \end{array} \right.$$

$$\left\{ \begin{array}{l} dH = TdS + VdP + \mu dN \quad \textcircled{2} \end{array} \right.$$

$$\left\{ \begin{array}{l} F = U - TS \end{array} \right.$$

$$\left\{ \begin{array}{l} dF = dU - TdS - SdT = TdS - PdV + \mu dN - TdS - SdT \end{array} \right.$$

$$\left\{ \begin{array}{l} dF = -SdT - PdV + \mu dN \quad \textcircled{3} \end{array} \right. \Rightarrow \left(\frac{\partial F}{\partial T} \right)_{VN} = -S \quad \left(\frac{\partial F}{\partial V} \right)_{TN} = -P \quad \left(\frac{\partial F}{\partial N} \right)_{TV} = \mu$$

$$\left\{ \begin{array}{l} G = U - TS + PV \end{array} \right.$$

$$\left\{ \begin{array}{l} dG = dU - TdS - SdT + PdV + VdP = TdS - PdV + \mu dN - TdS - SdT + PdV + VdP \end{array} \right.$$

$$\left\{ \begin{array}{l} dG = -SdT + VdP + \mu dN \quad \textcircled{4} \end{array} \right. \Rightarrow \left(\frac{\partial G}{\partial T} \right)_{PN} = -S \quad \left(\frac{\partial G}{\partial P} \right)_{TN} = V \quad \left(\frac{\partial G}{\partial N} \right)_{TP} = \mu$$

Qniz: Raise water from 25°C to 26°C, $S = 70 \text{ J/K}$.

$$\Delta G = \left(\frac{\partial G}{\partial T}\right)_{N,P} \cdot \Delta T = -S \cdot \Delta T = -70 \text{ J}$$

Qniz: $R = R(C, F)$ and $dR = B dC + E dF \Rightarrow dR = \left(\frac{\partial R}{\partial C}\right)_F dC + \left(\frac{\partial R}{\partial F}\right)_C dF$
 $B = \left(\frac{\partial R}{\partial C}\right)_F \Rightarrow \left(\frac{\partial B}{\partial F}\right)_C = \frac{\partial^2 R}{\partial F \partial C}$ $E = \left(\frac{\partial R}{\partial F}\right)_C \Rightarrow \left(\frac{\partial E}{\partial C}\right)_F = \frac{\partial^2 R}{\partial C \partial F}$
 \Rightarrow Always (might be an exception) $\left(\frac{\partial B}{\partial F}\right)_C = \left(\frac{\partial E}{\partial C}\right)_F$

$$\begin{cases} dU = T dS - P dV + \mu dN \\ \left(\frac{\partial U}{\partial S}\right)_{V,N} = T \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \\ \frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_{N,S} \quad \frac{\partial^2 U}{\partial V \partial S} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \\ \Rightarrow \left(\frac{\partial T}{\partial V}\right)_{N,S} = -\left(\frac{\partial P}{\partial S}\right)_{N,V} \end{cases}$$

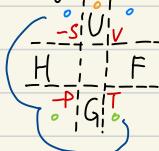
$$dH = T dS + V dP + \mu dN \\ \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dF = -S dT - P dV + \mu dN \\ \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial V}\right)_T$$

$$dG = -S dT + V dP + \mu dN \\ \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dU = T dS - P dV + \mu dN \\ \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Thermal dynamic square



$$dU = -P dV + T dS + \mu dN$$

Ignore the sign unless it is the coefficient.
 $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

Maxwell relations (fixed N)

o Free energy and equilibrium



System + environment = universe

let the environment be a reservoir entropy of system

↓ ↓ entropy of reservoir

System + environment are in thermal contact: $S_{univ} = S + S_R$

- If reservoir has constant $T, V, N \Rightarrow$ exchange is only of energy

$$dU_R = -dU$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \Rightarrow dS_R = \frac{dU_R}{T_R}$$

$$T_R = T \text{ at equilibrium} \Rightarrow dS_{univ} = dS + dS_R = dS - \frac{dU}{T} = -\frac{1}{T} (dU - T dS) = -\frac{dF}{T} \xrightarrow{o} \text{from negative } (dS > 0)$$

Thus, F_{system} tends to a minimum.

- If reservoir has fixed $T, P, N \Rightarrow$ exchange energy and volume

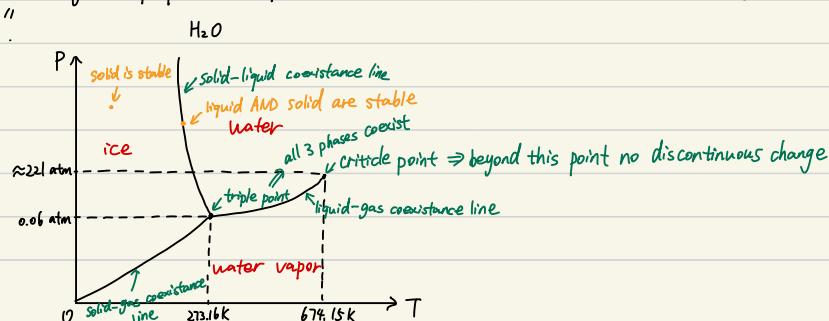
$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \Rightarrow dS_{\text{res}} = \frac{1}{T_{\text{res}}} dU_{\text{res}} + \frac{P_{\text{res}}}{T_{\text{res}}} dV_{\text{res}}$$

$$\text{Since } dV_{\text{res}} = -dV, P_{\text{res}} = P, T_{\text{res}} = T, \text{ then } dS_{\text{res}} = -\frac{dU}{T} - \frac{P dV}{T}$$

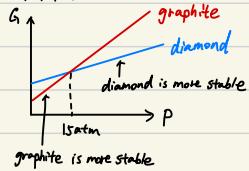
$$dS_{\text{univ}} = dS_{\text{res}} + dS = dS - \frac{dU}{T} - \frac{dV}{T} = -\frac{1}{T} (dU + P dV - T dS) = -\frac{1}{T} dG$$

Thus, G_{system} tends to a minimum.

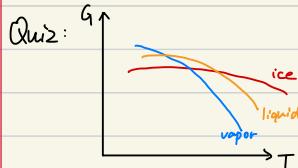
o Phase transitions: a discontinuous change in properties of a substance as its environment is changed infinitesimally. Solid, liquid, gas are all "phases".



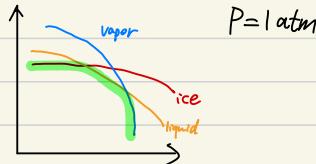
$(\frac{\partial G}{\partial P})_{T,N} = V \Rightarrow$ we can plot G vs P if V is constant this will be a straight line.



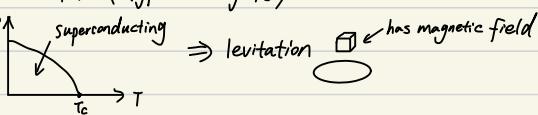
example carbon at fixed temperature - room temperature here.



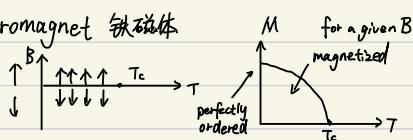
True when $P \ll 1 \text{ atm}$
 \Rightarrow liquid is never stable.



Superconductor (Type I e.g. Pb)



Ferromagnet

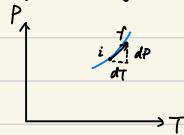


o Clausius-Clapeyron equation

boundary between liquid and gas phase $\Rightarrow G_L = G_g$: both phases are equally stable on the phase boundary also known as coexistence curve. if a change is made in some parameter but the system stays on the phase boundary then

$$\begin{aligned} dG_L &= dG_g \\ -S_L dT + V_L dP &= -S_g dT + V_g dP \\ (-S_L + S_g) dT &= (V_g - V_L) dP \end{aligned}$$

slope of the phase boundary $\frac{dP}{dT} = \frac{S_g - S_L}{V_g - V_L}$ difference in entropy difference in volume



In a phase transition, the heat transferred is "L" "latent heat", also $\Delta S = \frac{Q}{T} = \frac{L}{T}$.

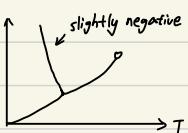
$$\frac{dP}{dT} = \frac{L}{T \Delta V} \leftarrow \text{Clausius-Clapeyron equation}$$

o Solid \leftrightarrow liquid transition

$$\frac{dP}{dT} = \frac{S_s - S_l}{V_s - V_l} \quad S_s < S_l \Rightarrow \Delta S \text{ is negative}$$

if $\frac{dP}{dT}$ is positive then ΔV must be negative $\Rightarrow V_s < V_l$ and $P_s > P_l$

For water,



□ Chapter 6 Boltzmann Statistics

The probability of finding a system in a particular state when it is in contact with a thermal reservoir depends on temperature.

- 2 state system: state 0 energy E_0 $E_1 > E_0$.
state 1 energy E_1 .

System is in contact with a thermal reservoir at T , $\frac{Pr(E_1)}{Pr(E_0)} = \frac{\Omega_{\text{sys+res},1}}{\Omega_{\text{sys+res},0}}$
Since $\Omega_{\text{sys+res}} = \Omega_{\text{sys}}\Omega_{\text{res}}$ and $\Omega_{\text{sys}} = 1$, then $\frac{Pr(E_1)}{Pr(E_0)} = \frac{\Omega_{\text{res},1}}{\Omega_{\text{res},0}}$.

$$S_{\text{res}} = k \ln(\Omega_{\text{res}}) \Rightarrow \Omega_{\text{res}} = e^{S_{\text{res}}/k}$$

$$\frac{Pr(E_1)}{Pr(E_0)} = \frac{e^{S_{\text{res},1}/k}}{e^{S_{\text{res},0}/k}} = e^{\Delta S_{\text{res}}/k} \quad \text{if } \Delta S_{\text{res}} = S_{\text{res},1} - S_{\text{res},0}$$

From state 0 \rightarrow state 1, $\Delta E_{\text{res}} = -E_1 + E_0$ and $\Delta E_{\text{sys}} = E_1 - E_0$.

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Rightarrow \Delta S = \frac{\Delta U}{T}$$

$$\frac{Pr(E_1)}{Pr(E_0)} = e^{-(E_1 - E_0)/kT} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}} \Rightarrow Pr(E_j) \propto e^{-E_j/kT} \quad \text{Boltzmann Factor}$$

$$Pr(E_j) = \frac{e^{-E_j/kT}}{\sum e^{-E_i/kT}} \quad \text{Boltzmann Distribution}$$

"partition function"
sum over all possible states of system, denoted Z .

We can find the average value of any* quantity by weighting the value of that quantity with the Boltzmann factor. e.g. $\bar{E} = \frac{\sum E_i e^{-E_i/kT}}{Z}$

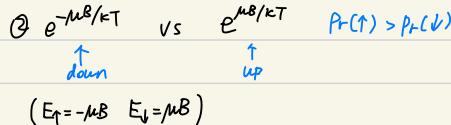
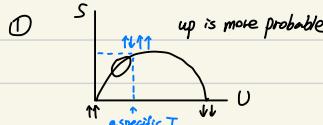
Ex. a system (an atom) has 2 possible levels. $E_0=0$ $E_1=0.02 \text{ eV}$ | $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ $k_B = 8.6 \times 10^{-5} \text{ eV/K}$

at equilibrium, what is the average value of E ?

$$\begin{aligned} \bar{E} &= \frac{1}{Z} \sum E_i e^{-E_i/kT} \\ &= \frac{1}{Z} (0) e^{-0/kT} + (0.02) e^{-0.02/kT} \\ &= 6.3 \times 10^{-3} \text{ eV} \end{aligned}$$

an ensemble of N such atoms at 300K will have $U = N\bar{E}$.

Quiz: UP is more probable in a paramagnet at a given temperature.



○ Paramagnetism

$$\begin{aligned} \uparrow \text{up} \quad E = -\mu B \\ \downarrow \text{down} \quad E = \mu B \end{aligned}$$

$$Z = e^{-(-\mu B)/kT} + e^{-(\mu B)/kT} = 2 \cosh\left(\frac{\mu B}{kT}\right)$$

$$P_{\text{up}} = \frac{e^{\mu B/kT}}{2 \cosh\left(\frac{\mu B}{kT}\right)} > P_{\text{down}} = \frac{e^{-\mu B/kT}}{2 \cosh\left(\frac{\mu B}{kT}\right)}$$

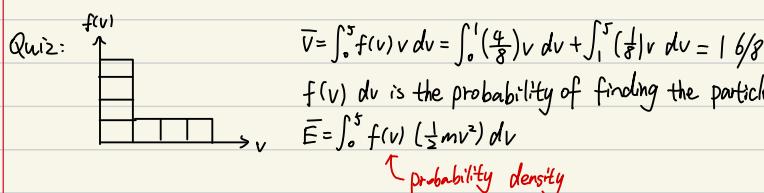
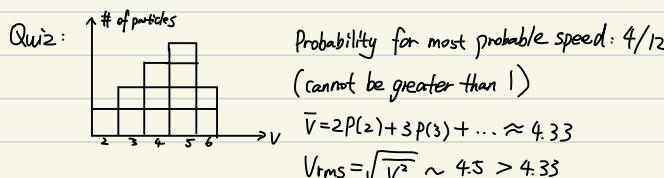
$$\begin{cases} \bar{E} = \frac{(-\mu B)e^{\mu B/kT} + (\mu B)e^{-\mu B/kT}}{2 \cosh\left(\frac{\mu B}{kT}\right)} \\ = -\mu B \tanh\left(\frac{\mu B}{kT}\right) \end{cases}$$

$$U = N\bar{E} = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

as $T \rightarrow \infty$, $U \rightarrow 0$, $M \rightarrow 0$.

○ Maxwell speed distribution

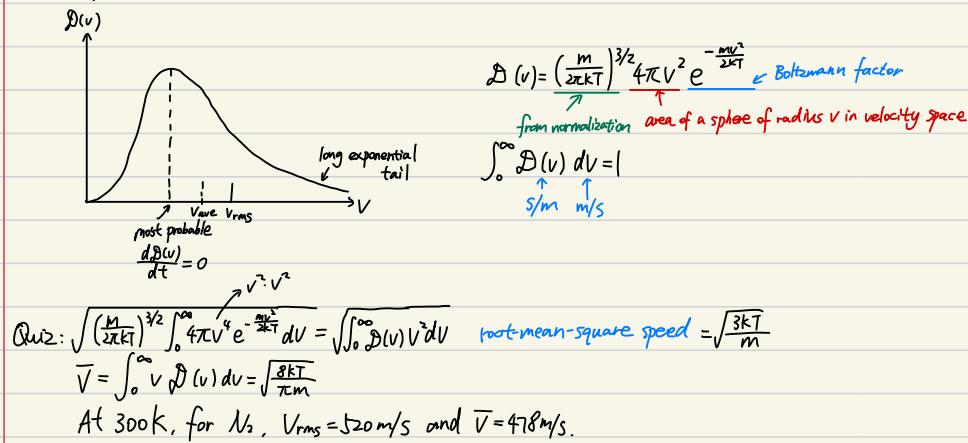
The root-mean-square speed of a gas molecule at temp T is $V_{\text{rms}} = \sqrt{\frac{3kT}{m}}$.



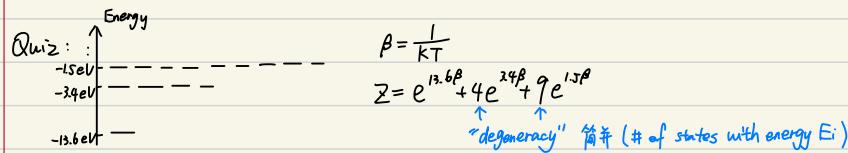
Quiz: $V = L \times L \times L$ probability density is uniform
 $P(\text{finding } r \text{ from the lower left-hand corner}) \propto \frac{\pi r^2 dr}{2}$ (surface area \times thickness)



o Maxwell aka Maxwell-Boltzmann distribution



e.g. At 300K, $P(v > 1000) = \int_{1000}^\infty D(v) dv \approx 1\%$



$$\bar{E} = \frac{1}{Z} \sum_i E_i e^{-E_i/kT} = \frac{1}{Z} \sum_i E_i e^{-\beta E_i}$$

$$\frac{\partial Z}{\partial \beta} = \sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i} = -\sum_i E_i e^{-\beta E_i}$$

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$