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Today's topics:

(1) Extensive vs intensive thermodynamic variables

(2) More on entropy:

- calculating entropy experimentally from heat capacities
- third law of thermodynamics: $S(T=0)=0$
  implies $C(T) \to 0$ as $T \to 0$

(3) Return to implications of entropy being maximum in equilibrium

$$\left.\begin{aligned} P &= T\left(\frac{\partial S}{\partial V}\right)_{N,U} \\ \mu &= -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \end{aligned}\right\}$$

must be same for all subsystems

Examples using P, μ

(4) The thermodynamic identity $dU = TdS - PdV + \mu dN$

(5) Paramagnet: system with negative temperature states
violates equipartition at high temperatures
use as low-T refrigerator

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Intensive vs Extensive Thermodynamic Variables

In Sackur-Tetrode equation,

$$S(U,V,N) = Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right)\right]$$

mixing identical gases led to additivity of entropy because of way U, V, N enter into equation. $N \to 2N$, $V \to 2V$, $U \to 2U$

If doubling amount of system causes thermodynamic variable to double, call variable <u>extensive</u> examples: N, U, V, S

If doubling amount of system leaves variable unchanged, call variable <u>intensive</u> examples: $\frac{N}{V}$ = density, $T = \frac{\partial U}{\partial S}$, Pressure P

Simple rules:

$$\text{extensive} + \text{extensive} = \text{extensive}$$

$$\frac{\text{extensive}}{\text{extensive}} = \text{intensive}$$

$$\text{extensive} \times \text{intensive} = \text{extensive}$$

can <u>not</u> mix extensive and intensive variables, $S + cP$ makes no sense, doesn't behave in reasonable way when varying amount of system, provides way to see if various algebraic expressions or guesses of algebraic forms make sense.

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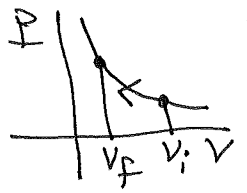
Calculating Entropy Changes From Heat Capacities

If we had to rely on theory, e.g. calculating Ω, then $S = k \ln \Omega$, then $\frac{1}{T} = \frac{\partial S}{\partial U}$, etc., would not be able to study most problems of interest.

Fortunately, possible to calculate changes in entropy and value of entropy itself by measuring heat capacities as f^n of temperature.

Starting point was our recent observation that, for isothermal expansion or compression of an ideal gas



$$\boxed{\Delta S = \frac{Q}{T}} \qquad Q = NkT \ln\left(\frac{V_f}{V_i}\right)$$

This relation holds generally for constant volume processes

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} \Rightarrow \frac{1}{T} \simeq \frac{\Delta S}{\Delta U} \Rightarrow \Delta S = \frac{\Delta U}{T}$$

for constant volume process

$$\Delta U = Q + W = Q \quad \text{since } W = 0$$

so

$$\boxed{\Delta S = \frac{Q}{T}}$$

good for solids, liquids, isothermal expansions of ideal gases at const. temp

Entropy in terms of heat capacity

What if temperature of system changes substantially during transfer of heat, then can't use $\Delta S = Q/T$.
But can imagine taking small steps in temperature and adding effects by calculus

$$\Delta S = \frac{Q}{T}$$

For constant volume process, if temperature changes by small amount ΔT

$$C_V = \frac{Q}{\Delta T} \Rightarrow Q = C_V \Delta T \Rightarrow \Delta S = C_V \frac{\Delta T}{T}$$

So change in entropy <u>of system</u> over temperature range T_i, T_f given by

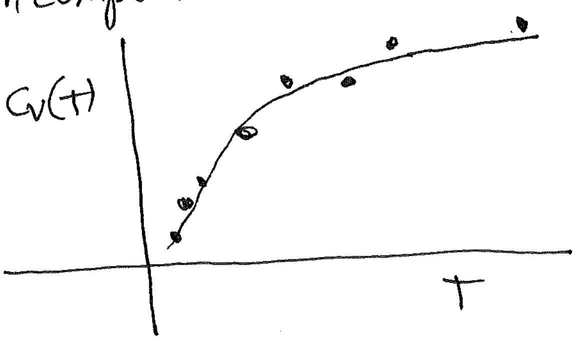
$$\boxed{\Delta S = \int_{T_i}^{T_f} \frac{C_V(T)}{T}\, dT}$$

Similar formula holds for quasistatic constant pressure process

$$\boxed{\Delta S = \int_{T_i}^{T_f} \frac{C_P(T)}{T}\, dT}$$

Use numerical approximations to estimate $\int_{T_i}^{T_f} \frac{C_v(T)}{T} dT$

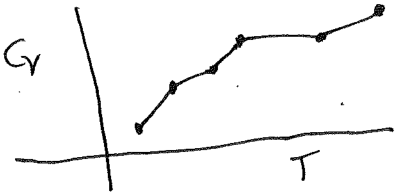
As side comment, experimental data for $C_v(T)$ might be noisy and incomplete



all we know are the measured points

could estimate $\int_{T_i}^{T_f} \frac{C_v(T)}{T} dT$ in two steps:

(1) <u>interpolate data</u> to get some simple function that approximates unknown curve over desired temperature range



E.g. use linear interpolation

use least-squares fit of f(x) some curve like polynomial

use <u>splines</u> (piece-wise cubics that are continuously diff.)

(2) use discrete numerical approximation to integral, e.g. box rule:

$$\int_{T_i}^{T_f} \cong \Delta T\left[f_0(T_i) + f(T_i+\Delta T) + f(T_i+2\Delta T) + \cdots\right]$$

or Simpson's rule (trapezoidal rule)

Entropy Change For Approximately Constant T Systems

In some cases, systems brought together, say two blocks of metal, are so big that small amount of heat transferred does not change temperature substantially

bring into thermal contact for short time

what is entropy change? assume $T_1 > T_2$, that amount of heat Q transfers from system 1 to system 2

$$\Delta S_1 = -\frac{Q}{T_1} < 0$$

$$\Delta S_2 = \frac{Q}{T_2} > 0$$

$$\Delta S_{total} = \frac{Q}{T_2} - \frac{Q}{T_1} = Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) > 0$$

total entropy change is (not suprisingly) positive so process is spontaneous and <u>irreversible</u>

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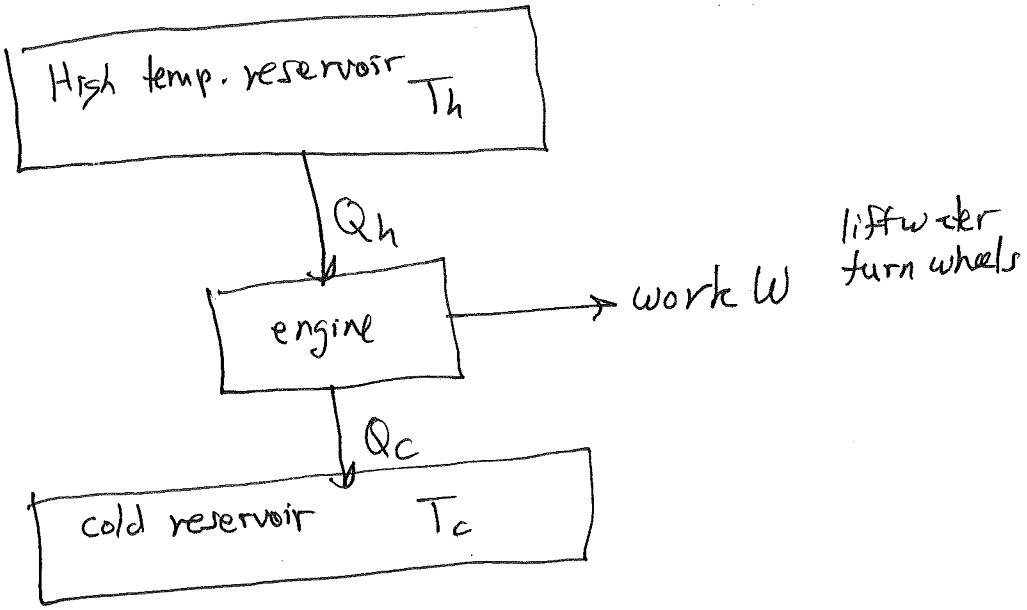
Theoretical Efficiency of Heat Engine
Section 4.1 of Schroeder



lingo: <u>reservoir</u> is system so large that properties like T, P don't change during some process

definition: efficiency ϵ of engine is $\epsilon = \frac{W}{Q_h}$

But conservation of energy gives

$$Q_h = Q_c + W$$

so

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

efficiency of engine

So far, have used just first law of thermodynamics, conservation of energy

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Heat engine efficiency continued

But we can see impact of second law of thermodynamics,

$\Delta S_{total} \geq 0$ for any process

$$\Delta S_{total} = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} \geq 0 \Longrightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$$

so

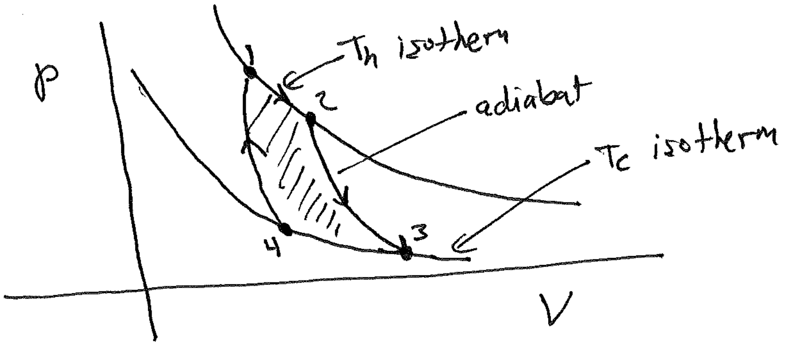
$$\boxed{\epsilon = 1 - \frac{Q_c}{Q_h} \leq 1 - \frac{T_c}{T_h}}$$

Very important 19th century achievement

Says to get good efficiency, want hottest possible hot reservoir coldest possible cold reservoir

Typical power plants will have $T_h \simeq 600$ K (superheated steam), $T_c \simeq 300$ K (dump heat into local river), so theoretical efficiency $\epsilon \simeq 0.5$. Actual efficiencies about 40%, not much room for improvement, we are already doing pretty well.

Carnot cycle achieves theoretical efficiency but useless from engineering point of view, involves two superslow isothermal steps



closed cycle one can endlessly repeat

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

$$Q_h = |W_{12}| = \int_{V_1}^{V_2} P\,dV = NkT_h \ln\left(\frac{V_2}{V_1}\right)$$

$$Q_c = |W_{34}| = \int_{V_1}^{V_2} P\,dV = NkT_c \ln\left(\frac{V_3}{V_4}\right)$$

$$\epsilon = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \times \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)}$$

But we know for adiabatic process $VT^{f/2} = \text{const}$

so $$V_2 T_h^{f/2} = V_3 T_c^{f/2}$$

$$V_1 T_h^{f/2} = V_4 T_c^{f/2}$$

taking ratio: $V_3/V_4 = V_2/V_1$ so $\frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} = 1$ QED

Discussion question for class

For Carnot cycle:

what is ΔS_{total} after one cycle?

what is ΔS for each of the four steps?

Note: Physics GRE exam loves to ask questions about Carnot cycles

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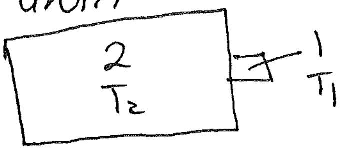
Example of Entropy Change Formulas

An object with constant heat capacity C_P and temperature T_1 is brought into contact with a thermal reservoir with constant temperature $T_2 \neq T_1$ until object reaches equilibrium.



1. What is total change of entropy ΔS_{total} of object and reservoir?
2. Is $\Delta S_{total} \geq 0$ as we would hope physically?

What is entropy change of object? Its temperature changes from T_1 to T_2 so

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

Entropy change of reservoir will be

$$\Delta S_{reservoir} = \frac{Q}{T_2}$$

where heat Q is transferred from reservoir to object. But this amount of heat is given by

$$Q = \int_{T_2}^{T_1} C_p(T) dT = C_p(T_1 - T_2)$$

this is just using defn $C = \frac{Q}{\Delta T}$

(cont)

Example continued

$$\Delta S_{total} = \Delta S_{object} + \Delta S_{reservoir}$$

$$= C_p \ln\left(\frac{T_2}{T_1}\right) + \frac{C_p(T_1-T_2)}{T_2}$$

$$\boxed{\Delta S_{total} = C_p\left[\ln\left(\frac{T_2}{T_1}\right) - 1 + \frac{T_1}{T_2}\right]}$$

answer

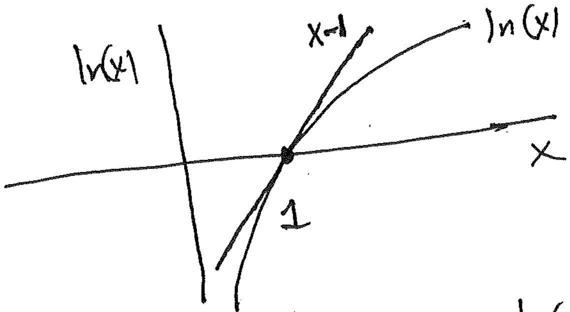
Does this answer make physical sense?

(1) what if $T_1 = T_2$? Then $\Delta S_{total} = 0$, makes sense ✓

(2) what if $T_2 \neq T_1$? Bit trickier to see if $\Delta S_{total} > 0$ but let's give it a try. note ΔS_{total} depends on T_1, T_2 only through ratio $x = \frac{T_1}{T_2}$ which can take on all possible positive values as T_1, T_2 varied over all positive values.

so look at

$$\Delta S_{total} = C_p\left[\ln\left(\frac{1}{x}\right) - 1 + x\right] = C_p\left[x - 1 - \ln x\right]$$



equiv to $e^x \geq ex$

not too hard to see that $x-1$ lies above $\ln(x)$ everywhere.

(a) touches $\ln(x)$ at $x=1$

(b) $\frac{d}{dx}\left[x-1-\ln(x)\right] = 1 - \frac{1}{x}$ changes sign at $x=1$ so $x-1$ always lies above

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Example of Entropy Change Formula

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V(T)}{T}\, dT$$

Problem 3.11 of Schroeder, p. 97:

50 l of water for bath at 55°C mixed with 25 l of water at 10°C. What is ΔS?

need to determine final equil temp T_f, then apply formula to each mass of water separately;

$$\Delta S = \int_{\underset{\approx 55+273\,K}{T_1}}^{T_f} \frac{C_V(T)}{T}\, dT + \int_{\underset{\approx 10+273\,K}{T_2}}^{T_f} \frac{C_V(T)}{T}\, dT$$

note: why ok to use C_V here, not C_P?

$$(2m)\, \underset{\substack{\uparrow \\ \text{specific} \\ \text{heat}}}{C_V} (55 - T_f) = m \cdot C_V (T_f - 10) \qquad \begin{matrix}\text{heat loss} \\ = \text{heat gained}\end{matrix}$$

$$\Rightarrow T_f = 40°C$$

$$\Delta S_1 = 25\,\text{kg} \times 4200 \frac{J}{K\,\text{kg}} \cdot \int_{283}^{313} \frac{dT}{T} \approx 10{,}550 \frac{J}{K}$$

$$\Delta S_2 = 50\,\text{kg} \times 4200 \frac{J}{K\,\text{kg}} \cdot \int_{328}^{313} \frac{dT}{T} \approx -9800 \frac{J}{K}$$

$$\Delta S_{total} = \Delta S_1 + \Delta S_2 = 750 \frac{J}{K}$$ (positive as expected)

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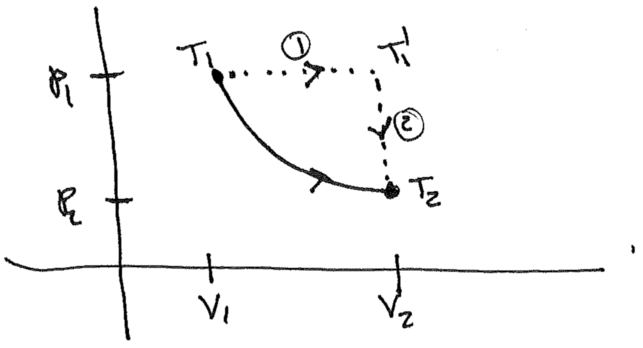
Entropy Change For Polyatomic Ideal Gas, General Case



any process can be decomposed into constant pressure and constant volume process

Can get entropy change by adding entropy change for constant pressure process followed by constant volume process, since S is state function, path doesn't matter

To go from P_1, V_1 to $P_1 V_2$, temperature increases to $T_1' = \left(\frac{V_2}{V_1}\right) T_1$

$$\Delta S_{①} = \int_{T_1}^{T_1'} \frac{C_P(T)}{T}\, dT = Nk\left(1+\frac{f}{2}\right) \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{②} = \int_{T_1'}^{T_2} \frac{C_V(T)}{T}\, dT = \left(Nk\frac{f}{2}\right) \ln\left(\frac{T_2}{T_1'}\right)$$

$T_2 = \frac{P_2}{P_1} T_1'$

$$= \left(Nk\frac{f}{2}\right) \ln\left[\frac{P_2}{P_1}\right]$$

$$\boxed{\Delta S_{total} = Nk\left(1+\frac{f}{2}\right) \ln\left(\frac{V_2}{V_1}\right) + \frac{Nkf}{2} \ln\left(\frac{P_2}{P_1}\right)}$$

$$= Nk\frac{f}{2} \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{V_2}{V_1}\right)$$

exact same expression as adiabatic followed by isothermal

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Third Law of Thermodynamics

$$S(T=0)=0 \Rightarrow C_V, C_P \to 0 \text{ at } T=0$$

What is entropy at $T=0$? Can't answer this by calculating multiplicities since need to know properties of quantum ground state of system. With a few rare exceptions, $\Omega=1$ for ground state so we conclude:

$$\boxed{S(T=0) = k\ln\Omega = k\ln(1) = 0}$$

Not easy to achieve $S=0$ if molecules not spherical, structure gets frozen in as $T \to 0$ and quantum tunneling times are too long.

Example: C≡O molecule acts like asymmetrical dumbbell

O—C C—O O—C
C—O C—O O—C C—O O—C
C—O O—C O—C C—O O—C

For N molecules, $\Omega = 2^N$ possibilities so <u>residual entropy</u> for CO crystal at $T=0$ could be as big as

$$S_{\text{residual}}(T=0) = k\ln(2^N) = Nk\ln 2 \simeq 6\,\frac{J}{K} \quad \text{for one mole}$$

Why $C_v, C_p \to 0$ as $T \to 0$

Once we know that $S(T=0)=0$, we can use heat capacity formulas to calculate actual entropy, not change in entropy

$$S(T)-S(0) = S(T) = \int_0^T \frac{C_p(T)}{T}\,dT$$

But entropy must be finite for all T, consider above integral for $T=\epsilon$ tiny

$$S(\epsilon) \simeq \int_0^\epsilon \frac{C_p(T)}{T}\,dT$$

The $\frac{1}{T}$ is diverging to ∞ as $T \to 0$ so $C_p(t)$ must go to zero fast enough to lead to finite answer, ~~A~~ If

$$C_p(T) = cT^\beta \qquad \beta > 0$$

$$\int_0^\epsilon \frac{T^\beta}{T}\,dT = \int_0^\epsilon T^{\beta-1}\,dT = \left.\frac{T^\beta}{\beta}\right|_0^\epsilon \simeq \frac{\epsilon^\beta}{\beta}$$

which is convergent (finite) for any $\beta > 0$, not $\beta \geq 1$ as you might expect. we conclude

$$C_p(T) \to 0 \text{ as } T \to 0 \quad \text{and similarly for } C_V$$

Entropy and Pressure

Recall our important central argument of two subsystems that can exchange "stuff" but total system is isolated so stuff is conserved

$$S_{total} = S_1(x_1) + S_2(x_2) \qquad x_1 + x_2 = \text{const}$$

$$x = U, V, N, \ldots$$

Equilibrium requires

$$0 = \frac{dS_{total}}{dx_1} = \frac{dS_1}{dx_1} - \frac{dS_2}{dx_2} = 0 \qquad \frac{dS_1}{dx_1} = \text{constant}$$

same for all subsystem

For $x = U$, we concluded that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} = \text{const}$$

For $x = V$, we get

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} = \text{const}$$

if we <u>define</u> $$\boxed{P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}}$$

why reasonable? $T\,dS$ has units of kT = units of energy so

$$T\frac{\partial S}{\partial V} \text{ has units of } \frac{\text{energy}}{\text{volume}} = \frac{F \times \text{dis}}{A \times \text{dist}} = \text{pressure}$$

See if formula makes sense for ideal gas

$$S = Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right)\right]$$

$$T\left(\frac{\partial S}{\partial V}\right)_{N,U} = T\frac{\partial}{\partial V}\left[\overset{Nk}{\cdot}\ln(V) + f(V,U)\right]$$

$$= \frac{NkT}{V}$$

This is exactly the pressure of an ideal gas, so works out

Can't apply to Einstein solid, which has no volume in discussion

Similarly, we can apply $\frac{\partial S}{\partial X}$ = constant for $X = N$ and discover

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$ <u>chemical potential</u>

must be constant for equilibrium system across all subsystems.

The Thermodynamic Identity

Relations $\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{N,U}$ $\frac{P}{T}=\left(\frac{\partial S}{\partial V}\right)_{U,N}$ $\frac{\mu}{T}=-\left(\frac{\partial S}{\partial N}\right)_{U,V}$

can be conveniently summarized in term of a differential called the thermodynamic identity

$$\boxed{dU = TdS - PdV + \mu dN}$$

get by thinking of entropy as f^n of U,V,N

$$S=S(U,V,N)$$

so small change in S arises from small changes in U,V,N

$$dS=\left(\frac{\partial S}{\partial U}\right)_{N,V}dU+\left(\frac{\partial S}{\partial V}\right)_{U,N}dV+\left(\frac{\partial S}{\partial N}\right)_{U,V}dN$$

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

which is traditionally rewritten to mimic 2^{nd} law of thermo:

$$dU=\underbrace{TdS}_{\substack{\text{looks}\\\text{like } Q}}-\underbrace{PdV}_{\substack{\text{work}\\\text{term}}}+\underbrace{\mu dN}_{\text{something new}}$$

Note how coeffs T,P,μ are all intensive variables, else extensive dU on left would be inconsistent with extensive dS, dV, dN on right

Thermodynamic Identity

Useful in several ways

(1) as mnemonic to recover defns, e.g.

$$\underbrace{dU = dN = 0}_{\text{hold } U,N \text{ constant}} \Rightarrow TdS - PdV = 0$$

$$\text{or} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$$

$$dU = dV = 0 \Rightarrow TdS - \mu dV = 0$$

$$dS = dV = 0 \Rightarrow dU = \mu dN \quad \text{or} \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

this is interesting, says μ is change in energy when particle added at constant entropy
helps motivate choice of ~~sign~~ minus sign

(2) cross-derivatives lead to useful identities known as Maxwell relation.
For smooth enough functions $f(x,y)$,
$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial y \partial x}$$

For example:
$$\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right) = \frac{\partial^2 U}{\partial S \partial V} = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)$$

$$\text{or} \quad \boxed{-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)}$$

Chemical potential Section 3.5

$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \Rightarrow \mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$ chemical potential

units of energy

meaning? $dU = TdS - PdV + \mu dN$

$dS = dV = 0 \qquad \boxed{\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}}$ increase ΔU in energy when add at constant S

$$S = Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m U}{3h^2 V}\right)^{3/2}\right)\right]$$

$\uparrow \qquad \uparrow$

S constant, V const, if we increase N, S constant $\Rightarrow U\downarrow$

so $\mu < 0$ generally

$e^{S/k} = \Omega(N,q) = \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N = \text{const} \qquad N\uparrow,\ q\downarrow \Rightarrow \mu < 0$

paramagnet: $S(U) = Nk\left[\ln(2) - \frac{1}{2}\ln(1-x^2) + \frac{x}{2}\ln\left(\frac{1-x}{1+x}\right)\right]$

$x = \frac{U}{N\mu B} \qquad N\uparrow$ and S constant

$\mu = -kT\ln\left(\frac{N+q}{N}\right)$ Einstein solid

$N+q > N \Rightarrow \mu < 0$

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μ for ideal monoatomic gas

$$S = Nk\left[\frac{5}{2} - \ln\left(N^{5/2}\right) + \underbrace{\ln\left[V\left(\frac{4\pi m U}{3h^2}\right)^{3/2}\right]}_{\text{const}}\right]$$

$$\boxed{\mu = -T\left(\frac{\partial S}{\partial N}\right)_{V,U} = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]}$$

$PV = NkT$

$$= -kT\ln\left[\frac{V/N}{\lambda_D^3}\right]$$

at STP, $\frac{V}{N} = \frac{kT}{P} \approx 4\cdot 10^{-26}\,m^3$

$\lambda_D^3 \simeq 10^{-31}\,m^3$

$1eV = 1.6\cdot 10^{-19}\,J$

$\mu = -0.32\,eV$ He $300K$, $10^5 \frac{N}{m^2}$

for fixed T, if $\frac{N}{V}$ increased, $\mu = kT\ln\left(\frac{N}{V}\right) + \cdots$ increases
becomes less negative

more generally,

$$\boxed{dU = TdS - PdV + \sum_i \mu_i dN_i}$$

one μ_i for each kind of particle

μ_i = constant separately

μ used in chemical reactions:

$N_2 + 3H_2 \leftrightarrow 2NH_3$

$\mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$

$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$ gibb's free en $G(T,P)$

Applicatn of μ

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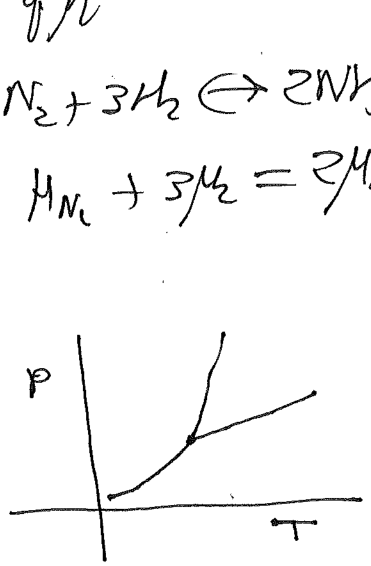
chemical reactions: $N_2 + 3H_2 \leftrightarrow 2NH_3$

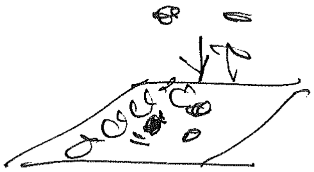
$$\mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$



phase transitions:

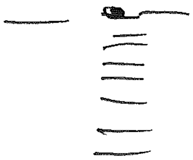
slopes of ~~[illegible]~~ lines,
properties near triple point



gas-liquid, gas-solid, liquid-solid eq'n

$\mu_{gas} = \mu_{2D\ gas}$ Langmuir isotherms

metals, semiconductors:

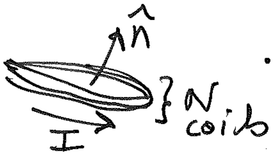


add electron, how does energy change?

Spin $\frac{1}{2}$ Paramagnet: Third System We Can Solve Completely

Consider N non-interacting spin-$\frac{1}{2}$ magnetic dipoles $\vec{\mu}$

Some review: $\vec{\mu} = NIA\hat{n}$



use right hand rule to get $\hat{n}$

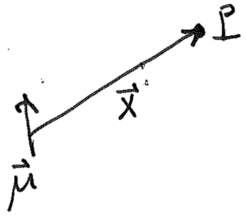
$\vec{\tau} = \vec{\mu} \times \vec{B}$

$U = -\vec{\mu} \cdot \vec{B}$ favors $\vec{\mu} \parallel \vec{B}$

classically without friction, torque causes oscillations, not alignment. QM'ly cause discrete transition ↑ → ↓ or ↓ → ↑

$\vec{F} = \nabla(\vec{\mu} \cdot \vec{B}(x))$ inhomogeneous magnetic field causes net force

$$\vec{B}(\vec{x}) = \frac{\mu_0}{4\pi} \frac{3\hat{n}(\hat{n}\cdot\vec{\mu}) - \vec{\mu}}{|\vec{x}|^3}$$



field far from dipole

tells strength of field on some other dipole, distance must be big enough that influence of dipoles on each other small compared to influence of external field

$$\|B_\mu\| \ll B_{uniform}$$

Spin $\frac{1}{2}$ Particles

Particles can have intrinsic magnetic moment, even in absence of current, e.g. electron is point particle with magnetic moment

Intrinsic angular momentum called spin, comes in multiples of $\frac{\hbar}{2}$ where $\hbar$ = Planck's constant

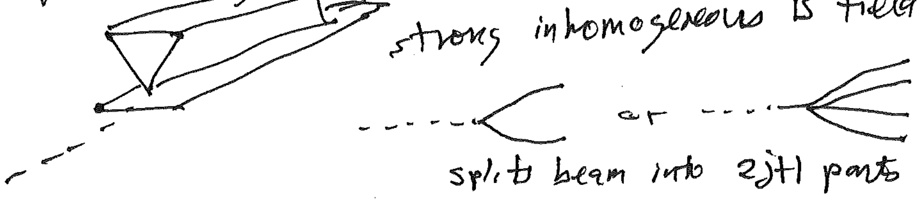
spin 0 particles: H atom, He^4 atom
$\frac{1}{2}$: e, p, n, quarks, neutrino
1 : photon
3/2 : some nuclei, atoms
2 : graviton

will soon see that spin plays profound role in properties of macroscopic systems:

odd multiples of $\frac{\hbar}{2}$ = fermions obey exclusion principle

even multiples of $\frac{\hbar}{2}$ = bosons can condense into same energy level

determine spin by spectroscopy or by Stern-Gerlach device



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Paramagnet: Solution

Given: N non-interacting magnetic dipoles μ in thermodynamic equilibrium with constant uniform external magnetic field $\vec{B} = B\hat{z}$,

calculate: $U(T)$

$C(T)$

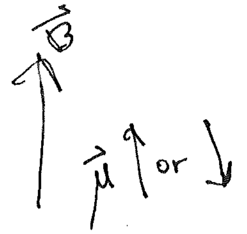
$M(T) = \mu(N_\uparrow - N_\downarrow)$ = magnetization

Strategy: $\Omega \rightarrow S = k\ln\Omega \rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,B}$

$\rightarrow U = U(T) \rightarrow C = C(T) = \frac{dU}{dT}$

Basic identities: ↑ ↓ ↓ ↑ ↓ ↑ ↑ ↑ ↓ ↑ ↓ ↓ ↑ ↑

$N_\uparrow + N_\downarrow = N$ # dipoles conserved



$\vec{\mu}$ ↑ or ↓

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

$N_\uparrow = \frac{N}{2} - \frac{U}{2\mu B} \qquad N_\downarrow = \frac{N}{2} + \frac{U}{2\mu B}$

$M = \mu(N_\uparrow - N_\downarrow) = -\frac{U}{B}$ so get magnetization from energy

Paramagnet: Multiplicity and S

$$\Omega(N, N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\, N_\downarrow!}$$ since $N_\downarrow = N - N_\uparrow$

We are well trained for approximating multiplicity provided

$N_\uparrow, N_\downarrow \gg 1$ good for macroscopic syst

$$\ln \Omega = \ln N! - \ln N_\downarrow! - \ln N_\uparrow!$$

$$\boxed{S = k \ln \Omega \cong k\left[N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow)\ln(N - N_\uparrow)\right]}$$

Substitute: $N_\uparrow = \frac{N}{2} - \frac{U}{2\mu B}$

define $x = \frac{U}{N\mu B}$ dimensionless energy $|x| \le 1$

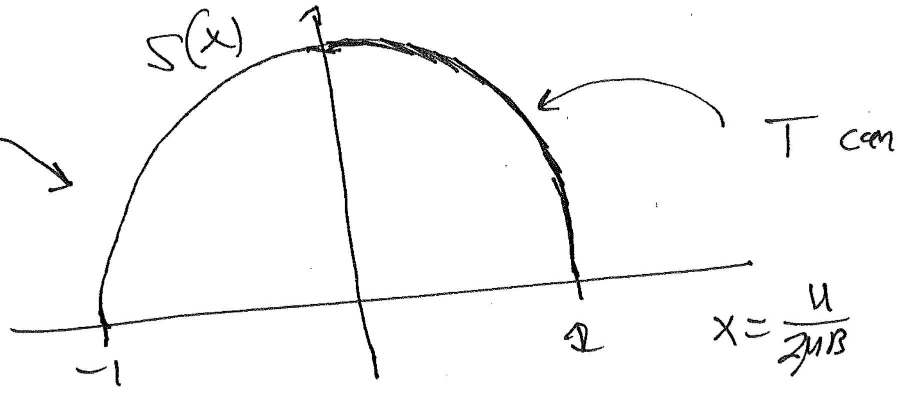
$$S = k\left[\ln 2 - \frac{1}{2}\ln(1-x^2) + \frac{x}{2}\ln\left(\frac{1-x}{1+x}\right)\right]$$

$$\frac{dS}{dx} = \frac{k}{2}\ln\left(\frac{1-x}{1+x}\right)$$ helps in plotting

$dS/dx = \infty \quad x \to -1$

$= 0 \quad x \to 0$

$= -\infty \quad x \to 1$



T can be negative

This is curve you explored in class, so you know $U(T)$, $C(T)$ without doing math

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Paramagnet: T, U(T), M(T)

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N = \frac{\partial S}{\partial x}\frac{\partial x}{\partial U} = \frac{1}{N\mu B}\frac{\partial S}{\partial x}$$

$$= \frac{1}{N\mu B}\cdot\frac{Nk}{2}\ln\left(\frac{1-x}{1+x}\right)$$

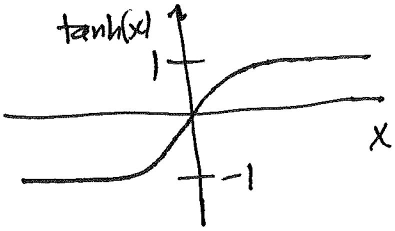
$$= \frac{k}{2\mu B}\ln\left[\frac{1-U/N\mu B}{1+U/N\mu B}\right]$$

Solve for $U = U(T)$, find

$$\boxed{\begin{aligned} U &= -N\mu B\tanh\left[\frac{\mu B}{kT}\right] \\ M &= -\frac{U}{B} = N\mu\tanh\left[\frac{\mu B}{kT}\right]\end{aligned}}$$

M(T) interesting: tells us how ordering by magnetic field B competes with disorder of temperature T

Comments:



increasing T means decreasing x, means decreasing M

$$\cosh = \frac{e^x + e^{-x}}{2} \quad \sinh = \frac{e^x - e^{-x}}{2} \quad \tanh = \frac{\sinh}{\cosh} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

$$\frac{d\sinh}{dx} = \cosh \quad \frac{d\cosh}{dx} = \sinh$$

$$\sin(x) = \frac{e^{ix} - e^{-ix}}{2i}$$

$$\sin(ix) = -\sinh x \quad \cos(ix) = \cosh(x)$$

Insight About M(T) for Paramagnet

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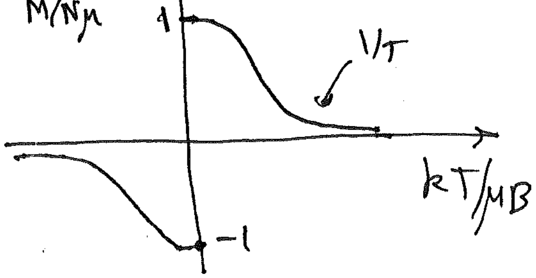


note: infinite temperature does not mean $M \to -1$ with all dipoles reversed, high T means most random arrangement of spins, $M \simeq 0$

$M = N\mu \tanh\left[\frac{\mu B}{kT}\right]$: increasing T ⇒ M decreases towards zero

Look at high T behavior: T big ⇒ $\frac{\mu B}{kT}$ small

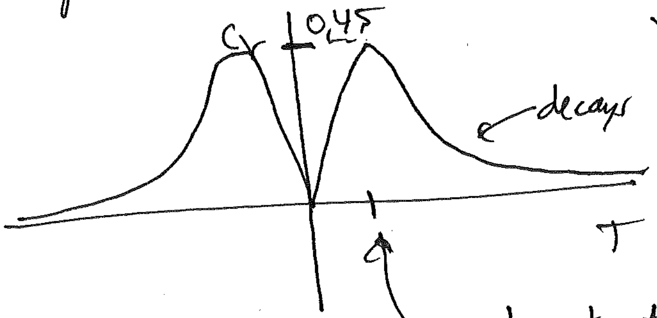
$\tanh(x) \simeq x$ for small x

conclude: $\boxed{M \sim \frac{N\mu^2 B}{k} \frac{1}{T} \propto \frac{1}{T}}$ Curie's law discovered exptlly

$M \propto B$ for fixed T large

Heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk \cdot \underbrace{\frac{y^{-2}}{\cosh^2(y^{-1})}}_{\Downarrow} \quad y = \frac{kT}{\mu B}$

C is even f^n of temp T



decays as $\frac{1}{T^2}$ for large T

peak not at $1 = \frac{kT}{\mu B}$, $\simeq 1.2$ instead

Energy Scales of Paramagnet

$T = 300K \equiv \frac{1}{40}\, eV$

For large B field, $T = 1$ tesla $\simeq 10^5$ gauss

Bohr magneton: $\mu_B = \frac{e h}{4\pi m_e} \sim 6\cdot 10^{-5} \frac{eV}{Tesla}$ T
of electron

$$\mu_B B \sim 6\cdot 10^{-5}\, eV \ll kT \sim \frac{1}{40}\, eV$$

so Curie's law should be quite accurate at room

$$\frac{\mu B}{kT} \ll 1$$

For nuclear paramagnets, $\mu_{nuclear} \simeq \frac{1}{2000}\mu_{electron}$

have to go to quite low temperatures to see substantial magnetization since can't increase B beyond ~10 Tesla

$T \sim 1\, mK$ to align nuclear spins

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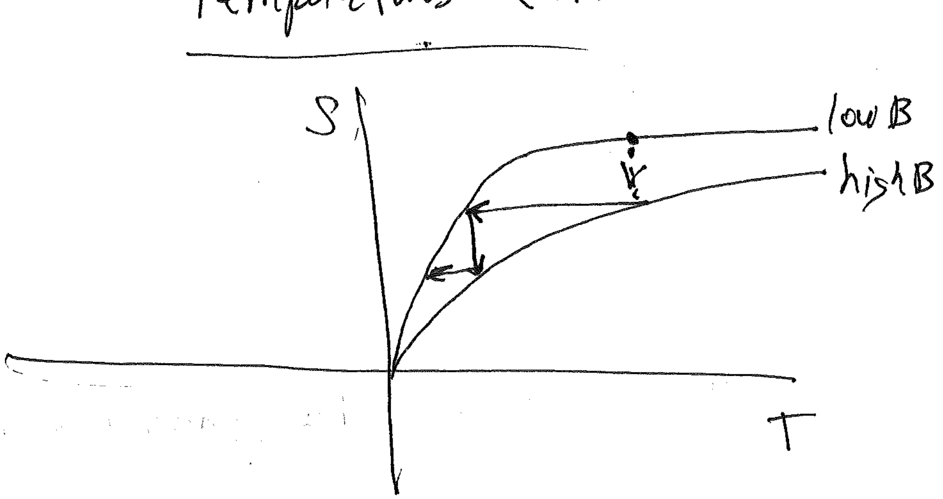
Using Paramagnet To Achieve Temperatures < 1K



Schroeder pages 144–148, Chapter 4

Key insights: entropy decreases with increasing B
in adiabatic process, $Q=0 \Rightarrow \Delta S=0$
so decreasing B field for thermally isolated paramagnet causes temperature to drop

similar to adiabatic expansion (cooling) followed by isothermal compression

$$M = N\mu \tanh\left[\frac{\mu B}{kT}\right]$$

adiabatic change, S fixed ⇒ M fixed ⇒ B decreases
⇒ T decreases by same factor as B