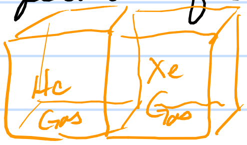
Chapter 1 Energy in Thermal Physics

Section 1.1 Thermal Equilibrium

Temperature = T is nonintuitive but simple if you don't think hard.

Thermometer = object whose properties depend on T. Examples: pressure of gas at fixed volume, volume of material at fixed pressure, color of light, ...

When 2 inert objects are in thermal contact, object at higher T loses energy to the object at lower T. Concept of heat. True, independent of the properties of each material!!!!



Xe mass >> He mass   Same T means what?

speed Xe = speed He ???

momentum Xe = momentum He ???

KE of Xe = KE of He ???

What is meant by saying two objects are at the same T ??

Section 1.2 The Ideal Gas

We'll used the measured properties of ideal gases and derivations to connect microscopic properties of the gas to macroscopic quantities.

As gas density gets smaller and T is not too low or high

Ideal Gas "Law" $\underset{\text{pressure}}{P}\ \underset{\text{Volume}}{V} = \underset{\text{\# of moles}}{n}\ \underset{8.31\,\frac{J}{mol\cdot K}}{R}\ T \leftarrow$ Temperature in K

SI units $P = N/m^2 = Pa$, $V = m^3$, $T = K$

1 mole of molecules or atoms $= 6.022 \times 10^{23} = N_A$ Avogadro's number

Convert the Ideal Gas Law to use number of atoms/molecules N

$PV = nN_A \frac{R}{N_A} T = N\ \underset{\uparrow}{k_B}\ T$

Boltzmann's const $= 1.381 \times 10^{-23} \frac{J}{K} = \overset{\text{book uses}}{k}$ or k_B

Prob 1.9 Volume of 1 mole at room temp and 1 atmosphere pressure

$T = 300\,K$ $P = 1.01 \times 10^5\,Pa$

$V = 1\,mol\ 8.31\,\frac{J}{mol\,K}\ 300\,K / 1.01 \times 10^5\,Pa \doteq 0.025\,m^3 = \frac{1}{40}\,m^3$

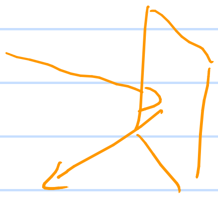
$\Rightarrow 1\,m^3$ contains $\simeq 40$ moles

Prob 1.10 number of air molecules in class room

Derivation of Ideal Gas Law

Assume: 1 type of atom, distance between atom-atom collisions is large, atom has specular reflection off wall

See book for different derivation



Before $\vec{V}_b = (v_x, v_y, v_z)$ After $\vec{V}_a = (-v_x, v_y, v_z)$

momentum impulse to wall $I = 2 m v_x$

Random collisions of atoms with wall gives pressure $P = \frac{F}{A}$

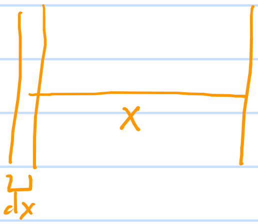
F = total I during time δt divided by δt

The atoms have a distribution function of v_x : $P(v_x)$

$1 = \int_{-\infty}^{\infty} P(v_x)\,dv_x$

$\overline{v_x} = \int_{-\infty}^{\infty} v_x P(v_x)\,dv_x$ $\overline{v_x^2} = \int_{-\infty}^{\infty} v_x^2 P(v_x)\,dv_x$ etc.

Examine a small slice dx of gas a distance x from the wall



Atoms that hit the wall during time δt have $v_x \geq x/\delta t$

$$I = \underbrace{\frac{N}{V} A\,dx}_{\text{number of atoms in slice}} \ \underbrace{\int_{x/\delta t}^{\infty} 2 m v_x P(v_x)\,dv_x}_{\text{impulse from atoms that reach wall}}$$

$$I_{TOT} = \text{sum all slices} = 2m\frac{N}{V}A\int_0^{\infty}\left[\int_{x/\delta t}^{\infty} v_x P(v_x)\,dv_x\right]dx$$

change variables $x = v_e\,\delta t$ $dx = \delta t\,dv_e$

$$= 2m\frac{N}{V}A\,\delta t\int_0^{\infty}\left[\int_{v_e}^{\infty} v_x P(v_x)\,dv_x\right]dv_e$$

chain rule $f\,dg = d(fg) - g\,df$ $f = \int_{v_e}^{\infty} v_x P(v_x)\,dv_x$ $g = v_e$

$$= 2m\frac{N}{V}A\,\delta t\left\{ v_e \int_{v_e}^{\infty} v_x P(v_x)\,dv_x \Big|_{v_e=0}^{v_e=\infty} + \int_0^{\infty} v_x^2 P(v_x)\,dv_x \right\}$$

$$= 2m\frac{N}{V}A\,\delta t\left\{ 0 + \frac{1}{2}\overline{v_x^2} \right\}$$

Plug into above $F = \frac{N}{V}A\,m\overline{v_x^2} \Rightarrow P = \frac{F}{A} = \frac{N}{V}m\overline{v_x^2}$

It must be true $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{(v_x^2 + v_y^2 + v_z^2)} = \frac{2}{3m}\overline{KE}$

$$\left.\begin{array}{ll}\text{Derivation gives} & PV = N\frac{2}{3}\overline{KE} \\ \text{Ideal gas law gives} & PV = NkT\end{array}\right] \Rightarrow \begin{array}{c}\overline{KE} = \frac{3}{2}kT \\ \frac{1}{2}m\overline{v_x^2} = \frac{1}{2}k_B T\end{array}$$

$\frac{3}{2}k_B$ is the conversion factor between T and $\overline{KE}$!!

Use this to compute $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}}$

Prob 1.18 Air is mostly N_2 $M = 4.65 \times 10^{-26}$ kg $v_{rms} \simeq 517\,\frac{m}{s}$ at 300K

Section 1.3 Equipartition Theorem

The average energy of any quadratic degree of freedom is $\frac{1}{2}k_BT$

KE examples $\frac{1}{2}\frac{\overline{p_x^2}}{m} = \frac{1}{2}k_BT$ $\frac{1}{2}\frac{\overline{L_z^2}}{I_z} = \frac{1}{2}k_BT$ . . .

PE example Harmonic oscillator $\overline{\frac{1}{2}m\omega^2 y^2} = \frac{1}{2}k_BT$

E + M $\frac{1}{2}\,Q^2/C = \frac{1}{2}kT$

For N molecules, each with f quadratic degrees of freedom

$U_{Therm} = N \cdot f \cdot \frac{1}{2}kT$

Important: The equipartition theorem is an approximation. It only works to the extent that quantum effects are unimportant.

First quantum effect discovered was through a violation of the equipartition thm

Quantum effects can freeze out motion

Example harmonic has f = 2 $U_{eg.} = 2\,\frac{1}{2}kT$ $U_{gm} \simeq \frac{1}{2}\hbar\omega$ if $kT \ll \hbar\omega$

Example particle in box f = 1 $U_{eg.} = \frac{1}{2}kT$ $U_{gm} \simeq \frac{h^2}{8mL^2}$ if $kT \ll \frac{h^2}{2mL^2}$

Equipartition examples

monatomic ideal gas He, Ne, Ar, ... f = 3

N_2 3 (translation), 2 (rotation), 2 (vibration)

rotation isn't 3 because rotation around symmetry axis frozen out

The 2 vibration are frozen out until high T

The 2 rotation are only frozen out at low T

In a solid $f \to 0$ as $T \to 0$, $f \simeq 6$ for medium T (every atom H.O.)

Prob 1.24 Calc U for 1g lead at room temp (no frozen out modes)

Atomic mass 207 => for 1g $N = \frac{6.02 \times 10^{23}}{207} = 2.9 \times 10^{21}$ atoms

$U = 2.9 \times 10^{21} \cdot 6 \cdot \frac{1}{2}\,1.38 \times 10^{-23}\,\frac{J}{K}\,300\,K = 36\,J$

Suppose you add 1 J to the 1g of lead. What's the new T?

$1\,J = 2.9 \times 10^{21} \cdot 6 \cdot \frac{1}{2} \cdot 1.38 \times 10^{-23} \frac{J}{K} \Delta T \Rightarrow \Delta T = 8\,K$

How T changes with U is important.

Prob 1.25 List all degrees of freedom for H_2O molecule in gas

3 - translation, 3 - rotation, 2 x 3 vibrations = 12 tot

Section 1.4 Heat and Work

Temperature - gives relative tendency for energy flow

Energy - measure of amount of damage that can be done

Heat and work - how energy is added/removed from system

Heat - spontaneous flow of energy from high T to low T

Work - all other methods, usually active agent manipulating system

U = total energy inside system, internal energy

A 1g lead ball at 300 K travelling at 100 m/s

$U = 36\,J \qquad KE = \frac{1}{2} 10^{-3} kg (100\, m/s)^2 = 5\,J$

Q = amount of heat that enters the system

W = amount of energy that enters the system by work

$\Delta U = Q + W$ = 1st Law of Thermodynamics = conservation of energy

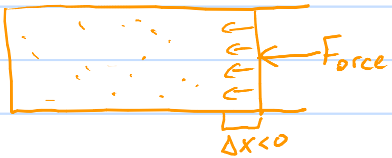
** Many authors W = work done by the system $\Rightarrow \Delta U = Q - W$

** For infinitesimal changes, book uses dU but not dQ or dW because these are already changes Many authors use $\text{đ}Q$ or $\text{đ}W$

Heat transfer can occur by conduction, convection, or radiation.

Section 1.5 Compression Work

Work done on object $W = \vec{F}\cdot d\vec{r}$



move to left

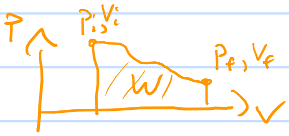
No friction, pushing slow constant speed $|\vec{F}| = PA$

$W = -PA\,\Delta x = -P\,\Delta V$

$\Delta V < 0$ positive work done on gas

$\Delta V > 0$ negative 〃 〃 〃 〃

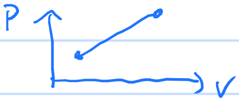
What if P depends on V?



$$W = -\int_{V_i}^{V_f} P(V)\,dV$$

Prob 1.31 1 liter of He at 1 atm goes to 3 liters so $P(V) \propto V$

a)



$$P(V) = \frac{1.01\times10^{5}\,\text{Pa}}{10^{-3}\,\text{m}^3}\,V$$

b) $W = -\int_{V_i}^{V_f} P(V)\,dV = -1.01\times10^{8}\,\frac{\text{Pa}}{\text{m}^3}\left(\frac{V_f^2 - V_i^2}{2}\right) = -404\,\text{J}$

c) $\Delta U = \frac{3}{2}Nk(T_f - T_i) = \frac{3}{2}(P_f V_f - P_i V_i) = 1212\,\text{J}$

d) $Q = \Delta U - W = 1616\,\text{J}$

e) heat source

Work done on ideal gas provides examples with closed expressions

Isothermal compression – $T = \text{const} \Rightarrow P \propto 1/V$

$W = -\int_{V_i}^{V_f} P(V)\,dV = -\int_{V_i}^{V_f} \frac{NkT}{V}\,dV = Nk_BT\ln(V_i/V_f)$

Since $\Delta U = \Delta\left(\frac{f}{2}NkT\right) = 0 \Rightarrow Q = \overset{\to 0}{\cancel{\Delta U}} - W = Nk_BT\ln(V_f/V_i)$

For isothermal compression, $Q = -W$ (heat input is minus work done on gas)

Adiabatic compression $Q = 0$ (no heat in/out) $\Rightarrow \Delta U = W$

$U = \frac{f}{2}NkT \Rightarrow dU = \frac{f}{2}Nk_B\,dT = -P\,dV$

For ideal gas $P = \frac{N}{V}kT \Rightarrow \frac{f}{2}\cancel{N}\cancel{k}\,dT = -\frac{\cancel{N}}{V}\cancel{k}T\,dV \Rightarrow \frac{f}{2}\frac{dT}{T} = -\frac{dV}{V}$

$\frac{f}{2}\ln(T_f/T_i) = \ln(V_i/V_f) \Rightarrow V_f T_f^{f/2} = V_i T_i^{f/2} = \text{const}$

Prob 1.35 if $VT^{f/2} = \text{const}$ then $V^{\gamma}P = \text{const}$ $\gamma = ?$

$T = \text{const}\ VP \Rightarrow V^{(1+f/2)}P^{f/2} = \text{const}$ $V^{(2+f)/f}P = \text{const}$

$\gamma = (2+f)/f$

Prob 1.37 In diesel engine, fast compression => $Q \cong 0$

$T_f = T_i \left(V_i/V_f\right)^{2/f}$ for N_2 $f = 5$ $T_f = 300\,K\,(20)^{2/5} \cong 994\,K$

Prob 1.40 adiabatic: show $\frac{dT}{dP} = \frac{2}{f+2}\frac{T}{P}$

$V T^{f/2} = const$ $V = \frac{NkT}{P}$ => $T^{\frac{f}{2}+1}\frac{1}{P} = const$ => $T = const\; P^{\frac{2}{f+2}}$

$\frac{dT}{dP} = \frac{2}{f+2}\, const\; P^{\frac{2}{f+2}}\,\frac{1}{P} = \frac{2}{f+2}\, T/P$ ✓

From prob 1.16 $\frac{dP}{dz} = -\frac{mg}{k_B}\frac{P}{T}$ => $\frac{dT}{dz} = \frac{dP}{dz}\frac{dT}{dP} = -\frac{mg}{k_B}\cancel{\frac{P}{T}}\,\frac{2}{f+2}\,\cancel{\frac{T}{P}}$

use $f=5$ $m = 4.65\times10^{-26}\,kg$ $\frac{dT}{dz} \cong -9.4\times10^{-3}\,\frac{K}{m} = -9.4\,\frac{K}{km} = -9.4\,\frac{°C}{km}$

If $\frac{dT}{dz}$ decreases faster than this, then warm low density air will rise and cold high density air will sink giving convection. Smog - temperature inversion.

Section 1.6 Heat Capacity

Heat capacity is the proportionality constant between Q and ΔT

$C \equiv Q/\Delta T$

C is proportional to the amount of material $C = \overset{\text{specific heat capacity}}{c} \cdot \underset{\text{mass of object}}{m}$

This definition is ambiguous because could be doing work as well.

$$C = \frac{\Delta U - W}{\Delta T} = \frac{\Delta U}{\Delta T} - \frac{W}{\Delta T}$$

$W = 0$ => heat capacity at constant volume $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ what is this math object?

If object expands when heat added at constant P: $W = -P\Delta V$

Heat capacity at constant pressure $C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$

Partial derivatives holding different quantities fixed is important for this topic

Example $F = r^2 z$ $rsz = 5$

$$\left(\frac{\partial F}{\partial r}\right)_z = 2rz = 10/s \qquad \left(\frac{\partial F}{\partial r}\right)_s = \frac{\partial}{\partial r}\left(r^2\frac{5}{rs}\right) = 5/s$$

$\longleftrightarrow$ not the same

For solids and liquids $\frac{\partial V}{\partial T}$ small $\Rightarrow$ $C_V \doteqdot C_P$

For gasses $C_P \neq C_V$. For ideal gas

Constant volume $U = \underbrace{\frac{f}{2}NkT = \frac{f}{2}PV}_{\text{ideal gas}} \Rightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{f}{2}V\left(\frac{\partial P}{\partial T}\right)_V = \frac{f}{2}Nk$

Constant pressure $C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{f}{2}+1\right)P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{f}{2}+1\right)Nk$

For ideal gas $C_P - C_V = Nk_B = nR$

Prob 1.43 for 1g $C_V = 4.2\ \text{J}/{}^\circ\text{C}$ $\quad$ $1\text{g} = \frac{1}{18}\text{mol} = 3.34\times10^{22}$ molecules

C_V/molecule $= 1.26\times10^{-22}\ \text{J/K} = 9.1\,k \overset{?}{=} f/2\,k \Rightarrow f = 18$?

Prob 1.41 $Q_{metal} + Q_{H_2O} = 0$

$C_{metal}(24^\circ C - 100^\circ C) + C_{H_2O}(24^\circ C - 20^\circ C)$

$C_{metal}(-76^\circ C) + 250\,g\ 4.2\frac{J}{^\circ C\,g}\ 4^\circ C = 0$ $\quad$ $C_{metal} = 55\frac{J}{^\circ C}$

$c_{metal} = 55\ \text{J}/{}^\circ\text{C}\ /100\,g = 0.55\ \text{J}/{}^\circ\text{C}\,g$

Latent heat at phase transition, $Q \neq 0$ but $\Delta T = 0$ until all material has made the transition

At the transition $\underset{\text{latent heat}}{L} = \overset{\text{heat added}}{Q}/\underset{\text{mass of material that made transition}}{m}$

Example: You have 1 kg ice at 0°C, you add 333 J and melt 1 g.
If you add 333 J to 2 kg " " ", how much melts?

Enthalpy $H \equiv U + \overbrace{PV}^{\text{work needed to make room for the system at constant } P}$

Look at change in H if do something to system at constant P

$U + \Delta U + P(V + \Delta V) = U + PV + \Delta U + P\Delta V = H + \Delta H$

If only compressional work is allowed $\Delta U = Q + W = Q - P\Delta V$

$\Rightarrow Q = \Delta H$

If other processe do work $\Delta H = Q + \underset{}{W_{other}}^{\leftarrow\text{not compression}}$

This leads to $C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$

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

Since constant pressure $\Delta H = \Delta U + P\Delta V$, the enthalpy can change either because of changes to internal energy or to compression work.

Latent heat at constant pressure $Q = \Delta H$

For example: Boil 1g H_2O at 100°C and 1 atm pressure needs 2260J

$Q = \Delta H = \Delta U + P\Delta V$

$\Delta V = V_{steam} - V_{liq} \cong V_{steam} \Rightarrow P\Delta V \cong \frac{1}{18}\text{mol}\ 8.31\frac{J}{\text{mol}\,K}\ 373 = 172\ J$

$\Delta U = 2260J - 172\ J = 2088\ J$

Prob 1.49 1mol H_2 + $\frac{1}{2}$mol $O_2 \rightarrow$ 1mol H_2O liquid $Q = ?$, $\Delta U = ?$, $P\Delta V = ?$

Pg 405 $\Delta H(H_2O\ liq) = -285.83 \times 10^3\ J/\text{mol}$ $\Delta H(O_2) = \Delta H(H_2) = 0$

$Q = -285.83 \times 10^3\ J$

$\Delta V = \sim 0 - V_{init} \Rightarrow P\Delta V = -\frac{3}{2}\text{mol}\ 8.31\frac{J}{\text{mol}\,K}\ \overset{\text{Table}}{298K} = -3.71 \times 10^3\ J$

$\Delta U = Q - P\Delta V = -285.83 \times 10^3\ J + 3.71 \times 10^3\ J = -282.1 \times 10^3\ J$

Prob 1.51 ΔH for $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Check before after 6C, 12H, 18O $\rightarrow$ ✓6C, 12H, 18O

$C_6H_{12}O_6$ $\Delta H = -1273$ kJ

O_2 $\Delta H = 0$ $\Delta H_{TOT} = \Delta H_{fin} - \Delta H_{init}$

$H_2O(l)$ $\Delta H = -285.8$ kJ $= 6(-393.5\ kJ) + 6(-285.8\ kJ) - (-1273\ kJ) - 0$

$CO_2(g)$ $\Delta H = -393.5$ kJ $= -2803$ kJ per mole

Problem 1.53 Determine the energy to dissociate 1 H_2 molecule in vacuum

ΔU for 1 Find $\Delta H \longrightarrow$ Find ΔU for 1mol $\longrightarrow$ Find ΔU for 1

$H_2(g)$ $\Delta H = 0$ $H(g)$ $\Delta H = 217.97$ kJ $\Delta H_{TOT} = 2 \cdot 217.97\ kJ - 0 = 435.94\ kJ$

$P\Delta V = (PV)_{2mol} - (PV)_{1mol} = 1\text{mol}\ 8.31\frac{J}{\text{mol}\,K}\ 298\ K = 2.48\ kJ$

$\Delta U = 435.94\ kJ - 2.48\ kJ = 433.46\ kJ$

$\Delta U_{1\,molecul} = 433.46 \times 10^3\ J / 6.02214 \times 10^{23} = 7.198 \times 10^{-19}\ J / 1.6022 \times 10^{-19}\ J/eV$

$= 4.4925\ eV$ $7.175 \times 10^{-19}\ J$ spectroscopic

I'm not sure why 0.3% difference.