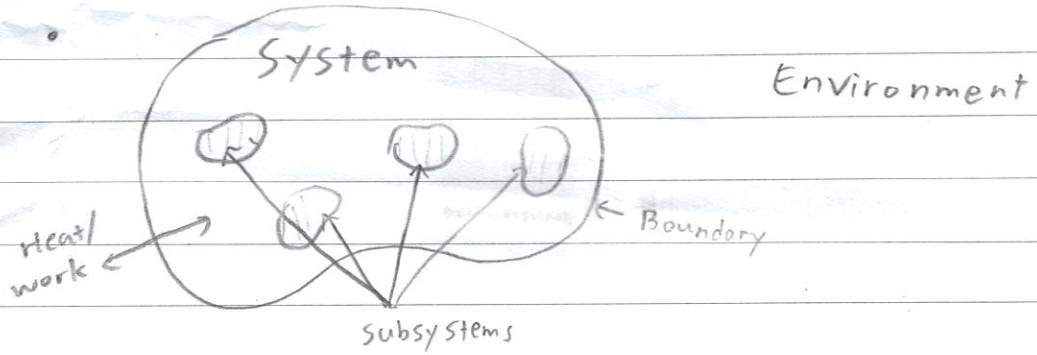


Light & Heat

week 0 Notes

*Classical Thermodynamics



- Types of systems (what can be exchanged)

- ↳ Open: heat, work, matter exchange

- ↳ Closed: heat, work, matter ~~exchange~~

- ↳ Thermally isolated: heat, work, matter exchange

- ↳ Mechanically isolated: heat, work, matter ~~exchange~~

- ↳ Isolated: heat, work, matter ~~exchange~~

※ Work: a deformation of the boundary

$$w = \int P dV \quad (\text{valid if system remains in equilibrium})$$

(ex. gas piston)

- ↳ If focus on understanding properties of system:

$$w=w_{on} = - \int P dV \quad \text{work done by system on gas}$$

- ↳ If focus is on efficiency (max W done) of system

$$w=w_{by} = \int P dV \quad \text{work done by gas on system}$$

※ Heat: microscopic, randomized energy transferred across boundary

- ↳ process, not property ("heating")

Transfer of matter across boundary

↳ ΔN (or Δm) = amt. of matter transferred

- Ignoring transfer of matter, change in internal energy of a system is defined as

$$\Delta U = Q + W \quad (\text{1st Law of Thermodynamics})$$

*Energy

- What the heck is it?
 - A property of objects, systems, and fields
 - Human-constructed property fashioned so as to be conserved
 - Not a thing or entity that exists independent of objects and systems.

Light & Heat

Week 0 Notes

*Statistical Mechanics

- Organizing distinguishable particles into boxes

$$\hookrightarrow \# \text{ of ways} = W = \frac{N!}{n_1! n_2! n_3! \dots n_i!}, \quad W = \frac{N!}{\prod n_i!}$$

↳ n_1 particles in box 1, n_2 in box 2, etc.

- Distributing particles into energy levels

↳ If E equal quanta are distributed among N distinguishable particles,

$$W_{\text{tot}} = \frac{(N+E-1)!}{(N-1)! E!}$$

⊗ The greater the # of particles, the probability of the most probable state approaches certainty. ($w/w_{\text{tot}} = 1$)

⊗ Different distributions are macrostates/configurations. Different ways of realizing the same macrostates are microstates/complexions.

↳ $W = \# \text{ of microstates for 1 macrostate}$

↳ Macrostates = distinguishable experimentally, microstates aren't.

- Most probable macrostate

$$\hookrightarrow n_i = N \left\{ \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \right\} \quad \begin{aligned} k &= 1.38066 \times 10^{-23} \text{ J/K} \\ n_i &= n_0 e^{-E_i/kT} \end{aligned}$$

Boltzmann constant

⊗ Particle Partition Function: $q = \sum_i e^{-E_i/kT}$

$$\hookrightarrow n_i = \frac{N}{q} e^{-E_i/kT}$$

Light & Heat

week 1 notes

* Statistical & Classical Thermodynamics

- Microstate: set of all properties of the molecule

↳ Statistical mechanics uses only position & momentum

$$\{\vec{r}_i, \vec{p}_i\}; i=1\dots N$$

- Macrostate: small set of properties of system with many constituents

↳ Energy, Volume, # of molecules, etc.

※ Postulate: probability for $\omega(t)$ to be in any microstate is the same.

↳ Under constraint of macrostate energy, volume, and # of molecules (E, V, N)

※ Phase space (Ω): space of all microstates

- Macroscopic variables

1. Extensive variables: these are sums over the macrostate.

- Mass, energy, volume..

- Combine 2 identical systems → value of property doubles

$$X(\lambda E, \lambda V, \lambda N) = \lambda X(E, V, N)$$

2. Intensive variables: these are averages over the macrostate.

- Temperature, pressure, density, etc.

- Combine 2 identical systems → Value of property is the same.

• Equilibrium: state of macrosystem achieved when all macroscopic variables are stable over time and through the system.

- Adiabatic process: process w/ no heat transfer between system & surroundings

- Isothermal process: process occurring at const. T

- Isochoric process: process occurring at const. V

- Isobaric process: process occurring at const. P

- Isentropic process: process in which entropy(s) is const.

• Multiplicity: $\Omega(E, V, N)$ is the # of microstates that yield the macrostate with E, V, N.

- For ideal gases:

1. Molecules making up the gas don't interact, except through direct collisions (no PE)

2. Molecules are points with no internal degrees of freedom except mass (energy is solely kinetic)

$$\therefore \Omega_T = \Omega_{\text{pos}}(r) \Omega_{\text{mom}}(p)$$

$$\Omega_T = \Omega_{\text{pos}}(v, N) \Omega_{\text{mom}}(E, N)$$

$$\log \Omega(E, V, N) = \log \Omega_{\text{pos}}(v, N) + \log \Omega_{\text{mom}}(E, N)$$

(base is conventionally defined as e)

$$\log \Omega(E, V) = N \log \frac{V}{N} \left(\frac{E}{N}\right)^{\frac{3}{2}} + \frac{3}{2} N \log \frac{4m\pi}{3h^3} + \frac{5}{2} N$$

↳ m=mass

↳ h= small voxel of hyperspace

• More on the derivations..

1. Position multiplicity

$$\Omega_{\text{pos}}(V, N) = \frac{1}{N!} \left(\frac{V}{h^3}\right)^N \quad \text{Indistinguishable particles}$$

$$\log \Omega_{\text{pos}} = N \log V - 3N \log h_r - \log N!$$

Use Stirling approximation: $\log N! \approx N \log N - N$

$$\log \Omega_{\text{pos}}(V, N) = N \log \frac{V}{N} + N - 3N \log(h)$$

2. Momentum multiplicity

Consider shape of Ω_{mom} in 2D:

$$E = \frac{1}{2m} (p_1^2 + p_2^2), \quad p_1^2 + p_2^2 = 2mE$$

Ω_{mom} is 3N-dimensional. Shape is a sphere of dimension 3N that has radius $\sqrt{2mE}$

$$\text{Volume of sphere in } d \text{ dimensions: } V_d = \frac{\pi^{d/2}}{\Gamma(\frac{d}{2}+1)} R^d$$

$$\hookrightarrow A_d = \frac{\partial V_d}{\partial R} = \frac{d\pi^{d/2}}{\Gamma(\frac{d}{2}+1)} R^{d-1}$$

\hookrightarrow Approximate Gamma function w/ $(\frac{3N}{2})!$

Area of 3N-dimensional sphere of radius $\sqrt{2mE}$:

$$\Omega(E) = \frac{1}{h_p^{3N}} \frac{\pi^{3N/2}}{\frac{3N}{2}!} (2mE)^{\frac{3N}{2}} \delta E$$

$$\log \Omega_{\text{mom}}(E) = N \log E^{\frac{3}{2}} + \frac{3}{2} N \log(2m\pi) - \log\left(\frac{3}{2}N\right)!$$

$\hookrightarrow \log \delta E$ ignored as small constant

\hookrightarrow Use Stirling on $\log\left(\frac{3}{2}N\right)!$

3. Overall multiplicity

$$\log \Omega(E, V, N) = \log \Omega_{\text{pos}}(V) + \log \Omega_{\text{mom}}(E)$$

does not depend
on E or V

$$= N \log \frac{V}{N} \left(\frac{E}{N} \right)^{\frac{3}{2}} + \underbrace{\frac{3}{2} N \log \left(\frac{4m\pi}{3h^2} + \frac{5}{3} \right)}_{\checkmark}$$

(number of microstates for the macrostate E, V, N is given by Ω)

$\checkmark \Omega(E, V, N) = \# \text{ of microstate configurations that have macrostate } E, V, N$

$\hookrightarrow \Omega_{\text{mom}}(E, N) = \# \text{ of ways to assign momenta to } N \text{ molecules with } (E, N)$

$\hookrightarrow \Omega_{\text{pos}}(V, N) = \# \text{ of ways to place } N \text{ molecules in volume } V$

$\checkmark \text{ Multiplicity of placing } N \text{ molecules into } M \text{ distinct states}$

$$\Omega_{\text{mom}} = \left(\frac{N!}{n_1!(N-n_1)!} \right) \left(\frac{(N-n_1)!}{n_2!(N-n_1-n_2)!} \right) \dots \left(\frac{(N-n_1-n_2)!}{n_3!(N-n_1-n_2-n_3)!} \right) \dots$$

$$= \frac{N!}{\prod_i n_i!}$$

$$\ln \Omega_{\text{mom}} = \ln N! - \sum_i \ln(n_i!)$$

$$= N \ln N - \sum_i n_i \ln(n_i)$$

$\checkmark \text{ Entropy: } S(E, V, N) = k \log \Omega(E, V, N)$

$$= S_{\text{pos}}(V, N) + S_{\text{mom}}(E, N) + \sigma$$

"Accessible part of phase space"

$$= Nk \log \frac{V}{N} + \frac{3}{2} Nk \log \frac{E}{N} + \sigma$$

$$\uparrow$$

$$\frac{3}{2} Nk \left(\log \frac{4m\pi}{3h^2} + \frac{5}{3} \right)$$

Light & Heat

Week 1 Notes

* Maximizing Multiplicity: Boltzmann Distribution

- When system reaches equilibrium, the state is in portion of phase space with max. # of microstates corresponding to that macrostate.

- Goal: find distribution of molecules into states with E_i

$$\hookrightarrow \text{Constraints: } \sum_{i=1}^M n_i = N, \quad \sum_{i=1}^M E_i n_i = E$$

$$\hookrightarrow \Omega_{\text{mom}} \text{ from Combinatorics: } \Omega_{\text{mom}}(E, N) = \frac{N!}{\prod_i n_i!}$$

$$\log \Omega_{\text{mom}} = \log N! - \sum_i \log n_i!$$

$$= N \log N - \sum_i n_i \log n_i \quad (\text{Stirling's approx.})$$

\hookrightarrow Maximizing Ω_{mom} with LaGrange Multipliers:

$$\frac{\partial \Omega_{\text{mom}}}{\partial n_r} = 0, \quad n_r = e^{-\alpha} e^{-\beta E_r}$$

- Probability for a molecule to be in state r : $p_r = \frac{n_r}{N}$

$$\hookrightarrow p_r = \frac{e^{-\beta E_r}}{\sum_i e^{-\beta E_i}} \quad \text{The Boltzmann Distribution}$$

$$\hookrightarrow Z \equiv \sum_i e^{-\beta E_i}, \quad \text{Partition Function, so } p_r = \frac{e^{-\beta E_r}}{Z}$$

※ Boltzmann Distribution is molecular distribution of KE of ideal gas at equilibrium

※ Maximizes multiplicity

$$\begin{aligned} \ast \ln \Omega &= N \ln(Z) + E \beta \\ &= N \ln Z + \frac{E}{kT} \end{aligned} \quad \left. \right\} \quad \begin{aligned} \beta &= \frac{1}{kT}, \quad k = 1.381 \times 10^{-23} \frac{\text{J}}{\text{K}} \\ &\uparrow \quad \text{Boltzmann constant} \end{aligned}$$

* A bit on Entropy

$$\bullet S = k \ln \Omega$$

$$\hookrightarrow S = kN \ln Z + \frac{E}{T}$$

$$\hookrightarrow \text{so } \left. \frac{\partial S}{\partial E} \right|_{V,N} = \frac{1}{T}, \quad \left. \frac{\partial E}{\partial S} \right|_{V,N} = T$$

≈ Stat. Mech. description of T: "rate of change of internal energy w.r.t. entropy"

Light & Heat

week 2 Notes

* The ideal gas

• Requirements

- Elastic collisions
- Volume of particles is negligible
- Large N of particles
- Random motion of particles

$$\bullet PV = Nk_B T$$

$$\hookrightarrow k_B = 1.38 \times 10^{-23} \text{ J/K}$$

* Kinetic theory of gases

• Gas pressure

↳ Specular collisions: $\vec{p}_{\parallel i} = \vec{p}_{\parallel f}$ (parallel momentum before & after)

$\vec{p}_{\perp i} = -\vec{p}_{\perp f}$ (momentum normal)

↳ With each collision with wall, $\Delta \vec{p}_{xi} = 2m\vec{v}_{xi}$ imparted

↳ Pressure due to 1 particle: $P_i = \frac{F_i}{A_i} = \frac{mV_{xi}^2}{V}$

↳ Averaging over other particles (x)

↳ $P = \rho_m \langle V_x^2 \rangle$, ρ_m = mass density

↳ Over all 3 directions: $P = \frac{\rho_m}{3} \langle V^2 \rangle$

∴ Avg. KE of particles in box: $\frac{1}{2} m \langle V^2 \rangle = \frac{3}{2} k_B T$

* Mean Free Path

• Distance between collisions (dist. traveled in $\Delta t \div \# \text{ of collisions}$)

↳ $\lambda = \frac{1}{\sqrt{2}\pi d_0^2 \rho_N}$, ρ_N = Number density

Probability that a particle travels distance r before colliding:

$$\hookrightarrow \frac{dr}{\lambda}$$

Number of particles that go without collision in a distance $r+dr$:

$$N(r+dr) = N(r) - N(r) \frac{dr}{\lambda}$$

that survive through distance r

that collide within distance dr

$$N(r) = N_0 e^{-r/\lambda}, N_0 = \text{total \# of particles}$$

Application: atmospheric pressure

Temp. is constant throughout atmosphere

$$P(h+dh) - P(h) = -g \rho_m(h) dh \quad \text{From Bernoulli's Equation}$$

$$dP = -\frac{gmP}{k_B T} dh \quad \text{Atmosphere is ideal gas, } P = \rho_N k_B T$$

$$\rho_m = m \rho_N$$

$$P(h) = P_0 e^{-\frac{mgh}{k_B T}} \quad P_0 = \text{Pressure at } h=0$$

Light & Heat

week 2 Notes

* Boltzmann's Law $\xrightarrow{\frac{mgh}{k_B T}}$ Gravitational PE

• Previous: $P(h) = P_0 e^{-\frac{mgh}{k_B T}}$

- Boltzmann generalized the PE part:

↳ $P_n = \text{Constant} \cdot e^{-\frac{PE}{k_B T}}$

- Probability to find the particle with particular value of potential energy

• Distribution of speeds: $P(v) d\vec{v} = A e^{-\frac{mv^2}{2k_B T}} d\vec{v}$

↳ where $\int_{\text{all } \vec{v}} P(v) d\vec{v} = 1$

↳ Change to spherical: $d\vec{v} = dV_x dV_y dV_z \rightarrow v^2 \sin\theta \ dv \ d\theta \ d\phi$

↳ $\int_{-\infty}^{+\infty} P(v) d\vec{v} = \int_0^\infty \int_0^\pi \int_0^{2\pi} P(v) v^2 \sin\theta \ dv \ d\theta \ d\phi$

$$\therefore A = \left(\frac{2\pi k_B T}{m} \right)^{3/2}, \quad P(v) d\vec{v} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} v^2 dv$$

IMPORTANT

Let $f(v) dv = P(v) dv$ to find Maxwell-Boltzmann

distribution: $f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} v^2$

⊗ RMS velocity: $\sqrt{\langle v^2 \rangle} = \sqrt{3} \sqrt{\frac{k_B T}{m}}$

⊗ Velocity at peak in distribution: $v_{\text{peak}} = \sqrt{2} \sqrt{\frac{k_B T}{m}}$

↳ Most common velocity

↳ So $v_{\text{peak}} < \langle v \rangle < v_{\text{rms}}$

* Nonideal gases, van der Waals Equation

• Ideal: $PV = nRT$

• Van der Waals Equation of state

1. Finite volume: $P(V - nb)$

↳ b = volume occupied by 1 mole of gas

2. Interparticular interactions tend to slow molecules

prior to striking walls: $\Delta P = -a\rho_N^2 = -a\left(\frac{n^2}{V^2}\right)$

∴ Combining the two, $P = \frac{nRT}{V - nb} - a\left(\frac{n^2}{V^2}\right)$

$$\hookrightarrow a = 0.141 \frac{m^3 Pa}{mol^2}$$

* Heat, Transfer of Thermal Energy

• Property

↳ Extensive: property is proportional to amt. of substance

↳ Intensive: property is independent to amt. of substance

※ Extensive property = sums over microstates

Intensive property = average over microstates

Important Terms

• Thermal energy: energy associated with motion of molecules within object (extensive)

• Temperature: measure associated with avg. kinetic energy of molecules (intensive)

• Heat: energy that is transferred in a thermal process

↳ Not a property of objects

↳ Think of it as a process: use the term "heating"

• 3 mechanisms for heating

1. Conduction: heat consists of diffusion of thermal energy through a substance.

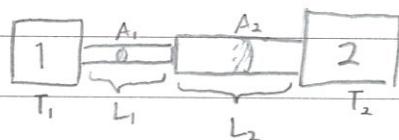
↳ TE only flows when there's a temperature gradient

$$\dot{Q} = -kA \frac{dT}{dx}, \quad k = \text{Thermal conductivity}$$

$$P_{\text{cond}} = \frac{\dot{Q}}{\Delta t} = -k \frac{A}{L} \Delta T, \quad P_{\text{cond}} = \text{Conduction rate}$$

※ 2 infinite thermal reservoirs:

$$P = \frac{T_1 - T_2}{R_1 + R_2}$$



$$\hookrightarrow R = \text{thermal resistance} = \frac{L}{kA}$$

$$\hookrightarrow R_{\text{eff}} = \sum_i R_i, \quad \text{just like resistors in circuits.}$$

2. Convection: transfer of thermal energy by transport of material

↳ Proportional to ΔT^2

3. Radiation

↳ Hot objects glow - emit electromagnetic radiation

↳ $P_{\text{rad}} = \text{rate of TE radiated} = E\sigma_{\text{SB}}T^4A$

↳ $\sigma_{\text{SB}} = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4$, Stefan-Boltzmann const.

↳ E = emittance of surface

↳ $E=1$: blackbody

↳ $E=0$: perfect mirror

* First Law of Thermodynamics

• Basically conservation of energy

$$\cdot \Delta U_{\text{internal}} = Q + W$$

* Conventions

↳ Q is \oplus if heat into body, \ominus if out

↳ W is \oplus for work done on body, \ominus for work done by body

* 0th Law of Thermodynamics

• If 2 objects are in thermal equilibrium with a 3rd object, all 3 objects are in thermal equilibrium with each other

Light & Heat

Week 3 Notes

*Heat Capacity, Latent Heat

- 1st law of Thermodynamics: $\Delta U = Q + W$

↳ (Except near 1st order phase transition) Adding heat increases temp. if W is negligible.

- Heat capacity: $Q = C\Delta T$

$$\hookrightarrow \text{Specific heat: } c \equiv \frac{C}{m} \quad \text{or} \quad Q = mc\Delta T$$

$$\hookrightarrow \text{molar heat capacity: } c_n = \frac{C}{\text{moles}}$$

$$\circlearrowleft C_p = \text{const. pressure}, C_v = \text{const. volume}$$

- Heat capacities:

↳ Solids: expansion ignored, measured at C_p

$$Q = \Delta U \quad (\text{since } W \text{ is negligible})$$

For simple metals & elemental solids near room temp, $c_n \sim 25 \frac{\text{J}}{\text{mol} \cdot \text{K}}$

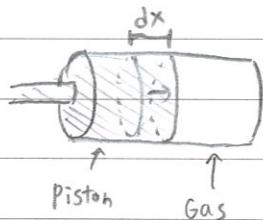
- Latent heat

↳ heat required for a 1st order phase transition

$$\hookrightarrow Q = mL \quad [\text{J/kg}] \quad \text{or} \quad Q = nL \quad [\text{J/mol}]$$

* Work via Ideal Gases

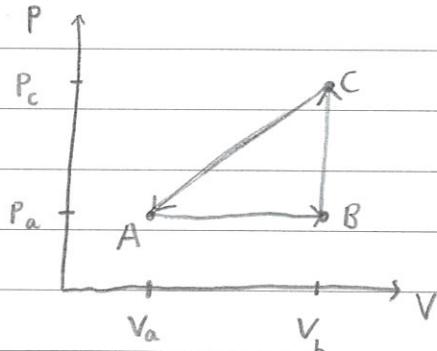
- Gas expanding against piston



$$W = \int F_x dx = \int -(pA) dx = - \int p dV$$

(work done by gas on piston)

- Multistep process



$$W_{AB} = -(V_b - V_a) p_a$$

$$W_{BC} = 0 \quad b.c. \quad \Delta V = 0$$

$$W_{CA} = -(V_b - V_a) \left(p_a + \frac{p_c - p_a}{2} \right)$$

$$W_{\text{total}} = (V_b - V_a) \frac{p_c - p_a}{2}$$

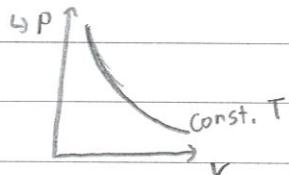
(work done on system = area of triangle)

⊗ At const. V (isochoric), $W=0$

⊗ At const. P (isobaric), $W = -p \Delta V$

⊗ At const. T (isothermal), $W = -nRT \ln\left(\frac{V_f}{V_i}\right)$

↳ Using ideal gas law



⊗ Work done in thermal isolation (adiabatic): $W = -p_i V_i^{\gamma} \int_{V_i}^{V_f} \frac{dV}{V^{\gamma}}$

↳ $\Delta Q = 0$

↳ pV^{γ} remains const., $\gamma = \frac{5}{3}$ for ideal gas, $\gamma = \frac{4}{3}$ for polyatomic gas at room temp.

↳ Alt. form: $W = \frac{p_i V_i}{\gamma-1} \left[\frac{V_i^{\gamma-1}}{V_f^{\gamma-1}} - 1 \right] = \frac{1}{\gamma-1} [p_f V_f - p_i V_i]$

$$\text{⊗ } \gamma = 1 + \frac{nR}{C_v}$$

Light & Heat

Week 3 Notes

* Internal energy of gases

- Molecules can have energy in different modes

↳ Modes: independent ways in which energy can be stored

↳ 3 translational modes: K_{Ex} , K_{Ey} , K_{Ez}

↳ 3 rotational modes: rotational KE about each axes

↳ 1 kinetic vibrational mode along axis of molecule

↳ 1 PE mode for vibrations

- Rotational modes: $E_{rot} = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$

↳ $I = \sum_{atoms} m r_i^2$, r_i is dist. from center of atom to axis of rotation.

↳ $L = I\omega$, If $v_i = r_i\omega$, $E_{rot} = \frac{1}{2} m v^2$

$$E_{transl} = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

$$E_{rot} = \frac{1}{2} \left(\frac{L_x^2}{I_x} + \frac{L_y^2}{I_y} + \frac{L_z^2}{I_z} \right)$$

$$E_{vib} = \frac{m}{8} \left(\frac{dr}{dt} \right)^2 + \frac{1}{2} k(r - r_0)$$

※ Equipartition theorem: each mode possesses the same energy $E_{mode} = \frac{1}{2} kT$

- Quantum effects

- Angular momentum, vibration are quantized

- Modes realized only when kT exceeds spacing between energy levels.

- At 300K, only transl & rot. modes contribute.

↳ $E_{internal} = \frac{3}{2} nRT$ (monoatomic gases He, Ne, Ar...)

$$= \frac{5}{2} nRT$$
 (diatomic gases N₂, O₂...)

$$= \frac{6}{2} nRT$$
 (polyatomic gases CO₂...)

※ Solids: 3 kinetic & potential vibrational modes, $E_{internal} = \frac{6}{2} nRT$

*Heat Capacity at const. V & const. P

• Heat Capacity (C) : $Q = C\Delta T$

• At const. V : $Q_v = C_v \Delta T$

↳ $\Delta V = 0$, so $W = 0$

↳ 1st Law gives $\Delta U = \Delta E_{internal} = Q_v$, $\Delta U = C_v \Delta T$

$$C_v = \left(\frac{dU}{dT} \right)_V \quad \text{means held at const. } V$$

↳ Simple solids (expansion negligible): $U = 3nRT \rightarrow C_v = 3nR$

↳ Gases near 300K

$$\hookrightarrow \text{Monoatomic: } C_v = \frac{3}{2}nR$$

$$\hookrightarrow \text{Diatomeric: } C_v = \frac{5}{2}nR$$

$$\hookrightarrow \text{Polyatomic: } C_v = 3nR$$

• At const. P: $Q_p = C_p \Delta T$

↳ $C_p > C_v$ b.c. gas expands, does work on environment

$$\hookrightarrow \Delta U = Q_p + W = C_p \Delta T - p \Delta V$$

$$\hookrightarrow \text{Now use } pV = nRT \longrightarrow pdV + Vdp = nRdT$$

$$dU = C_p dT - nRdT, \quad dU = C_v dT$$

$$\therefore C_p = C_v + nR$$

$$\text{Monoatomic: } C_v = \frac{3}{2}nR, \quad C_p = \frac{5}{2}nR$$

$$\text{Diatomeric: } C_v = \frac{5}{2}nR, \quad C_p = \frac{7}{2}nR$$

$$\text{Polyatomic: } C_v = 3nR, \quad C_p = 4nR$$

$$\bullet \text{ Isothermal: } Q_{in} = nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$\bullet \text{ Isobaric: } Q_{in} = C_p \Delta T$$

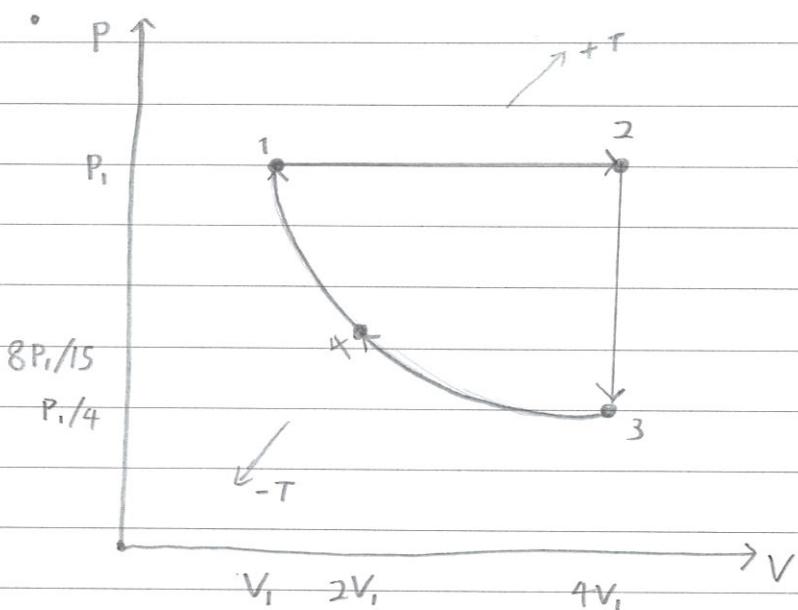
$$\bullet \text{ Isochoric: } Q_{in} = C_v \Delta T$$

$$\bullet \text{ Adiabatic: } Q_{in} = 0$$

Light & Heat

week 3 notes

* PV diagrams + reversible cycles



$$PV = NkT$$

$$\Delta E = Q - P\Delta V \\ = Q + W$$

$$E_1 = \frac{3}{2}NkT_1 = \frac{3}{2}P_1V_1$$

- 1 → 2: isobaric process, $\Delta E = Q - P\Delta V$

$$\hookrightarrow W = -P_1 \Delta V = -3P_1V_1$$

$$\hookrightarrow E_2 = 4E_1$$

$$\hookrightarrow Q_{1-2} = \Delta E - W = 6P_1V_1$$

$$E_2 = \dots$$

- 2 → 3: isochoric process, $\Delta E = Q + 0$

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

Just use

$$E_1 = \frac{3}{2}NkT_1$$

$$= \frac{3}{2}P_1V_1$$

- 3 → 4: isothermal process, $0 = Q - PdV$

$$\hookrightarrow PV = \text{const.}$$

and

$$\Delta E = Q_{in} + W_{on}$$

$$W = -P\Delta V$$

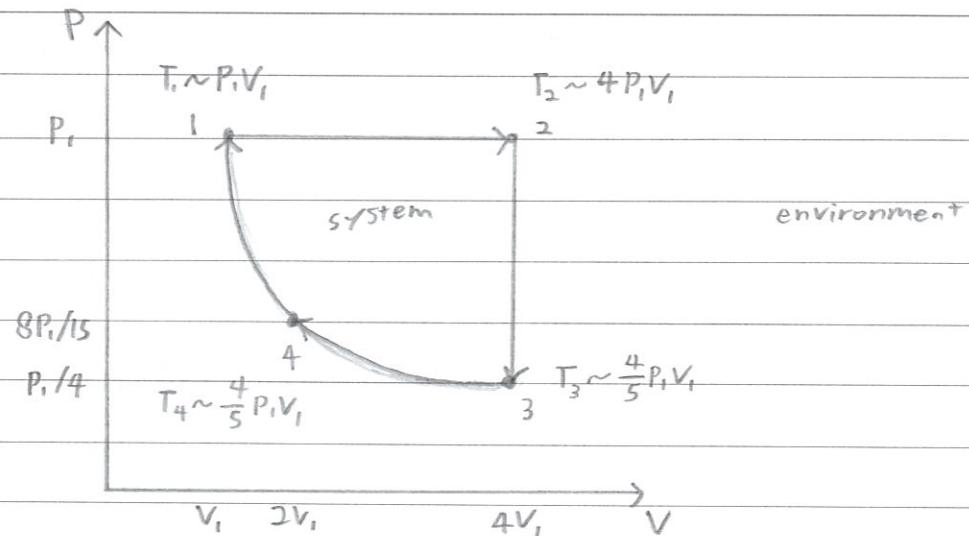
- 4 → 1: adiabatic process, $dE = 0 - PdV$

$$\hookrightarrow PV = NkT$$

\hookrightarrow Steeper than isothermal processes

$\ddot{\times}$ If reversible: adiabatic = isentropic

$\ddot{\times}$ Entropy of ideal gas: $\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$



	ΔV_{System}	Q or W	Q or W	$\Delta V_{\text{Environment}}$
1 - 2 isobaric	$3P_1 V_1$	$6P_1 V_1$	$-6P_1 V_1$	$-3P_1 V_1$
2 - 3 isochoric	$-\frac{16}{5}P_1 V_1$	$3P_1 V_1$	Q	$\frac{16}{5}P_1 V_1$
3 - 4 isothermal	0	$-\frac{4}{5}P_1 V_1 \ln(2)$	$\frac{4}{5}P_1 V_1 \ln(2)$	0
4 - 1 adiabatic	$\frac{1}{5}P_1 V_1$	W	$-\frac{4}{5}P_1 V_1 \ln(2)$	$-\frac{1}{5}P_1 V_1$
Net Cycle	0	0	0	0

Light & Heat

week 4 Notes

* Applications of the 1st law

- Review:

↳ Isochoric $\Delta V = 0$ $W = 0$, $dU = Q$

↳ Isobaric $\Delta P = 0$ $W = -pdV$

↳ Isothermal $\Delta T = 0$ $W = -nRT \ln\left(\frac{V_f}{V_i}\right)$

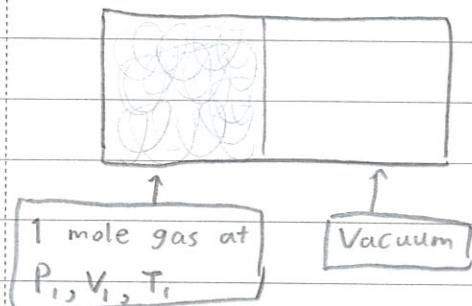
↳ Adiabatic $Q = 0$ $W = \frac{1}{\gamma-1} (P_f V_f - P_i V_i) = -C_v(T_f - T_i)$

$dU = W$, $PV^\gamma = \text{const.}$

↳ Closed cycle $\Delta U = 0$ $W = -Q$

*Free expansion & irreversibility

- Perfectly insulated container, thin barrier



↳ Small opening made in barrier...

↳ No work done; no objects are being "pushed," $F_{\text{net}} = 0$

↳ No heat exchanged

$$\Delta U = Q + W = 0$$

↳ What's wrong here?

↳ Irreversible process.

↳ Not in equilibrium during the process; can't find P or V during that time.

※ Free expansion (irreversible processes can't be represented on PV diagram): $W \neq -\int pdV$

Light & Heat

week 4 Notes

* Second Law of Thermodynamics

Empirical
statements

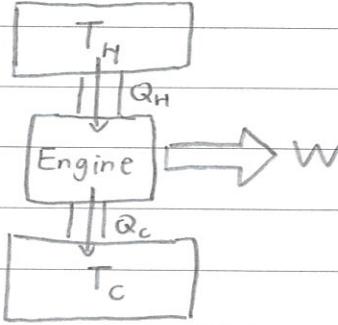
• Statement 1 (Clausius statement)

- Impossible for any cyclic set of thermodynamics processes (machine) to produce no other effect than to convey heat from 1 body to another that's at a higher temperature.

• Statement 2 (Kelvin-Planck statement)

- Process whose only final result is to transform heat extracted from an isothermal source into work is impossible.

• Heat engines:

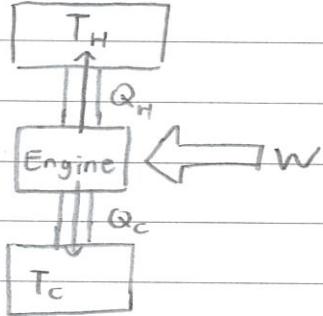


$$|Q_H| = |Q_c| + W$$

$$\epsilon \equiv \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_c|}{|Q_H|}$$

(efficiency)

• Refrigerator:



• Heat engines run backwards

• Work done on system ($w > 0$)

$$\kappa \equiv \frac{|Q_c|}{|W|} = \frac{|Q_c|}{|Q_H| - |Q_c|}$$

(coeff. of performance)

* Statement 3 (Carnot)

- Carnot engine has max. efficiency.

* Reversible processes, Carnot cycle

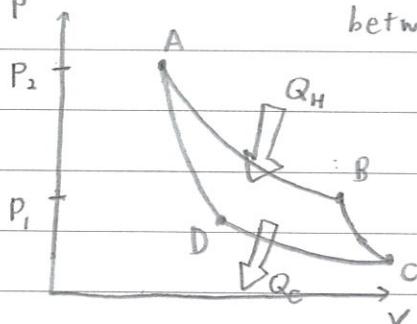
- Reversible cycles

↳ Want most efficient cycle

↳ Need to do process as slowly as possible

↳ e.g. 2 isothermals process

- Carnot cycle (max. possible efficiency for heat engine working between 2 heat reservoirs)



$A \rightarrow B$: isothermal expansion at T_H

$B \rightarrow C$: adiabatic expansion $T_H \rightarrow T_C$

$C \rightarrow D$: isothermal compression at T_C

$D \rightarrow A$: adiabatic compression $T_C \rightarrow T_H$

$$e = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

- Details

1. $A \rightarrow B$: $Q_H = nRT_H \ln\left(\frac{V_B}{V_A}\right)$ $P_A V_A = P_B V_B$

2. $B \rightarrow C$: N/A $P_B V_B^\gamma = P_C V_C^\gamma$

3. $C \rightarrow D$: $Q_C = -nRT_C \ln\left(\frac{V_D}{V_C}\right)$ $P_C V_C = P_D V_D$

4. $D \rightarrow A$: N/A $P_D V_D^\gamma = P_A V_A^\gamma$

∴ $V_A V_B^\gamma V_C V_D^\gamma = V_A^\gamma V_B V_C^\gamma V_D \rightarrow V_B^{\gamma-1} V_D^{\gamma-1} = V_A^{\gamma-1} V_C^{\gamma-1}$

$Q_h = nRT_h \ln(V_2/V_1) \dots$

Carnot efficiency: $E_c = 1 - \frac{T_C}{T_H}$

↳ Same for any reversible process

↳ Greater than any irreversible process

Efficiency = $\frac{\text{benefit}}{\text{cost}} = \frac{\sum Q_{in} - \sum Q_{out}}{\sum Q_{in}}$

= or $\frac{W}{Q_h}$

Light & Heat

week 5 notes

$$* \text{Entropy } (\Delta S = \int \frac{dQ_{\text{rev}}}{T})$$

• State variables (core, measurable macroscopic properties)

↳ Intensive: P, T

↳ Extensive: V

• State function

↳ Internal energy: U(P, V, T, N) (of a system)

↳ Internal energy of ideal gas: U(T, N)

⊗ Energy is defined for the microstate, but never measured directly.

⊗ $w = - \int pdV$ (for reversible processes)

⊗ For Q: $\Delta U = Q - pdV$, run experiments at const. V

↳ $\therefore Q \sim T$ (but U is extensive, T is intensive)

↳ New property: $\Delta S = \left(\frac{\Delta U}{T} \right)_V , Q = TdS$

• What is this S?

↳ Extensive

↳ Units J/K

↳ State function (like U) - we also don't measure it directly.

$$dU = TdS - PdV$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV = C_V \frac{dT}{T} + Nk \frac{dV}{V}$$

$$\text{Integrating, } \Delta S = C_V \ln\left(\frac{T_f}{T_i}\right) + Nk \ln\left(\frac{V_f}{V_i}\right)$$

$$\text{⊗ Extra: } \left. \frac{\partial U}{\partial S} \right)_V = T, \quad \left. \frac{\partial U}{\partial V} \right)_S = P$$

$$\text{Isothermal: } \Delta S = Nk \ln \frac{V_f}{V_i}$$

$$\text{Isochoric: } \Delta S = C_V \ln \left(\frac{T_f}{T_i} \right)$$

$$\text{Adiabatic: } \Delta S = 0$$

$$\text{Isobaric: } \Delta S = C_V \ln \left(\frac{T_f}{T_i} \right) + Nk \ln \left(\frac{V_f}{V_i} \right)$$

big C? $C = cm$.

* More with Carnot cycle (which is optimal)

• Carnot cycle: $\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}$ (not efficiency) $\leftarrow \Delta S = \frac{Q_H}{T_H} - \frac{Q_C}{T_C}$

↳ Since $Q_H > 0$ and $Q_C < 0$, $\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$

↳ Sum of $\frac{Q_i}{T_i}$ is 0 in any Carnot cycle.

• Approximate smooth curve by an arbitrarily large number of Carnot cycles.

↳ 2 adjacent isotherms: $\frac{Q_n}{T_n} + \frac{Q_{n+1}}{T_{n+1}} = 0$
(b.c. they're in opposite directions)

$$\sum_{i=1}^N \frac{Q_i}{T_i} = 0 \quad \text{in limit } N \rightarrow \infty, \Delta T \rightarrow 0$$

$$\oint \frac{dQ}{T} = 0$$

∴ $dS = \frac{dQ}{T}$, for any reversible process, $\oint dS = 0$,
entropy is conserved.

For irreversible processes, $\int dS > 0$

∴ In general, $\Delta S > 0$ when heat goes from high \rightarrow low temp.

$\Delta S < 0$ when heat goes from low \rightarrow high temp.

∴ 2nd Law of Thermodynamics (entropy form): A natural process that starts & ends in equilibrium will go in direction that causes entropy of system + environment to increase.

∴ S is a function only of the state of the system

- State function

- Path independent

- only depends on starting & ending points,

$$\hookrightarrow \Delta S = \int \frac{dQ_{rev}}{T}$$

• ΔS for

↳ Isothermal expansion

$$dS = \int \frac{dQ}{T} = \int \frac{PdV}{T} \quad (Q = -w)$$

$$= nR \int_{V_i}^{V_f} \frac{dV}{V} = nR \ln\left(\frac{V_f}{V_i}\right)$$

↳ Isochoric heating

$$dS = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{C_v dT}{T} = C_v \ln\left(\frac{T_f}{T_i}\right)$$

Use $C_v = \frac{1}{2}nRz$ ($z = \#$ of modes for gas)

Also $C_p = C_v + nR$, $\gamma = \frac{C_p}{C_v}$, $C_v = \frac{nR}{\gamma-1}$

$$dS = C_v \ln\left(\frac{T_f}{T_i}\right) = \frac{nR}{\gamma-1} \ln\left(\frac{T_f}{T_i}\right)$$

* Ideal gas: $dS_{gas} = nR \ln\left(\frac{V_f}{V_i}\right) + \frac{nR}{\gamma-1} \ln\left(\frac{T_f}{T_i}\right)$

$$= nR \ln V + \frac{nR}{\gamma-1} \ln T - (\text{constant})$$

↳ Adiabatic expansion

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{\gamma-1}$$

* Now:

$$dS_{gas} = nR \ln\left(\frac{V_f}{V_i}\right) + \frac{nR}{\gamma-1} \ln\left(\frac{V_f}{V_i}\right)^{\gamma-1}$$

$$dS_{gas} = 0 \text{ for adiabatic processes}$$

* ΔS when going through phase change

↳ Const. T

↳ $\Delta S = \frac{mL_f}{T}$ (melting m moles)

↳ $\Delta S = -\frac{mL_f}{T}$ (freezing m moles)

* Heat & Work are inexact differentials.

- Consider $\delta U = \delta Q + \delta W$

↳ U is an exact differential, b.c. it's an internal property of the system.

$$\int_i^f \delta U = \Delta U = U_f - U_i \quad (\text{independent of path})$$

↳ W & Q are not internal properties, but related to interactions.

$$\int_i^f \delta W = W_{i \rightarrow f} \neq W_f - W_i$$

w_f has no meaning, not a property.

Integration depends on path taken.

*Notes

- T increases when you cross isotherms.
- S increases when you cross adiabats.

• Interesting parallel: $W = -pdV$ (see PV diagram)

$Q = TdS$ (see TS diagram)

*3rd Law of Thermodynamics

- For solids,

$$Q = C_V dT = T dS$$

$$C_V = T \left(\frac{dS}{dT} \right)_V$$

For non-metal solids at low T ,

$$C_m = 234R \left(\frac{T}{\theta_D} \right)^3, \quad T \ll \theta_D$$

$$\text{Thus } S = \frac{234R}{\theta_D^3} \frac{T^3}{3} + \text{const.}$$

- For systems that stay in thermodynamics equilibrium down to $T=0K$,

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

(Q.M.: as $E \rightarrow E_0$, $S \rightarrow 0$)

(At very low $T \sim T_0$, system may be in ground state for d.o.f. involving spin)

(Number of states w/ different spin orientations \rightarrow sizable S)

(Thus as $T \rightarrow T_0$, S approaches a value S_0 only depending on spin d.o.f.'s)

- 3rd Law of Thermodynamics

↳ Entropy of a system has the limiting property that as $T \rightarrow 0_+$, $S \rightarrow S_0$

where S_0 is a constant independent of all (macroscopic) parameters of particular system

∴ S of system undergoing reversible processes approaches 0 as $T \rightarrow 0$

Light & Heat

Week 6 Notes

* Entropy - more on it (stat. mech view)

- Extensive property, measure of total available microstates
- Given a set of properties, how many corresponding microstates?
- Restrictions on $S(\Omega)$
 1. Monotonically increasing func. of multiplicity of states, Ω
 2. Extensive property, $S_{\text{trans}} = S(\Omega_1) + S(\Omega_2)$
 - ⊗ If systems are initially isolated, # of states = $\Omega_1 \Omega_2$
 3. If only 1 possible arrangement of microstate, measure is at a minimum, $S(1) = 0$.

↳ To satisfy all this: $S = k \ln(\Omega)$

- Stat. mech. 2nd Law: if a system begins in a state of low multiplicity, it will evolve to a probable state with higher multiplicity.
- ↳ At its core: probabilistic.

• Rise of entropy in universe

↳ Reversible process: $\Delta S = 0$

↳ Irreversible process: $\Delta S_{\text{universe}} > 0$

↳ Implications:

↳ Entropy of universe will eventually reach max

Heat death: no useful energy to do work anymore

↳ Big Bang was low entropy event - how did the universe get into that state?

* The H Theorem

- Probability to be in state r : P_r , func. of time

$$\sum_r P_r(t) = 1$$

- Transition probability per unit time for system to transition from $r \rightarrow s$: W_{rs}

↳ Reverse: W_{sr}

$$W_{rs} = W_{sr}$$

$$\frac{dP_r}{dt} = \sum_s P_s W_{sr} - \sum_s P_r W_{rs}$$

$$= \sum_s W_{rs} (P_s - P_r)$$

- Consider mean value of $\ln(P_r)$, or H .

$$\ln(P_r) = H = \sum_r P_r \ln(P_r)$$

$$\frac{dH}{dt} = \sum_r \frac{dP_r}{dt} (\ln P_r + 1)$$

$$\frac{dH}{dt} = \begin{cases} \sum_r \sum_s W_{rs} (P_s - P_r) (\ln P_r + 1) \\ \sum_r \sum_s W_{rs} (P_r - P_s) (\ln P_s + 1) \end{cases}$$

$$\frac{dH}{dt} = -\frac{1}{2} \sum_r \sum_s W_{rs} (P_r - P_s) (\ln P_r - \ln P_s)$$

- $\ln P_r > \ln P_s$ if $P_r > P_s$, then $(P_r - P_s)(\ln P_r - \ln P_s) \geq 0$
are equal only when $P_r = P_s$.

$W_{rs} > 0$ (it's a probability), so $\frac{dH}{dt} \leq 0$

$\therefore \frac{dH}{dt} = 0$ iff. $P_r = \text{const.}$ for all accessible states.

* Relating stat. mech & Classical entropies

- Stat. mech: $S = k \ln \Omega$

- Classical thermo: $\Delta S = Q/T$

- Derive ΔS expression:

$$dS = \frac{\delta Q}{T} = \frac{dE - \delta W}{T} = C_V \frac{dT}{T} + \frac{P dV}{T} = C_V \frac{dT}{T} + Nk \frac{dV}{V}$$

$$\Delta S = C_V \int \frac{dT}{T} + Nk \int \frac{dV}{V}$$

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

- Find multiplicity of states over differential region of phase space by discretizing phase space.

$$d\Omega = \frac{1}{h^{3N}} \omega(\vec{r}, \vec{p}) d^N \vec{r} d^N \vec{p}$$

$\omega(\vec{r}, \vec{p})$ = density of states over pos. & mom.

For an ideal gas, $\omega(\vec{r}, \vec{p}) = e^{-\sum_i p_i^2 / 2m kT}$

$$\Omega = \frac{1}{N! h^{3N}} \int \dots \int \omega(\vec{r}, \vec{p}) d^N \vec{r} d^N \vec{p}$$

For ideal gas, $\omega(\vec{r}, \vec{p}) = \omega(\vec{p})$ & all molecules independent.

$$\Omega = \frac{1}{N! h^{3N}} \left(\int d^N \vec{r} \right) \left(\int \dots \int e^{-\sum_i p_i^2 / 2m kT} d^N \vec{p} \right)$$

For momentum part

$$\left\{ \begin{aligned} \left[\int e^{-p_x^2 / 2m kT} dp_x \right]^N &= \left[\int e^{-p_x^2 / 2m kT} dp_x \right]^{3N} \\ &= \left[\sqrt{2\pi m kT} \int_{-\infty}^{\infty} e^{-q^2} dq \right]^{3N} \quad \text{where } q = \frac{p_x}{\sqrt{2m kT}} \\ &= (2\pi m kT)^{\frac{3N}{2}} \end{aligned} \right.$$

OK so now $S = k \ln \Omega = k [N \ln V - \ln N!]$

$$+ k \left[\ln (2\pi m kT)^{\frac{3N}{2}} - \ln (h^{3N}) \right]$$

$$\bullet S = Nk \ln \frac{V}{N} + \frac{3}{2} Nk \ln T + \frac{3}{2} Nk \left(\ln \frac{2\pi mk}{h^2} \right)$$

↳ Find that $\Delta S = S_f - S_i = \frac{3}{2} Nk \ln \left(\frac{T_f}{T_i} \right) + Nk \ln \left(\frac{V_f}{V_i} \right)$

which is the classical form for ΔS .

※ A more careful approach w/ quantum mechanics
(\hbar = Planck constant) yields Sackur-Tetrode relation.

$$S = Nk \ln \left(\frac{V}{N} \right) + \frac{3}{2} Nk \ln(T) + \frac{3}{2} Nk \ln \left(\frac{2\pi mk}{h^2} \right) + \frac{5}{2} Nk$$

※ Relationship:

$$\Delta S = k \ln(\Omega_{mom}) + k \ln(\Omega_{pos})$$

$$\Delta S = C_v \ln \left(\frac{T_f}{T_i} \right) + Nk \ln \left(\frac{V_f}{V_i} \right)$$

	$\ln \Omega_{mom}$	$\ln \Omega_{pos}$	$\ln \Omega$
Isothermal expansion:	0	>0	>0
Isochoric heating:	>0	0	>0
Iobaric expansion:	>0	>0	>0
Adiabatic expansion:	<0	>0	0