

Thermodynamics

Three Laws

1) Energy can't be created or destroyed.

$$\Delta U = Q - W \quad (\text{watch signs!})$$

↑ internal energy ↑ heat ↑ work in differential form, $dU = TdS - PdV$

2) no process can ^{solely} transfer heat from a body at a lower (refrigerator) temp to one at a higher temp. or no system can undergo (engine) a cyclic process where heat absorbed from a reservoir at a single temp is completely converted into mechanical work.

$$\Delta S \geq \frac{\delta Q}{T} \quad \text{entropy cannot decrease for isolated system}$$

3) Entropy is zero ^(or constant) at absolute zero temp.

$$\Rightarrow S = k_B \ln W, @ 0 \text{ K} \rightarrow \text{only 1 microstate!}$$

Prob 52 (pg 324) Which of the following is NOT true about the 3rd law?

A) it implies that the entropy of a perfect crystal of a pure substance must approach zero @ abs. zero

★ B) it implies that the entropy of an isolated system can sometimes decrease

C) it is a consequence of the fact that the ground state degeneracy of a system determines its entropy

D) it implies that abs. zero can never be reached in expts.

E) it permits the entropy of a system to be nonzero @ abs. zero

Equations of state

2

ideal gas: $PV = Nk_B T$ (know by heart)

vdW gas: $(P + N^2 a / V^2)(V - Nb) = Nk_B T$ recognize but don't memorize
 $a \rightarrow$ attraction, $b \rightarrow$ size

Ex: (18 from practice) IF one mole of an ideal gas doubles its volume as it undergoes an isothermal expansion, its pressure is
(A) quadrupled (B) doubled (C) unchanged (D) halved (E) quartered
 PV is constant; $V \times 2 \rightarrow P \times 1/2$

Types of processes

1) Reversible: infinitesimal steps, each can be undone by changing state variable

$$\delta W = PdV$$

$$\delta Q = TdS \rightarrow \Delta S = \int \frac{\delta Q}{T} \quad (\text{Note! } \Delta S \text{ does not have to be } 0)$$

2) Quasistatic: happens infinitely slowly; always in equilibrium
reversible is always quasistatic but reverse not always

3) Adiabatic: $\delta Q = 0$

4) Isentropic / reversible adiabatic: reversible $\rightarrow \Delta S = \int \frac{\delta Q}{T}$, adiabatic $\rightarrow \delta Q = 0$

$\Rightarrow \Delta S = 0$; Ex. compressing gas into a cylinder slowly

Also $PV^\gamma = \text{constant}$, $\gamma = C_p / C_v$

5) Iso-"something" process: isothermal - constant T , etc.

iso ~~thermal~~ ^{thermal} $\rightarrow P = \frac{Nk_B T}{V} \Rightarrow W = \int P dV = Nk_B T \int \frac{dV}{V} = Nk_B T \ln\left(\frac{V_2}{V_1}\right)$

6) Free expansion: adiabatic, but not reversible, e.g. gas released into room (also isothermal)

entropy change? can't use $\Delta S = \int \frac{\delta Q}{T}$! (only reversible)

$$dU = 0 \rightarrow TdS = PdV \rightarrow \Delta S = \int_{V_1}^{V_2} P \frac{dV}{T} = \int_{V_1}^{V_2} \frac{Nk_B T}{V} \frac{dV}{T} = Nk_B \ln\left(\frac{V_2}{V_1}\right)$$

We also know for ideal gas,
 $S = Nk_B \ln \left(\frac{V T^{3/2}}{N} \right) + \text{constants}$

Prob: Which of the following must be true of a closed system undergoing an adiabatic process?

- ★ A) no heat is exchanged w/environment
- B) entropy is constant (reversible)
- C) the system does no work on its environment
- D) entropy increases (irreversible)
- E) the system is at constant pressure

Heat Capacity

~~$\left(\frac{\partial Q}{\partial T} \right)_V = C_V$~~ ~~$\left(\frac{\partial Q}{\partial T} \right)_P = C_P$~~

$\hookrightarrow dU = TdS - PdV \stackrel{no}{=} \delta Q \quad \hookrightarrow \frac{\partial U}{\partial T} = \left(\frac{\partial Q}{\partial T} \right)_V = C_V$

Equipartition (classical)

Each quadratic term (degree of freedom) in the Hamiltonian for a particle contributes $\frac{1}{2}kT$ to the internal energy

Ex: ideal gas: 3 translational $\rightarrow U = \frac{3}{2}kT$
 $H = P_x^2/2m + \dots$

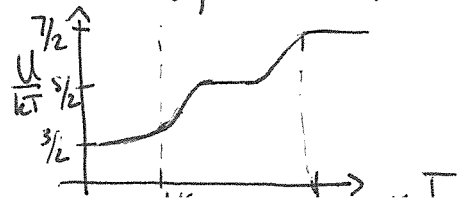
diatomic gas: 3 translational (CM) + 2 rotational (no $\odot \odot$ since pointlike) + 2 vibrational (kinetic and potential) $\Rightarrow U = \frac{7}{2}kT$

$$H = P_x^2/2m + P_y^2/2m + P_z^2/2m + L_1^2/2I_1 + L_2^2/2I_2 + \frac{P_s^2}{m} + \frac{1}{2}ks^2$$

temperature dependent! Breaks down when energy level spacing is large

$kT \sim \hbar \omega \Rightarrow T \sim 1000K$ (vibrational)

$kT \sim \hbar^2/2I \Rightarrow T \sim 1K$ (rotational)



Heat Capacity

$\left(\frac{\partial Q}{\partial T}\right)_V = C_V$ $\left(\frac{\partial Q}{\partial T}\right)_P = C_P$ $\frac{\partial}{\partial T}(dU = TdS - PdV = \delta Q)$
more common $\hookrightarrow \frac{\partial U}{\partial T} = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$

for ideal gas, $C_P - C_V = Nk_B$

for monoatomic ideal gas, $U = \frac{3}{2}kTN \rightarrow C_V = \frac{3}{2}Nk$, $C_P = \frac{5}{2}Nk$

$\gamma = C_P/C_V = 5/3$

C_P, C_V are extensive (depend on amount of substance)

normalize by mass to get c (specific heat)

~~$\left(\frac{\partial Q}{\partial T}\right)_V = C_V$~~

$Q = mc\Delta T$

watch units to tell the difference between spec. heat and heat capacity

Ex: A diatomic ideal gas of N particles is trapped on a layer of material, such that the gas molecules are free to move only in 2D. What is the heat capacity at constant volume of this gas at room temp? Assume $kT \ll \hbar\sqrt{k/m}$.

A) $\frac{1}{2}Nk_B$

B) Nk_B

★ C) $\frac{3}{2}Nk_B$

D) $2Nk_B$

E) $\frac{5}{2}Nk_B$

Remember! $C_V = \partial U / \partial T$

$U = \frac{kTN}{2} \cdot \left(\underset{\substack{\uparrow \\ 2D \text{ trans.}}}{2} + \underset{\substack{\uparrow \\ \text{rotational}}}{1} \right) = \frac{3}{2}kTN \rightarrow C_V = \frac{3}{2}Nk$

Ideal gases (monoatomic)

$U = \frac{3}{2}NkT$, $v_{rms} = \sqrt{\frac{3kT}{m}}$

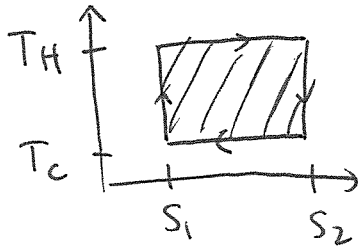
(all come from partition function)

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

PV diagrams

efficiency: $e = 1 - \left| \frac{Q_c}{Q_H} \right|$ for heat engine absorbing heat Q_H from hot reservoir @ T_H and expelling Q_c to cold one @ T_c

max efficiency: $e_{max} = 1 - T_c/T_H$ (idealized Carnot cycle)

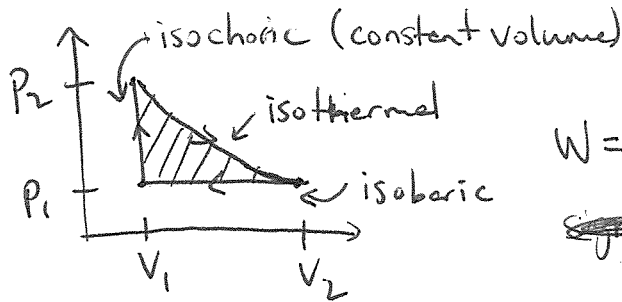


vertical legs are adiabatic
horizontal are isothermal > both reversible

returns to initial state $\rightarrow \Delta U = 0 \Rightarrow Q = W$

~~Q =~~ $dS = \frac{dQ}{T} \rightarrow Q = \int T dS = T_H(S_2 - S_1) + T_c(S_1 - S_2)$

$Q = W = (T_H - T_c)(S_2 - S_1)$



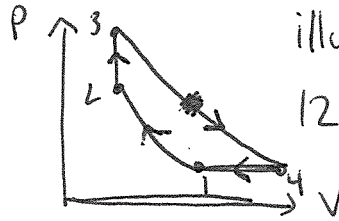
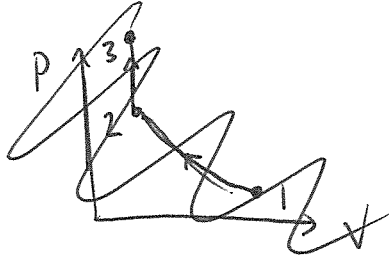
$W = \int P dV = \text{area}$

clockwise - $W > 0$

~~signs matter!~~ signs matter!

CCW - $W < 0$

Prob



illustrates Sargent cycle for ideal gas

1,2,3,4 - reversible adiabatic

2,3 - CV; 4,1 - CP

If T_i denotes temp @ point i , which is hottest?

- A) T_1 B) T_2 C) T_3 D) T_4 E) can't tell

What do we know? rev. adiabatic: $PV^\gamma = \text{constant}$, $\gamma = C_p/C_v = 5/3$

$PV = NkT \rightarrow (PV) V^{\gamma-1} = NkT V^{\gamma-1} = \text{constant}$

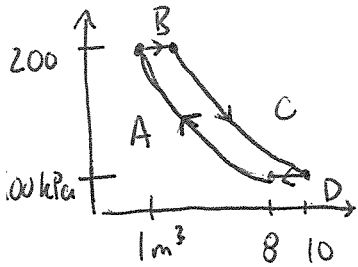
$\gamma > 1 \rightarrow V \downarrow \Rightarrow T \uparrow \Rightarrow T_2 > T_1$; $T_3 > T_4$, what about T_2, T_3 ?

$V(2 \rightarrow 3)$

$PV = NkT \rightarrow V = \text{constant} = \frac{NkT}{P}$ if $P \uparrow, T \uparrow \Rightarrow T_3 > T_2 \Rightarrow \boxed{C}$

Ideal gas undergoing Brayton ~~cycle~~ cycle.

A, C isentropic; B, D isobaric

~~is~~

10) What is the approximate work done during the cycle?

- A) -6200 kJ B) -3100 kJ C) 0 D) 3100 kJ E) 6200 kJ

rectangle $\approx 2 \text{ m}^3 \times 3100 \text{ kPa} = 6200 \text{ kPa} \cdot \text{m}^3 = 6200 \text{ kJ}$ + because CW!

11) The gas used is most likely

- A) monoatomic B) diatomic C) triatomic D) ionized E) heteronuclear

isentropic \rightarrow adiabatic, $PV^\gamma = \text{constant}$

$$100 \cdot 8^\gamma = 3200 \cdot 1^\gamma \rightarrow 8^\gamma = 32 \rightarrow \gamma = 5/3 \Rightarrow \text{monoatomic}$$

(9 practice) A ~~power~~ power plant takes in steam @ 527°C to power turbines and then exhausts the steam at 127°C . In any given time, it consumes 100 megawatts of heat energy from the steam. The maximum possible power output is

- A) 10 MW B) 20 MW C) 50 MW D) 75 MW E) 100 MW

$$P_{\text{max}} = 1 - \left(\frac{T_C}{T_H} \right) = 1 - \left| \frac{400\text{K}}{800\text{K}} \right| = 0.50 \rightarrow 100 \text{ MW} \cdot 0.50 = \underline{50 \text{ MW}}$$

↑ absolute temp!