Thermodynamics Review

temperature: $\boxed{A}\boxed{B}$ in "thermal" contact $T_A = T_B$ (thermal equilibrium)

"0"th Law: $T_A = T_C$ & $T_B = T_C \Rightarrow T_A = T_B$ (mercury in tube)

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equation of state T, P, V, N $\rho = \frac{N}{V}$

$\boxed{P = P(T, \rho)}$

boltzmann constant

e.g. $\boxed{PV = NkT}$ $P = kT\rho$ ideal gas

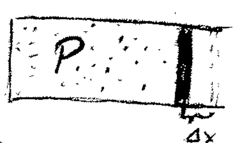
or V.d.W.: $\boxed{\left(P + a\left(\frac{N}{V}\right)^2\right)\left(V - bN\right) = NkT}$

Van der Wals

$(\rho + a\rho^2)\, V\, (1 - b\rho) = NkT$

Stat. Mech: to "derive" $P(T, \rho)$ $\rightarrow$ $P = kT\frac{\rho}{1 - b\rho} - a\rho^2$

Work



W = work done on system $= \int F_{ext}\, dx$

$\Delta V = A\Delta x$ pressure · Area

$= \int (-P \cdot A)\, dx = -\int P\, dV$

Small change in vol

$\boxed{\delta W = -p\,dV}$ infinitesimal work done on gas

can use equation of state

work done on system

e.g. quasistatic process: $P = P(T, V)$ $W = -\int P(T, V)\, dV$

ideal gas, compression at constant T: $P = \frac{NkT}{V}$

Slow-moving?

$V_1 \to V_2$ Expand or Compress

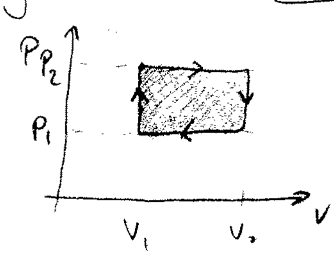
$W = -NkT\int_{V_1}^{V_2}\frac{dV}{V} = -NkT\ln\frac{V_2}{V_1}$

Work

* Constant temp & mass

"Verk"

$\oint \delta W \neq 0$ not a state function



$\oint \delta W = -P_2(V_2 - V_1) - P_1(V_1 - V_2) = -(P_2 - P_1)(V_2 - V_1) \neq 0$

Entropy & Enthalpy are state functions

Work is not

The first law of thermodynamics

Q is heat

thermally isolated system: $dE = \delta W$ adiabatic process

E is a state function, uniquely determined by $T, P, N, \ldots$

thermal contact: δQ heating — Oven / Fridge

$$\boxed{dE = \delta Q + \delta W}$$
$$\boxed{dE = \delta Q - p\,dV}$$

heating: $\delta Q > 0$
cooling: $\delta Q < 0$

$\oint \delta Q \neq 0$ (not a state function)

* can add additional terms for EM

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equation of state for the energy

$E(T,V)$ $N = \text{const.}$

ideal gas: $\boxed{E = \frac{3}{2} NkT}$ — energy doesn't depend on vol for monoatomic gas

V.d.W.: $\boxed{E = \frac{3}{2} NkT - N\left(\frac{N}{V}\right) a}$

Stat. Mech: to "derive" them from "microscopics"

isothermal process for ideal gas: $T = \text{const.}$

$$dE = \delta Q + \delta W = 0$$

$$\delta Q = -\delta W \qquad Q_{1\to2} = -W_{1\to2} = NkT \ln \frac{V_2}{V_1}$$

e.g. $V_2 < V_1$ (compressed, i.e., done work on gas

$Q_{1\to2} < 0$ gives up "heat" to its surroundings

Heat Capacity and Enthalpy

heat capacity (~specific heat) (normalized to unit mass, etc, ...)

$$C = \lim_{\delta T \to 0} \frac{\delta Q}{\delta T}$$

amount of heating needed to change the temperature by unit amount

$$\boxed{\delta Q = dE + \cancel{p\,dV}}$$ (always)

$V = \text{const}$: $C_V = \left.\frac{\delta Q}{\delta T}\right|_V = \left(\frac{\partial E}{\partial T}\right)_V$

example: monoatomic ideal gas: $C_V = \frac{3}{2} N k$

enthalpy $\longrightarrow$ Thermodynamic potential?

$$\boxed{H = E + pV}$$

$$dH = dE + p\,dV + V\,dp = \delta Q + V\,dp$$

$p = \text{const}$: $\left(\frac{\partial H}{\partial T}\right)_p = \left.\frac{\delta Q}{\delta T}\right|_p = C_p$

+ use Enthalpy to find heat capacity

General Relationship between C_p & C_V

C_V └ constant vol

C_p └ constant pres

$H = E + pV$ $\qquad E(T, V)$ $\qquad$ H.c

$C_V = \left(\frac{\partial E}{\partial T}\right)_V$ $\qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{C_p = C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right]}$$

example: ideal gas: (monoatomic $C_V = \frac{3}{2}Nk$) $\left(\frac{\partial E}{\partial V}\right)_T = 0$ $\qquad$ $PV = NkT \Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk}{p}$

$$\boxed{C_p = C_V + Nk} = \frac{5}{2}Nk$$

(obviously $C_p > C_V$ since when $V \neq$ const., work is done as well.)

Adiabatic Processes Meaning? → Exclusion of heat exchange. Perfectly insulated.

$$dE = \delta W + \delta Q$$

$\delta Q = 0$: adiabatic process

$\delta W = -PdV$: quasistatic proces

no energy exchange due to temperature difference

$$dE = dW = -pdV \quad : \text{quasi static adiabatic process}$$

ideal gas: (no V dependence) $\qquad dE = C_V\, dT$

$$C_v\, dT = -p\, dV \qquad pV = NkT$$

$$C_v\, dT = -NkT \frac{dV}{V}$$

$$C_v \frac{dT}{T} = -Nk \frac{dV}{V} \qquad C_p - C_v = Nk$$

$$C_v \frac{dT}{T} = -(C_p - C_v) \frac{dV}{V}$$

$$\frac{dT}{T} = -\left(\frac{C_p}{C_v} - 1\right) \frac{dV}{V} \qquad \gamma = C_p/C_v > 1$$

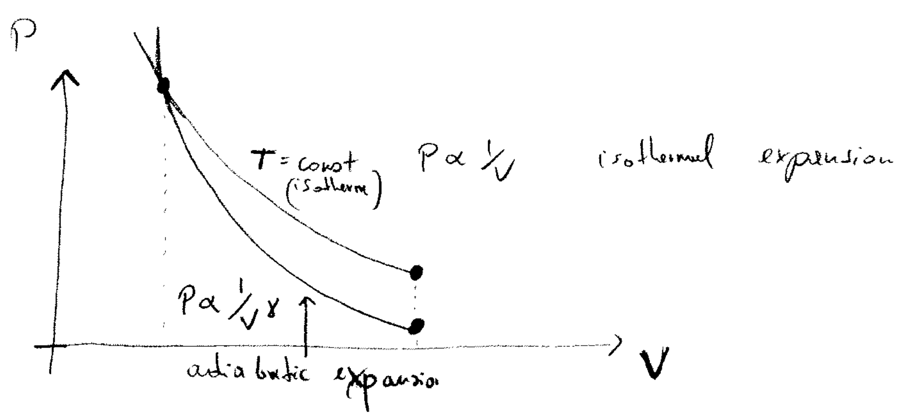
$$\ln T + \ln V^{\gamma-1} = \text{const}$$

$$\boxed{T \cdot V^{\gamma-1} = \text{const.}}$$

$$PV = NkT \Longrightarrow \boxed{PV^{\gamma} = \text{const.}} \quad , \quad \boxed{P^{\frac{1-\gamma}{\gamma}} \cdot T = \text{const.}}$$

adiabatic: $$\left(\frac{\partial P}{\partial V}\right)_{\text{adiab.}} = -\gamma \frac{\text{const.}}{V^{\gamma+1}} = -\gamma \frac{P}{V}$$

isothermal: $$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{V^2} = -\frac{P}{V}$$



The Second Law of Thermodynamics

$E, H, \ldots, S$(entropy) : state functions

W, Q : not properties of the system

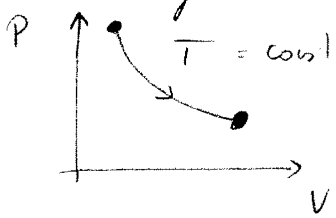
$\oint \delta W \neq 0, \quad \oint \delta Q \neq 0$ depends on the process

1) Kelvin: "No process is possible whose sole result is the complete conversion of energy transferred by heating into work."

isothermal expansion of ideal gas. $\Delta E = Q + W = 0$

work done by gas: $-W = Q$

full conversion but the gas is in a different state



cyclic operation:

$\sum W = 0$
$(\oint W = 0)$

2) Clausius: "No process is possible whose sole result is cooling a colder body and heating a hotter body"
(i.e., energy does not spontaneously go from a colder to hotter body)

3) "There exists an additive state function, the entropy S, that can never decrease for an isolated system"

since S cannot decrease, in equilibrium, it must have a maximum

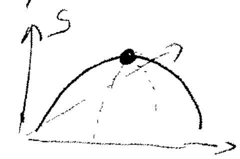
The thermodynamic temperature

$\boxed{A \,\vdots\, B}$ in thermal contact, but isolated from the rest of the world.

$$V = V_A + V_B = \text{const.}$$
$$N = N_A + N_B = \text{const}$$
$$E = E_A + E_B = \text{const.}$$

$$S = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_A)$$

only thermal contact: $V_A = \text{const}$, $N_A = \text{const}$, etc.



$dS = 0$ in equilibrium

$$dS = \left(\frac{\partial S_A}{\partial E_A}\right)_{V_A,N_A} dE_A + \left(\frac{\partial S_B}{\partial E_B}\right)_{V_B,N_B} dE_B$$

$E = E_A + E_B = \text{const.}$

$dE = 0 = dE_A + dE_B \Rightarrow dE_B = -dE_A$

$$dS = \Bigg[\underbrace{\left(\frac{\partial S_A}{\partial E_A}\right)_{V_A,N_A} - \left(\frac{\partial S_B}{\partial E_B}\right)_{V_B,N_B}}_{0}\Bigg] dE_A$$

in thermal equilibrium: $\left(\frac{\partial S_A}{\partial E_A}\right)_{V_A,N_A} = \left(\frac{\partial S}{\partial E_B}\right)_{V_B,N_B}$ $\qquad \frac{1}{T_A} = \frac{1}{T_B}$

$$\boxed{\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E}\right)_{V,N}}$$ thermodynamic temperature $\qquad T_A = T_B$

assume initially separated by an insulating wall $T_A > T_B$

after removing the constraint:

$$\Delta S \approx \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\Delta E_A > 0 \quad \Rightarrow \quad \Delta E_A < 0 \;\;\&\;\; \Delta E_B > 0$$

energy is transferred from hotter to colder system

recall. "heat does not spontaneously go from colder to hotter

The Second Law and Heat Engines

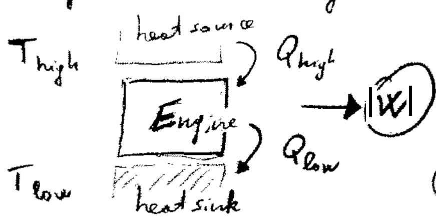
For pure heating/cooling $\quad dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE = \frac{1}{T}\, dE$

$V = \text{const.} \Rightarrow$ no work is done

$$dE = \delta Q = T\, dS \qquad \boxed{dS = \frac{\delta Q}{T}}$$

quasi-static $\overline{\text{reversible}}$ process

simplest heat engine



1. Q_{high} transferred to E by heat source
2. Engine does work $|W|$
3. Q_{low} is transferred to heat sink

"cycle": state variables E, S have the same values for the engine at the end of a cycle

First Law: $\quad Q_{high} - Q_{low} = |W|$ (done by eng.) $(Q_{high}, Q_{low} > 0)$
(energy conservation for cycle)

Second Law: (applied to a cycle)

$$\Delta S_{total} = \Delta S_{high} + \Delta S_{low} + \underbrace{\Delta S_{engine}}_{=0} = \Delta S_{high} + \Delta S_{low} = -\frac{Q_{high}}{T_{high}} + \frac{Q_{low}}{T_{low}} \geq 0$$

$$\boxed{\frac{Q_{low}}{Q_{high}} \geq \frac{T_{low}}{T_{high}}}$$

thermal efficiency: η

$$\eta = \frac{W}{Q_{high}} = \frac{Q_{high} - Q_{low}}{Q_{high}} = 1 - \frac{Q_{low}}{Q_{high}} \leq 1 - \frac{T_{low}}{T_{high}}$$

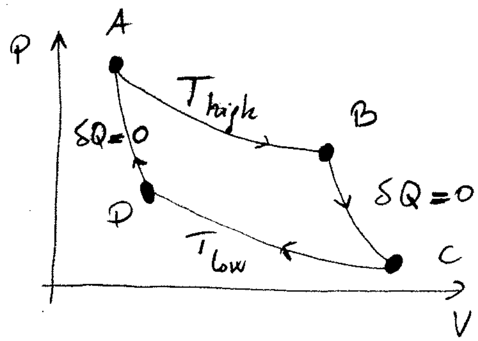
equality holds when $\frac{Q_{low}}{Q_{high}} = \frac{T_{low}}{T_{high}}$ i.e., reversible!!!!

Carnot principle: efficiency for reversible engines operating between the same pair T_{high}, T_{low} have the same efficiency $\boxed{\eta = 1 - \frac{T_{low}}{T_{high}}}$
(general Carnot engine)

Carnot cycle

(particular realization of the general reversible Carnot engine)

ideal gas



(adiabatic)

$dE = \delta Q - \delta W_E$

$(\delta W = -\delta W_E)$

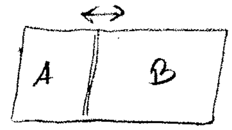
① $A \to B$ isothermal expansion (work done by engine) Q_{high} transferred to engine

② $B \to C$ (lower pressure by) adiabatic expansion (work done by engine) $(\delta Q = 0)$

③ $C \to D$ isothermal compression Q_{low} passed to heat sink (we must do work now on engine

④ $D \to A$ adiabatic compression $(\delta Q = 0)$

Thermodynamic Pressure



$S(E,V,N)$

$E_A + E_B = \text{const.}$
$V_A + V_B = \text{const.}$
$N_A, N_B = \text{const}$

$$S = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B)$$

also N_A, N_B fixed

$$dS = dS_A + dS_B = \left(\frac{\partial S_A}{\partial E_A}\right)_{V_A,N_A} dE_A + \left(\frac{\partial S_A}{\partial V_A}\right)_{E_A,N_A} dV_A + \left(\frac{\partial S_B}{\partial E_B}\right)_{V_B,N_B} dE_B + \left(\frac{\partial S_B}{\partial V_B}\right)_{E_B,N_B} dV_B$$

use $dE_B = -dE_A$ & $dV_B = -dV_A$

$$dS = \underbrace{\left[\left(\frac{\partial S_A}{\partial E_A}\right)_{V_A,N_A} - \left(\frac{\partial S_B}{\partial E_B}\right)_{V_B,N_B}\right]}_{\emptyset} dE_A + \underbrace{\left[\left(\frac{\partial S_A}{\partial V_A}\right)_{E_A,N_A} - \left(\frac{\partial S_B}{\partial V_B}\right)_{E_B,N_B}\right]}_{\emptyset} dV_A = 0$$

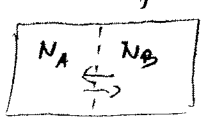
thermal equilibrium

$$\boxed{\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E}\right)_{V,N}} \qquad \boxed{\frac{P}{T} \equiv \left(\frac{\partial S}{\partial V}\right)_{E,N}}$$

$$\frac{1}{T_A} = \frac{1}{T_B} \qquad P_A = P_B$$

mechanical equilibrium

Chemical Equilibrium / Chemical potential



$N_A + N_B = \text{const.}$

(assume $T_A = T_B$, $P_A = P_B$ i.e. thermal & mechanical equilibrium is established)

$$dS = dS_A + dS_B = \left(\frac{\partial S_A}{\partial N_A}\right)_{E_A,V_A} dN_A + \left(\frac{\partial S_B}{\partial N_B}\right)_{E_B,V_B} dN_B = \left[\left(\frac{\partial S_A}{\partial N_A}\right)_{E_A,V_A} - \left(\frac{\partial S_B}{\partial N_B}\right)_{E_B,V_B}\right] dN_A$$

$$\frac{\mu}{T} \equiv -\left(\frac{\partial S}{\partial N}\right)_{E,V} \qquad \mu_A = \mu_B$$