Thermodynamics Review

temperature: $\boxed{A|B}$ 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 $\rho = \frac{N}{V}$

$$\boxed{P = P(T, \rho)}$$ e.g. $\boxed{PV = NkT}$ $P = kT\rho$

ideal gas

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

$$\boxed{\text{Stat. Mech: to "derive" } P(T,\rho)}$$

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

$$P = kT \frac{\rho}{1 - b\rho} - a\rho^2$$

Work

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

$\Delta V = A \Delta x$

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

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

can use equation of state

e.g. quasistatic process: $P = P(T, V)$ $W = -\int P(T, V) \, dV$
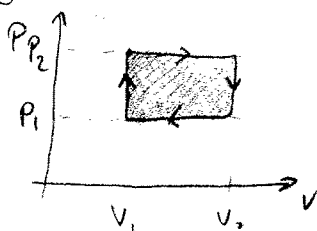
ideal gas, compression at constant T: $P = \frac{NkT}{V}$

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

$\oint \delta W \neq 0$ __not__ a state function

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

$\neq 0$

(1)

The first law of thermodynamics

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

$\underline{E \text{ is a state function}}$, uniquely determined by $T, P, N, \dots$

thermal contact: δQ ~~heating~~

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

$$\oint \delta Q \neq 0 \quad \text{(not a state function)}$$

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

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equation of state for the energy

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

ideal gas: $\quad \boxed{E = \tfrac{3}{2} N k T} \qquad$ for $\underline{\text{monoatomic}}$ gas

V. d. W.: $\quad \boxed{E = \tfrac{3}{2} N k T - N\left(\tfrac{N}{V}\right) a}$

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

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

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

$$\delta Q = -\delta W \qquad\qquad Q_{1\to 2} = -W_{1\to 2} = N k T \ln \frac{V_2}{V_1}$$

e.g. $V_2 < V_1$ (compressed, i.e., done work on gas
$Q_{1\to 2} < 0$ 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

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

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

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

enthalpy

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

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

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

General Relationship between C_p & C_V

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

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

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

③

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

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

$$C_P = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{C_P = C_V + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]}$$

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

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

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

Adiabatic Processes

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

$\delta Q = 0$: adiabatic process

$\delta W = -PdV$: quasistatic process

   no energy exchange due to temperature difference

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

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

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

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

$$c_V \frac{dT}{T} = -Nk \frac{dV}{V} \qquad\qquad c_p - c_V = Nk$$

$$c_V \frac{dT}{T} = -(c_p - c_V) \frac{dV}{V}$$

$$\frac{dT}{T} = -\left(\frac{c_p}{c_V} - 1\right) \frac{dV}{V} \qquad\qquad \gamma \equiv \frac{c_p}{c_V} > 1$$
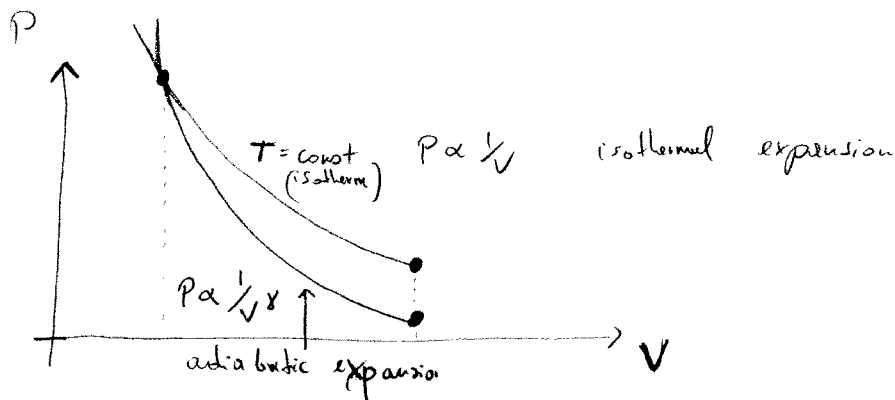
$$\ln T + \ln V^{\gamma-1} = \text{const}$$

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

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

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

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

P

$T = \text{const}$ (isotherm) $P \propto \frac{1}{V}$ isothermal expansion

$P \propto \frac{1}{V^\gamma}$

adiabatic expansion

V

The Second Law of Thermodynamics

E, H, ..., S (entropy) : state functions

W, Q : not properties of the system

$$\oint \delta W \neq 0, \qquad \oint \delta Q \neq 0 \qquad \underline{\text{depends on the process}}$$

1) $\underline{\text{Kelvin}}$: "No process is possible whose $\underline{\text{sole}}$ result is the $\underline{\text{complete}}$ 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:

$$P \uparrow \qquad T = \text{const.}$$
$$\xrightarrow{\qquad} V$$
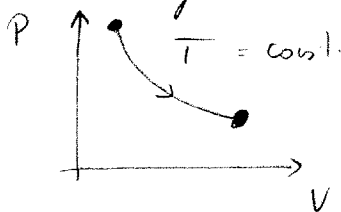
$\sum W = 0$
$(\oint W = 0)$

2) $\underline{\text{Clausius}}$: "No process is possible whose $\underline{\text{sole}}$ 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 $\underline{\text{equilibrium}}$, it must have a $\underline{\text{maximum}}$

The thermodynamic temperature

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

$V = V_A + V_B = $ const.

$N = N_A + N_B = $ const

$E = E_A + E_B = $ const.

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

only thermal contact: $V_A = $ const , $N_A = $ 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 = $ const.

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

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

$\underbrace{}_{0}$

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

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

assume initially separated by an insulating wall $T_A > T_B$
after removing the constraint:

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

energy is transferred from hotter to colder system

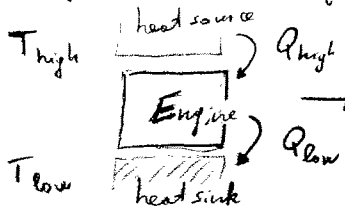recall: "heat does not spontaneously go from colder to hotter

The Second Law and Heat Engines

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

$V = $ const. $\Rightarrow$ no work is done

$$dE = \delta Q = T\, dS$$

$$\boxed{dS = \frac{\delta Q}{T}}\qquad \text{quasi-static} \frac{\text{reversible}}{\text{process}}$$

simplest heat engine

T_{high} heat source

T_{low} heat sink

Engine $\quad Q_{high} \quad Q_{low} \quad |W|$

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: $\qquad Q_{high} - Q_{low} = |W|$ (done by eng.) $(Q_{high}, Q_{low} > 0)$

(energy conservation) for cycle

Second Law: (applied to a cycle)

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

thermal efficiency: η

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

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

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

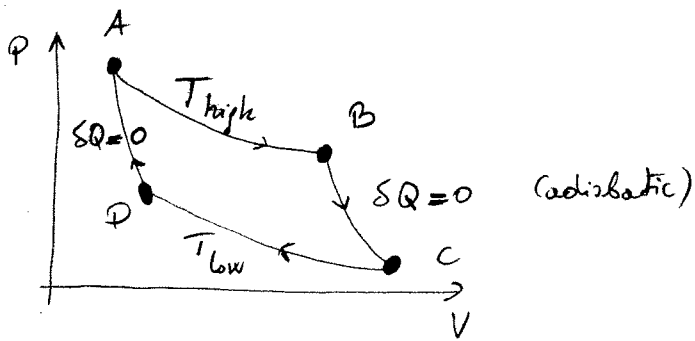Carnot principle: efficiency for __reversible__ engines operating between the same pair T_{high}, T_{low} have the same efficiency (general Carnot engine)

$$\boxed{\eta = 1 - \frac{T_{low}}{T_{high}}}$$

⑧

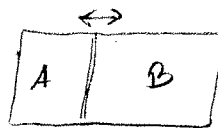Carnot cycle (particular realization of the general reversible Carnot engine)

ideal gas

$$dE = \delta Q - \delta W_E$$

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

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

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

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

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

Thermodynamic Pressure

$$S(E, V, N)$$

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

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

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 $\quad dE_B = -dE_A \qquad \& \qquad dV_B = -dV_A$

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

$\varnothing$ thermal equilibrium $\qquad\qquad \varnothing$

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

$$\frac{1}{T_A} = \frac{1}{T_B} \qquad\qquad\qquad P_A = P_B \qquad \underline{\text{mechanical equilibrium}}$$

Chemical Equilibrium / Chemical potential
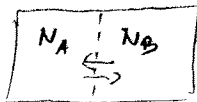
$$N_A \rightleftharpoons N_B \qquad\qquad N_A + N_B = \text{cost.}$$

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

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

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