

Reviews on Thermodynamics

SCPY152, Second Semester, 2021-22

Udom Robkob, Physics-MUSC

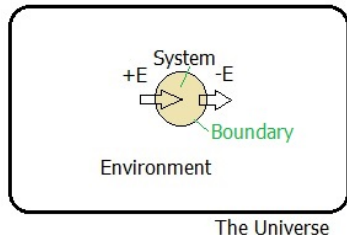
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Topics

1. Thermodynamic system
2. System of ideal gas
3. The first law of thermodynamics
4. Heat engines and refrigerator
5. The second law of thermodynamic

1 Thermodynamic Systems

- ▶ Thermodynamic system is characterized with equation of state $f(E, T, \dots) = 0$, where E is energy (work done/heat) in Joule, temperature T in Kelvin, and other.
- ▶ We are interested in thermal processes of the system, i.e., inside and transfer in/out of the system
- ▶ *The whole Universe* consists of the system (small), its environment (huge) and the boundary.
- ▶ In *canonical case*, we let only *energy* E can be transferred in to/out of the system



2 System of Ideal Gas

- ▶ System of ideal gas is characterized by its temperature T , pressure P , container volume V , , and the Number N of molecules inside the container. They satisfy the equation of state

$$pV = Nk_B T, \quad k_B = 1.38 \times 10^{-23} \text{ J/K}$$

(k_B is Boltzmann constant.) Or in the form

$$pV = nRT, \quad n = \frac{N}{N_A}, \quad N_A = 6.02 \times 10^{23} \text{ molecule/mol}$$

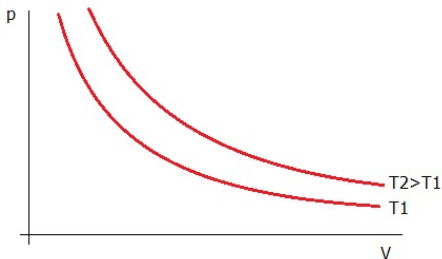
where N_A is Avogadro number, n is molar number of the gas and $R = N_A k_B = 8.314 [\text{J/mol} \cdot \text{K}]$ is the Universal gas constant.

- ▶ For canonical ideal gas system the number is fixed, so that

$$pV \propto T$$

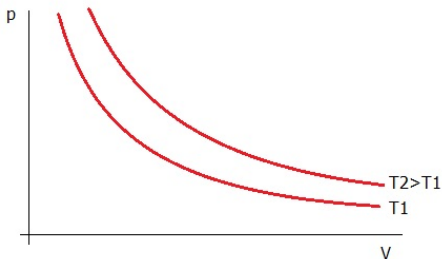
This is displayed as hyperbolic curve on the p-V diagram

- ▶ The p-V diagram of ideal gas system



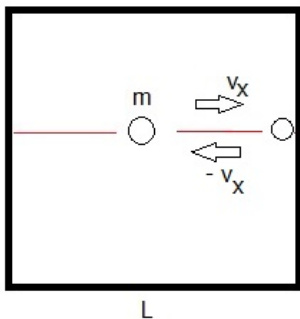
- ▶ This diagram is very useful for in studying thermal processes of the system, since all of them can be explained on this diagram

- ▶ The p-V diagram of ideal gas system



- ▶ This diagram is very useful for in studying thermal processes of the system, since all of them can be explained on this diagram
- ▶ We start with constructing mechanical description of the ideal gas system, from the fundamental level, by determining the system energy E .
- ▶ The ideal gas system consist of moving non-interacting gas molecules, so that the system energy is the summation of the kinetic energy of all molecules, by ignoring small gravitational potential energy.

- ▶ Let us check this picture, by determining motion of one gas molecule of mass m velocity v in side of cubic volume of side $L \rightarrow V = L^3$. Start from its motion in x-direction



$$K_x = \frac{1}{2}mv_x^2, \quad p_x = mv_x$$

- ▶ Once it hits the right wall and bounce back with velocity $-v_x$, the impulse of this hitting is $\Delta p_x = -2mv_x$

- ▶ The next hitting wait after the duration of $\Delta t = \frac{2L}{v_x}$, so that the average hitting force on the right wall will be

$$\bar{F}_x = \frac{-\Delta p_x}{\Delta t} = \frac{mv_x^2}{L} \rightarrow \bar{P}_1 = \frac{\bar{F}_x}{A} = \frac{mv_x^2}{V}$$

where \bar{P}_1 is the average pressure from single molecule. The average pressure from N molecules will be

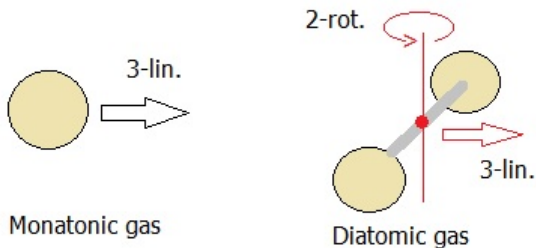
$$\bar{P} = \frac{m}{V} \sum_{n=1}^N v_{xn}^2 = \frac{mN\bar{v}_x^2}{V}, \text{ where } \bar{v}_x^2 = \frac{1}{N} \sum_{n=1}^N v_{xn}^2$$

$$\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 \rightarrow \bar{v}_x^2 = \frac{1}{3}\bar{v}^2 = \frac{1}{3}v_{rms}^2$$

$$\bar{P} = \frac{mNv_{rms}^2}{3V} = \frac{N}{V} \left(\frac{1}{3}mv_{rms}^2 \right) \rightarrow \frac{1}{3}mv_{rms}^2 = k_B T$$

$$\rightarrow \frac{1}{2}mv_{rms}^2 = \frac{3}{2}k_B T \text{ "kinetic theory"}$$

- **Kinetic theory** of ideal gas = *kinetic energy any one degree of freedom of ideal gas molecule equals to thermal energy $\frac{1}{2}k_B T$*



$$U_{mon} = \frac{3}{2} N k_B T = \frac{3}{2} n R T, \quad U_{dia} = \frac{5}{2} N k_B T = \frac{5}{2} n R T$$

From kinetic theory we can have $v_{rms} = v_{rms}(T)$.

- Anyway, we can have molecular velocity distribution from the following steps of analysis. Let $v = (v_x, v_y, v_z)$ be a molecular velocity and

$$v^2 = v_x^2 + v_y^2 + v_z^2 \rightarrow \text{constant}$$

$$d(v^2) = 0 = 2v_x dv_x + 2v_y dv_y + 2v_z dv_z$$

$$\rightarrow v_x dv_x + v_y dv_y + v_z dv_z = 0$$

Let $f(v^2) = f(v_x)f(v_y)f(v_z)$ be a velocity distribution function, it satisfies

$$df(v^2) = 0 = f'(v_x)dv_x[f(v_y)f(v_z)] + f'(v_y)dv_y[(f(v_x)f(v_z))] + f'(v_z)dv_z[f(v_x)f(v_y)]$$

$$\frac{f'(v_x)}{f(v_x)}dv_x + \frac{f'(v_y)}{f(v_y)}dv_y + \frac{f'(v_z)}{f(v_z)}dv_z = 0$$

From above $\alpha(v_x dv_x + v_y dv_y + v_z dv_z = 0) = 0$

After addition together, we have

$$\begin{aligned} \left(\frac{f'(v_x)}{f(v_x)} + \alpha v_x \right) dv_x + \left(\frac{f'(v_y)}{f(v_y)} + \alpha v_y \right) dv_y + \left(\frac{f'(v_z)}{f(v_z)} + \alpha v_z \right) dv_z &= 0 \\ \rightarrow \frac{f'(v_x)}{f(v_x)} + \alpha v_x = 0, \frac{f'(v_y)}{f(v_y)} + \alpha v_y = 0, \frac{f'(v_z)}{f(v_z)} + \alpha v_z &= 0 \end{aligned}$$

Let us determine

$$\begin{aligned} \frac{f'(v_x)}{f(v_x)} + \alpha v_x = 0 &\rightarrow d \ln f(v_x) = -\alpha v_x dv_x = -\frac{1}{2} \alpha dv_x^2 \\ \rightarrow \ln f(v_x) - \ln a &= -\frac{1}{2} \alpha v_x^2 \rightarrow f(v_x) = a e^{-\frac{1}{2} \alpha v_x^2} \\ \rightarrow f(v) &= f(v_x) f(v_y) f(v_z) = a^3 e^{-\frac{1}{2} \alpha v^2} \\ ?(a, \alpha) &\rightarrow \int f(v) d^3 v = 1 \text{ normalization} \end{aligned}$$

With an appearance of v^2 on the exponent, let us assign for convenient $\alpha = m/k_B T = \beta m$, with $\beta = 1/k_B T$.

Calculate the normalization

$$1 = \int f(v_x) dv_x = a \int dv_x e^{-\frac{1}{2}\beta m v_x^2} = a \sqrt{\frac{2\pi}{\beta m}}$$

$$\rightarrow a = \sqrt{\frac{\beta m}{2\pi}} = \sqrt{\frac{m}{2\pi k_B T}} \rightarrow f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m v_x^2}{2k_B T}}$$

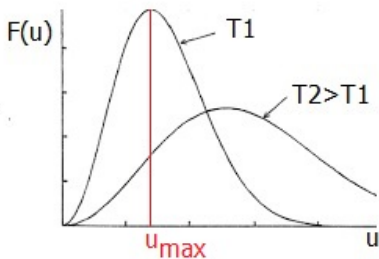
$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m v^2}{2k_B T}}$$

Isotropic velocity space volume in three dimensions in spherical coordinates $d^3v = 4\pi u^2 du$, $u = |v| \rightarrow u^2 = v^2$

$$f(v_x, v_y, v_z) d^3v = 4\pi v^2 f(u) du = F(v) dv$$

$$F(u) = 4\pi \sqrt{\frac{m}{2\pi k_B T}} u^2 e^{-\frac{m u^2}{2k_B T}}$$

$F(u)$ is called Maxwell-Boltzmann speed distribution function.



The average speed (with molecular mass m and molar mass M)

$$\bar{u} = \int_0^{\infty} uF(u)du = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

The most probable speed

$$F'(u_{\max}) = 0 \rightarrow u_{\max} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$

when compared to rms speed $u_{rms} = \sqrt{3k_B T/m} = \sqrt{3RT/M}$.

3 The First Law of Thermodynamics

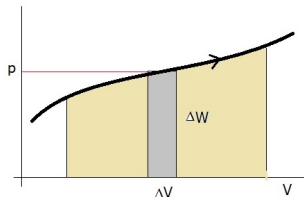
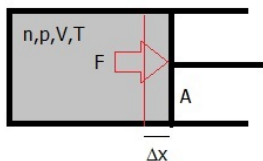
- ▶ Let U be total internal energy of thermodynamic system, its change ΔU results from heat absorption ΔQ into the system and work done ΔW by the system, i.e.,

$$\Delta U = \Delta Q - \Delta W$$

- ▶ Apply to ideal gas system of N particles

$$U = \frac{3}{2}Nk_B T = \frac{3}{2}nRT \rightarrow \Delta U = \frac{3}{2}nR\Delta T$$

Determine the work done by the gas in cylindrical piston
 $\Delta W = F\Delta x = p\Delta V$ It is area under curve on p-V diagram



- ▶ Thermodynamic processes of ideal gas system, according the first law

- ▶ constant volume (isochoric) process

$$\Delta W = 0 \rightarrow \Delta U = \Delta Q = \frac{3}{2}nR\Delta T \equiv nc_V\Delta T$$

$$c_V = \frac{3}{2}R$$

Molar specific heat at constant volume

- ▶ constant pressure (isobaric) process

$$\Delta U \equiv nc_V\Delta T = \Delta Q_P - p\Delta V \equiv nc_P\Delta T - nR\Delta T$$

$$\rightarrow c_P = c_V + R$$

Molar specific heat at constant pressure

- ▶ constant temperature (isothermal) process

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

The ideal heat engine!!!

► Thermodynamic processes of ideal gas system (cont.)

- adiabatic (no heat absorption) process

$$\Delta Q = 0 \rightarrow \Delta U = nc_V \Delta T = -\Delta W = -p\Delta V$$

$$pV = nRT \rightarrow \frac{c_V}{R}[p\Delta V + V\Delta p] = -p\Delta V$$

Divide through with pV : $\rightarrow c_V \frac{\Delta P}{p} + c_P \frac{\Delta V}{V} = 0$

$$\Delta(\ln p + \gamma \ln V) = 0, \quad \gamma = \frac{c_P}{c_V}$$

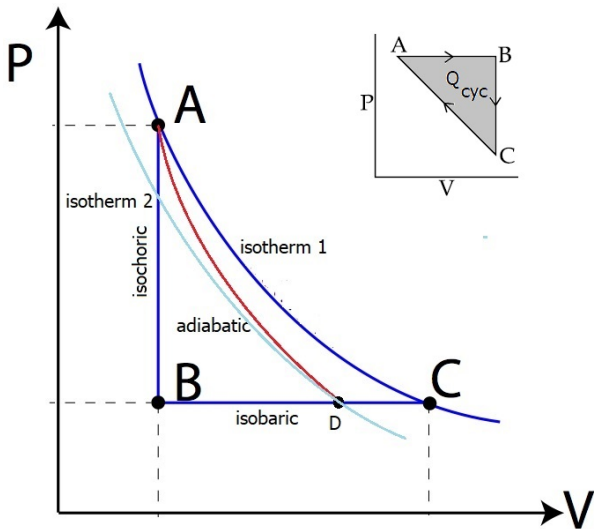
$$\Delta \ln(pV^\gamma) = 0 \rightarrow \ln pV^\gamma = C, \quad pV^\gamma = C$$

We do derive adiabatic process equations

$$pV^\gamma = C \rightarrow TV^{\gamma-1} = C, \quad p^{1-\gamma} T^\gamma = C$$

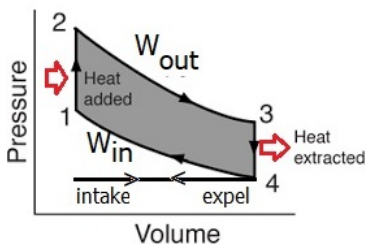
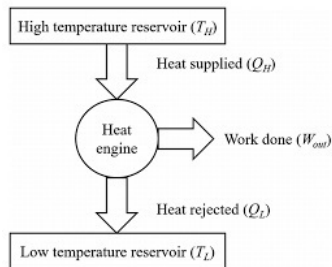
- cyclic process, after one cycle of change of state

$$\Delta U_{cyc} = 0 \rightarrow \Delta Q_{cyc} = \Delta W_{cyc}$$



4 Heat Engines and Refrigerator

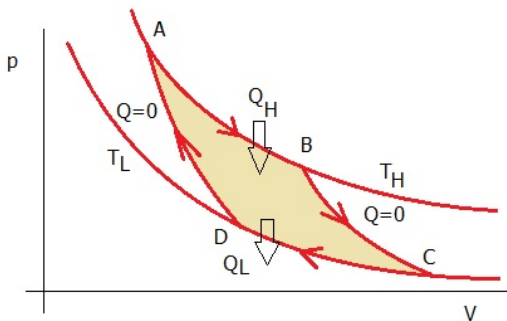
- Idea of heat engine is an ideal gas system, contained in a cylindrical piston, changes its state in cycle, with $W_{out} = W_{cyc}$, $Q_{cyc} = Q_H - Q_L$



- Efficiency

$$e(\%) = \frac{W_{cyc}}{Q_H} \times 100 = \frac{Q_{cyc}}{Q_H} \times 100\%$$

► Carnot engine



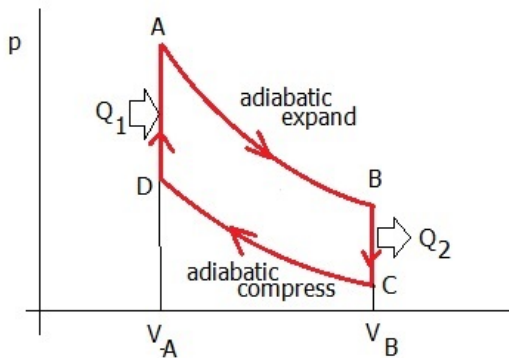
$$\Delta Q_H = \Delta W_{AB} = (p\Delta V)_{AB} = nRT_H \left(\frac{\Delta V}{V} \right)_{AB} = nR\Delta(\ln V)_{AB}$$

$$Q_H = nRT_H \ln \frac{V_B}{V_A} \rightarrow Q_L = nRT_L \ln \frac{V_D}{V_C}$$

$$\text{Adiabatic: } \frac{V_B}{V_A} = \frac{V_C}{V_D} \rightarrow Q_H + Q_L = nR(T_H - T_L) \ln(V_B/V_A)$$

$$e(\%) = \frac{T_H - T_L}{T_H} \times 100\%$$

► Otto engine



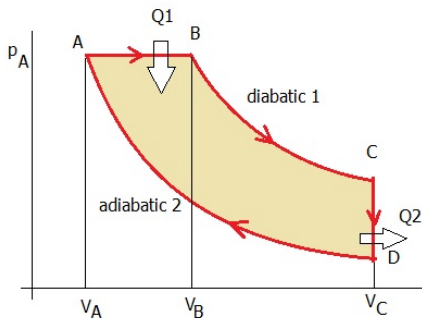
$$Q_1 = U_{DA} = nc_V(T_A - T_D) = nc_V T_D (T_A/T_D - 1)$$

$$Q_2 = \Delta U_{BC} = nc_V(T_C - T_B) = nc_V T_C (1 - T_B/T_C)$$

$$\text{Adiabatic : } \frac{T_A}{T_D} = \frac{T_B}{T_C} \rightarrow e = \frac{T_D - T_C}{T_D} = 1 - \frac{T_C}{T_D} = 1 - r_E^{\gamma-1}$$

$$\text{Vol. exp. ratio : } r_E = \frac{V_B}{V_A} \rightarrow e(\%) = (1 - r_E^{\gamma-1}) \times 100\%$$

► Diesel engine



$$Q_1 = n c_p (T_B - T_A), \quad Q_2 = n c_v (T_D - T_C)$$

$$e = \frac{Q_1 + Q_2}{Q_1} = 1 - \frac{1 (T_C - T_D)}{\gamma (T_B - T_A)} = 1 - \frac{1 V_C (p_C - p_D)}{\gamma p_A (V_B - V_A)}$$

$$= 1 - \frac{1 (p_C/p_A - p_D/p_A)}{\gamma (V_B/V_C - V_A/V_C)} = 1 - \frac{1 p_C/p_A - p_D/p_A}{\gamma (1/r_E - 1/r_C)}$$

► Diesel engine (cont.)

$$\text{Adiabatic : } p_A V_A^\gamma = p_D V_C^\gamma, \quad p_A V_B^\gamma = p_C V_C^\gamma$$

$$\frac{p_A}{p_D} = \left(\frac{V_C}{V_A} \right)^\gamma = r_C^\gamma, \quad \frac{p_A}{p_C} = \left(\frac{V_C}{V_B} \right)^\gamma = r_E^\gamma$$

$$\rightarrow e(\%) = \left(1 - \frac{1}{\gamma} \left[\frac{r_E^{-\gamma} - r_C^{-\gamma}}{r_E^{-1} - r_C^{-1}} \right] \right) \times 100\%$$

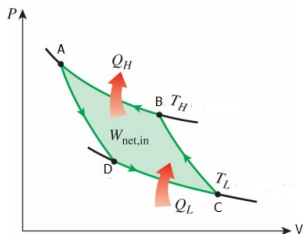
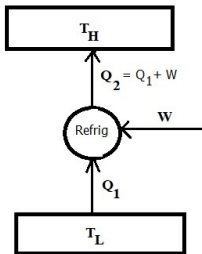
► Diesel engine (cont.)

$$\text{Adiabatic : } p_A V_A^\gamma = p_D V_C^\gamma, \quad p_A V_B^\gamma = p_C V_C^\gamma$$

$$\frac{p_A}{p_D} = \left(\frac{V_C}{V_A} \right)^\gamma = r_C^\gamma, \quad \frac{p_A}{p_C} = \left(\frac{V_C}{V_B} \right)^\gamma = r_E^\gamma$$

$$\rightarrow e(\%) = \left(1 - \frac{1}{\gamma} \left[\frac{r_E^{-\gamma} - r_C^{-\gamma}}{r_E^{-1} - r_C^{-1}} \right] \right) \times 100\%$$

► Carnot refrigerator



► Carnot refrigerator (cont.)

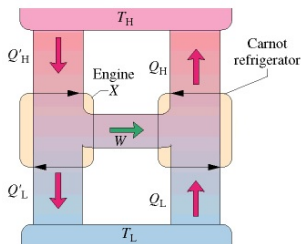
$$\text{Performance : } P = \frac{Q_1}{W} = \frac{Q_1}{Q_2 - Q_1}$$

$$Q_1 = Q_L = nRT_L \ln \frac{V_D}{V_C}, \quad Q_2 = Q_H = nRT_H \ln \frac{V_B}{V_A}$$

$$\rightarrow P = \frac{T_L}{T_H - T_L}$$

5 The Second Law of Thermodynamics

- ▶ Missing information from the first law, let us determine a work in Carnot refrigerator done by Carnot engine



We observe that

$$\lim_{T_L \rightarrow 0} e(\%) \rightarrow 100\% \text{ but } \lim_{T_L \rightarrow 0} P \rightarrow 0 \text{ then } T_L \neq 0$$

Conclusion: we cannot reach $T = 0K$, so that we will never have $e(\%) = 100\%$ heat engine and $P = \infty$ refrigerator

- ▶ How to state this fact in form of physical law with mathematical expression ?

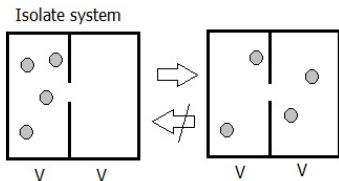
- ▶ Rudolf Clausius (1865) a German physicist was introduced *entropy* S to describe direction of transformation of state of thermal system, which is related to the change of entropy ΔS , by stating that

$$\Delta S = \frac{\Delta Q}{T} = \int \frac{dQ}{T} \geq 0$$

with the conditions

- ▶ $\Delta S = 0$ for reversible processes
- ▶ $\Delta S > 0$ for irreversible processes

This sets time direction (arrow) of all thermal processes, for example of free expansion $V \rightarrow 2V$ in isolate system (isothermal T)



$$\Delta Q = nRT \ln 2$$

$$\rightarrow \Delta S = nR \ln 2 > 0$$

- ▶ Cyclic process is observed to be reversible, from above

$$\Delta S_{cyc} = \sum_{cycle} \frac{\Delta Q}{T} = \oint \frac{dQ}{T} = 0$$

For example of Carnot cycle

$$\begin{aligned}\Delta S_{Carnot} &= \frac{\Delta Q_H}{T_H} + \frac{\Delta Q_L}{T_L} = nR (\ln(V_B/V_A) - \ln(V_C/V_D)) \\ &= nR \ln \left(\frac{V_B}{V_A} \frac{V_D}{V_C} \right) = nR \ln(1) = 0\end{aligned}$$

- ▶ Generic cyclic process $\Delta S_{cyc} = 0$ always

