Chapter 19 Key Words

Boltzmann constant k=1.38×10²³(J/K)
Gas constant R=8.31(J/mol.K)
Molar mass (M) 摩尔质量
Mole (n) 摩尔
Isothermal 等温的
Expansion 膨胀
Compression 压缩
Isochoric (Constant volume) 等容
Isobaric (Constant pressure) 等压
Adiabatic 绝热的
Root-mean-square speed v_{rms} 均方根速率
Average speed 平均速率
Translational kinetic energy 平动动能
Mean free path 平均自由程
Most probable speed 最概然速率
Molar specific heats (C_V,C_P) 摩尔比热

Degree of freedom 自由度
Monatomic 单原子的
Diatomic 双原子的
Polyatomic 多原子的
Translational freedom 平动自由度
Rotational freedom 转动自由度
Oscillatory freedom 振动自由度
Equipartition of energy theorem
能量均分定理
Ideal gas law 理想气体定律

Chapter 19 Mole and Ideal gas law

Avogadro's number: $N_A = 6.02 \times 10^{23}$ mol^{-1}

Mole : $\quad n = \dfrac{N}{N_A} = \dfrac{M_{Sam}}{M}$

Mole mass : $\quad M = mN_A$

Ideal gas law: $\quad pV = nRT = NkT$

$R = 8.31 J / mol \cdot K,$

$k = R / N_A = 1.38 \times 10^{-23} J / K$

Pressure, rms Speed:

$$\left. \begin{array}{l} pV = \dfrac{1}{3} nMv_{rms}^2 \\[2mm] pV = nRT \end{array} \right\} \Rightarrow v_{rms} = \sqrt{\dfrac{3RT}{M}}$$

Average translational kinetic energy:

$$K_{avg} = \left(\dfrac{1}{2} mv^2\right)_{avg} = \dfrac{1}{2} m(v^2)_{avg} = \dfrac{1}{2} mv_{rms}^2 = \dfrac{3}{2} kT$$

Fraction of gas particles with speed v centered in the speed interval dv is $P(v)dv$, where $P(v)$ is probability distribution function. 概率分布函数

Fraction of gas particles with speed in an interval between v_1 and v_2:

概率

$$\text{frac} = \int_{v_1}^{v_2} P(v)\, dv$$

Maxwell's speed distribution law:

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$
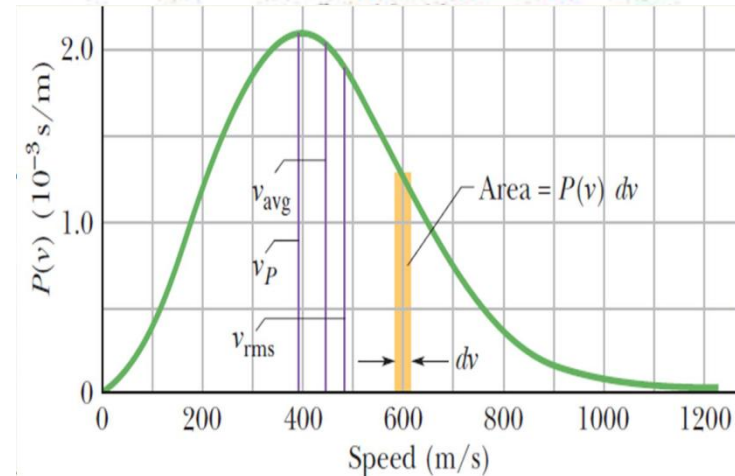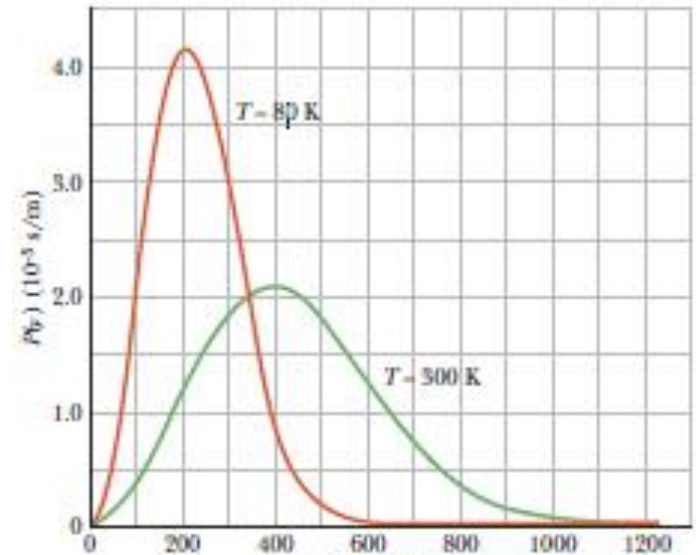
Average speed :

$$v_{avg} = \int_0^\infty v\, P(v)\, dv \implies v_{avg} = \sqrt{\frac{8RT}{\pi M}}$$

Root-Mean-Square speed：

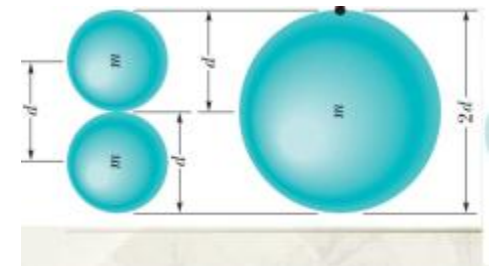$$(v^2)_{avg} = \int_0^\infty v^2 P(v)\, dv = \frac{3RT}{M} \implies v_{rms} = \sqrt{\frac{3RT}{M}}$$

Most probable speed：

$$dP/dv = 0 \implies v_P = \sqrt{\frac{2RT}{M}}$$

Chapter 19 Mean Free Path and Collision Rate

◆ Length of path during time interval Δt: $L = v_{avg}\Delta t$

◆ Number of collisions in Δt: $N_{col} = (N/V)[(\pi d^2)v_{rel}\Delta t]$

➢ d: diameter of gas particle.

➢ v_{rel}: **average relative** speed between particles. With Maxwell's distribution law, it can be shown that $v_{rel} = \sqrt{2}v_{avg}$.

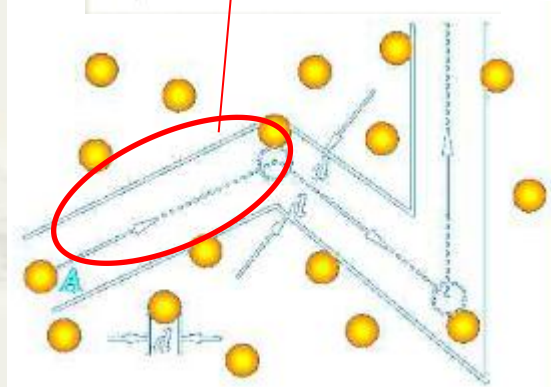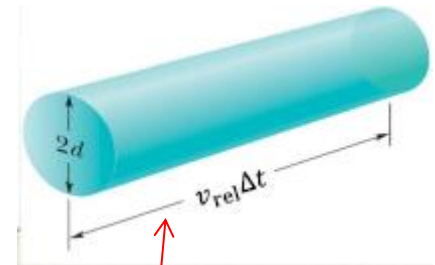**Mean free path λ:** average distance travelled by a gas particle between collisions.

$$\lambda = \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} = \frac{v_{avg}\Delta t}{v_{rel}\Delta t \pi d^2 N/V}$$

➡ $$\boxed{\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}}$$

▪ Depends on the gas density and size of gas particle.

Average time between collisions: $t = \dfrac{\lambda}{v_{avg}}$

Collision rate: $f = 1/t = v_{avg}/\lambda$

Assumption： The molecule can be treated as rigid ball with diameter d; The collisions between molecules are elastic collision; the velocity of the moving molecule relative to the others is average relative velocity and the speed of that moving molecule is v_{avg}

Chapter 19 Molar Specific Heats

◆ C_V: Molar specific heat at constant volume

◆ C_P: Molar specific heat at constant pressure

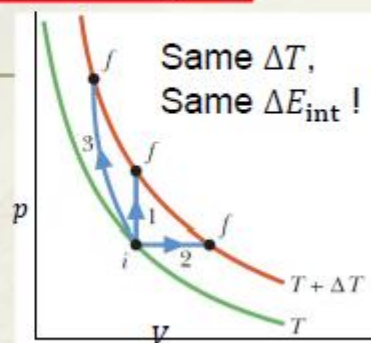$Q = nC_V\Delta T$

$Q = nC_P\Delta T$

Molar specific heat at constant volume

$Q = nC_V\Delta T$ and $W = 0$ ➡ $\boxed{\Delta E_{int} = Q - W = nC_V\Delta T}$

■ A change in the internal energy E_{int} of a confined ideal gas depends on only the change in the temperature, **not** on what type of process produces the change.

Same ΔT, Same ΔE_{int} !

Internal energy is a state function

Internal energy of ideal gas

$\boxed{E_{int} = nC_V T}$ (any ideal gas) Only depends on Temperature !!

Molar specific heat at constant pressure

$Q = nC_P\Delta T$

$W = \int p\,dV = p\int dV = p\Delta V,$

Ideal gas: $pV = nRT \rightarrow p\Delta V = nR\Delta T$

➡ $W = nR\Delta T$

➡ $\boxed{C_p = C_V + R}$

$\Delta E_{int} = nC_V\Delta T = Q - W = nC_P\Delta T - nR\Delta T$

Chapter 19 Equipartition of energy

□ Each degree of freedom has an average energy of $\frac{1}{2}kT$ per particle ($\frac{1}{2}RT$ per mole).

Every kind of molecule has a certain number of *degrees of freedom,* which are independent ways in which the molecule can store energy （translation(t)，Rotation(r), vibrate(v) (Very high temperature)

$$E_{\text{int}} = n\frac{f}{2}RT, \text{ and } C_V = \frac{f}{2}R = 4.16f \text{ J/mol}\cdot\text{K}, C_p = \left(\frac{f}{2} + 1\right)R$$

Only considered translational and rotational freedom:

Molecule	Degrees	C_V	C_P
Monatomic	$t = 3$	$3R/2$	$5R/2$
Diatomic	$t + r = 3 + 2 = 5$	$5R/2$	$7R/2$
Polyatomic （non-linear）	$t + r = 3 + 3 = 6$	$3R$	$4R$
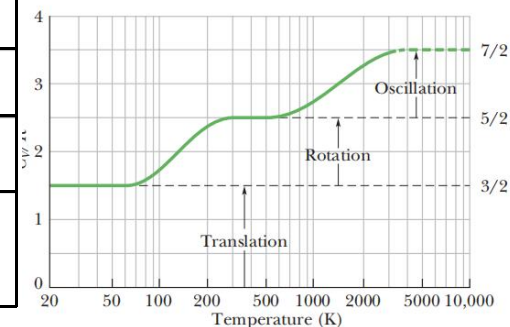
Chapter 19 Thermodynamic Processes

$$pV = nRT \Rightarrow pdV + Vdp = nRdT \qquad\qquad C_V = \frac{f}{2}R, \quad C_p = C_V + R$$

$$\Delta E_{int} = Q - W = Q - \int pdV = nC_V \Delta T$$

1，Isothermal process (T constant)

$$\Delta T = 0 \quad\Rightarrow\quad \Delta E_{int} = 0 \quad\Rightarrow\quad Q = W = \int pdV = \int \frac{nRT}{V}dV = nRT\int \frac{dV}{V} = nRT\ln\frac{V_f}{V_i}$$

2，Isobaric process (P constant)

$$W = p\Delta V = nR\Delta T \qquad Q = nC_p\Delta T = (C_p/R)p\Delta V \qquad \begin{aligned}\Delta E_{int} &= nC_V\Delta T \\ &= Q - W = (C_V/R)p\Delta V\end{aligned}$$
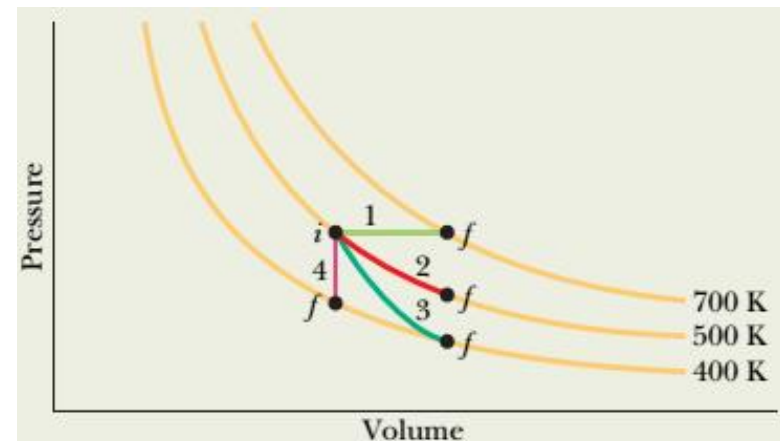
3，Isochoric process (V constant）

$$W = 0 \quad\Rightarrow\quad \Delta E_{int} = Q = nC_V\Delta T$$

4，Adiabatic process (Q=0)

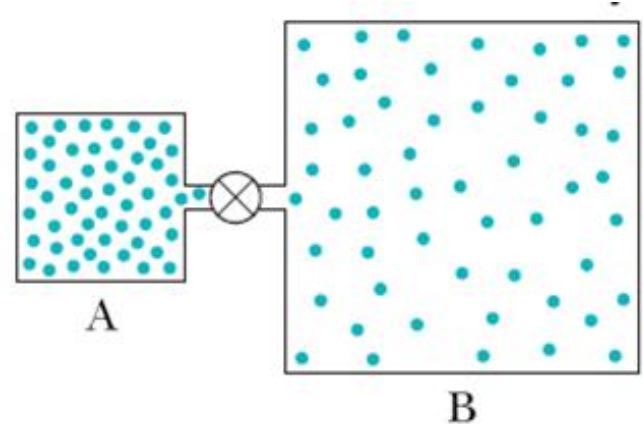$$W = \Delta E_{int} = nC_V\Delta T \qquad \boxed{pV^\gamma = \text{a constant}}$$

5，Free expansion

Container A holds an **ideal monatomic** gas at a pressure of 5.0×10^5 Pa and a temperature of 300 K. It is connected by a thin tube (and a closed valve) to container B, with four times the volume of A. Container B holds the same ideal gas at a pressure of 1.0×10^5 Pa and a temperature of 400 K. The valve is opened to allow the pressure to equalize, but the temperature of each container is maintained.

a) What then is the pressure?

b) If the volume $V_A = 1$ m³, what is the energy transferred as heat to the container during this process?

a) What then is the pressure?

The numbers of moles in A and B are
$$n_A = \frac{p_A V_A}{RT_A} \qquad n_B = \frac{4 p_B V_A}{RT_B}$$

The total number of moles is constant
$$n = n_A + n_B = \frac{V_A}{R}\left(\frac{p_A}{T_A} + \frac{4 p_B}{T_B}\right)$$

After the valve is opened
$$n'_A = \frac{p'_A V_A}{RT'_A} \qquad n'_B = \frac{p'_B V_B}{RT'_B}$$

And
$$p'_A = p'_B \qquad T'_A = T_A \qquad T'_B = T_B$$

Then we have
$$n'_A + n'_B = \frac{V_A}{R}\left(\frac{p'_A}{T_A} + \frac{4 p'_A}{T_B}\right)$$

a) What then is the pressure?

Then we can solve $\quad n'_A + n'_B = n_A + n_B$

$$\frac{p'_A V_A}{R}\left(\frac{1}{T_A} + \frac{4}{T_B}\right) = \frac{V_A}{R}\left(\frac{p_A}{T_A} + \frac{4p_B}{T_B}\right)$$

$$p'_A\left(\frac{1}{T_A} + \frac{4}{T_B}\right) = \left(\frac{p_A}{T_A} + \frac{4p_B}{T_B}\right)$$

$$p'_A = \frac{p_A + 4p_B T_A/T_B}{1 + 4T_A/T_B} = 2.0 \times 10^5\,Pa$$

b) What is the energy transferred as heat to the container during this process?

Because the volume of the containers A and B keep constant, so the work done on the system (A an B) is 0. The change in the internal energy only due to the energy exchanged as heat, so:
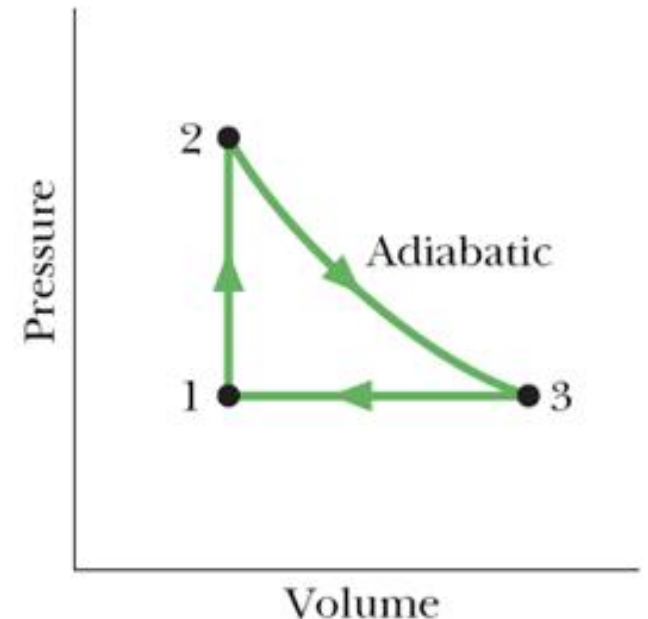
$$\Delta E_{int} = E_f - E_i = Q + W_{on} = Q$$

The total internal energy of the system is the sum of individual energy

$$Q = E_f - E_i = E_{Af} + E_{Bf} - E_{Ai} - E_{Bi}$$

$$= (n'_A - n_A)C_V T_A - (n_B - n'_B)C_V T_B = (n'_A - n_A)C_V (T_A - T_B)$$

$$= (p'_A - p_A)\frac{V_A}{RT_A}\frac{3}{2}R(T_A - T_B) = 1.5 \times 10^5 \, J$$

Chapter 19 Tutorial Problem 2

Figure shows a cycle undergo by 1.00 mol of an ideal diatomic gas with its molecules rotating but no vibrating. The initial pressure at point 1 is p_1. The temperatures at points 1 and 2 are T_1, T_2. In terms of these known values,

(a) What are volume V_2 and pressure p_2 at point 2 and

(b) Volume V_3, pressure p_3 and temperature T_3 at point 3?

(c) For $1 \rightarrow 2$, what are the change in internal energy ΔE_{12}, heat Q_{12} and the work W_{12} done by gas?

(d) and ΔE_{23}, Q_{23} and W_{23} for $2 \rightarrow 3$,

(e) ΔE_{31}, Q_{31} and W_{31} for $3 \rightarrow 1$

(f) ΔE, Q and W for the full cycle?

(g) What ΔE_{23}, Q_{23} and W_{23} if $2 \rightarrow 3$ changes to be isothermal?

For ideal diatomic gas, the molar specific heat at constant volume

is $C_V = \dfrac{5}{2}R,$ the molar specific heat atconstantpressure is $C_p = \dfrac{7}{2}R,$

and the ratio of the molar specific heat is $\gamma = \dfrac{C_p}{C_V} = \dfrac{7}{5}.$

The process $1 \rightarrow 2$ occurs at constant volume, $V_2 = V_1$

(a) At point 1, we have $(n = 1.00)$

$$p_1 V_1 = nRT_1 \quad \Rightarrow \quad V_2 = V_1 = R\frac{T_1}{p_1}$$

At point 2, $\quad p_2 V_2 = RT_2$

$$\frac{p_2 V_2}{T_2} = R = \frac{p_1 V_1}{T_1} \quad \Rightarrow \quad \frac{p_2}{T_2} = \frac{p_1}{T_1} \quad \Rightarrow \quad p_2 = p_1 \frac{T_2}{T_1}$$

The process $2 \rightarrow 3$ is adiabatic

(b) We have $pV^\gamma = \text{constant}$ and $pV = nRT$

$$p_3 V_3^{7/5} = p_2 V_2^{7/5}$$

And the process $3 \rightarrow 1$ occurs at constant pressure, $p_3 = p_1$

$$\begin{cases} \dfrac{p_3 V_3}{T_3} = \dfrac{p_2 V_2}{T_2} \\[3mm] p_3 V_3^{7/5} = p_2 V_2^{7/5} \end{cases} \Rightarrow \begin{cases} \dfrac{p_1 V_3}{T_3} = \dfrac{p_2 V_2}{T_2} \\[3mm] p_1 V_3^{7/5} = p_2 V_2^{7/5} \end{cases}$$

$$\Rightarrow \begin{cases} V_3 = V_2 \left(\dfrac{p_2}{p_1} \right)^{5/7} = V_1 \left(\dfrac{T_2}{T_1} \right)^{5/7} = R \dfrac{T_1}{p_1} \left(\dfrac{T_2}{T_1} \right)^{5/7} \\[5mm] T_3 = T_2 \dfrac{p_1 V_3}{p_2 V_2} = T_1 \dfrac{V_3}{V_1} = T_1 \left(\dfrac{T_2}{T_1} \right)^{5/7} \end{cases}$$

(c) The process $1 \rightarrow 2$ occurs at constant volume, so the increased heat is

$$Q_{12} = nC_V \Delta T = \frac{5}{2} R(T_2 - T_1)$$

The process with costant volume means no work is done by gas $W_{12} = 0$, then from the first law of thermaldynamics, the increased internal energy is $\Delta E_{12} = Q_{12}$,

it can also directly be calculated $\Delta E_{12} = nC_V \Delta T = \frac{5}{2} R(T_2 - T_1)$

(d) The process $2 \rightarrow 3$ is adiabatic, $Q_{23} = 0$

$$\Delta E_{23} = nC_V \Delta T = \frac{5}{2} R(T_3 - T_2) \Rightarrow \Delta E_{23} = \frac{5}{2} R \left[T_1 \left(\frac{T_2}{T_1} \right)^{5/7} - T_2 \right] = \frac{5}{2} RT_2 \left[\left(\frac{T_1}{T_2} \right)^{2/7} - 1 \right]$$

From the first law of thermaldynamics the work done by the gas is

$$W_{23} = Q_{23} - \Delta E_{23} = -\frac{5}{2} RT_2 \left[\left(\frac{T_1}{T_2} \right)^{2/7} - 1 \right]$$

The work can also directly be calculated by integral

$$W_{23} = \int_{V_2}^{V_3} p\,dV = \int_{V_2}^{V_3} \frac{p_2 V_2^{7/5}}{V^{7/5}}\,dV \qquad \left(pV^{\gamma} = p_2 V_2^{\gamma} \;\Rightarrow\; p = \frac{p_2 V_2^{\gamma}}{V^{\gamma}} \right)$$

$$= p_2 V_2^{7/5} \int_{V_2}^{V_3} V^{-7/5}\,dV = \frac{p_2 V_2^{7/5}}{-7/5 + 1}\left[V_3^{-7/5+1} - V_2^{-7/5+1} \right]$$

$$= -\frac{5}{2} p_2 V_2^{7/5}\left[V_3^{-2/5} - V_2^{-2/5} \right] = -\frac{5}{2} p_2 \left[V_2^{2/5} V_3^{-2/5} - V_2 \right]$$

$$= -\frac{5}{2} p_2 V_2 \left[\left(\frac{V_3}{V_2} \right)^{-2/5} - 1 \right] \qquad \left(V_3 = V_1\left(\frac{T_2}{T_1} \right)^{5/7}, \; V_2 = V_1 \right)$$

$$= -\frac{5}{2} R T_2 \left[\left(\frac{T_1}{T_2} \right)^{2/7} - 1 \right]$$

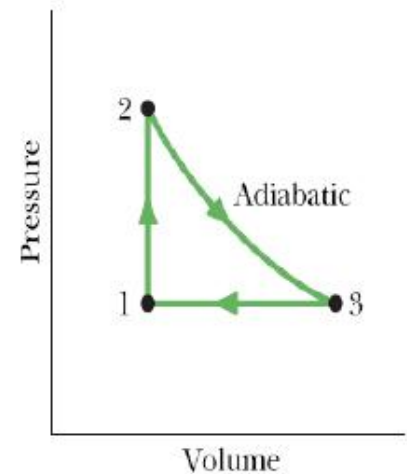(e) The process $3 \rightarrow 1$ occurs at constant pressure, $p_3 = p_1$

$$Q_{31} = nC_p\Delta T = \frac{7}{2}R(T_1 - T_3) = \frac{7}{2}RT_1\left[1 - \left(\frac{T_2}{T_1}\right)^{5/7}\right]$$

$$\Delta E_{31} = nC_V\Delta T = \frac{5}{2}R(T_1 - T_3) = \frac{5}{2}RT_1\left[1 - \left(\frac{T_2}{T_1}\right)^{5/7}\right]$$

$$W_{31} = Q_{31} - \Delta E_{31} = RT_1\left[1 - \left(\frac{T_2}{T_1}\right)^{5/7}\right]$$

The work can also directly be calculated by integral

$$W_{31} = \int_{V_3}^{V_1} p_1 dV = p_1 V_1 - p_1 V_3 = RT_1 - RT_1\left(\frac{T_2}{T_1}\right)^{5/7}$$

$$= RT_1\left[1 - \left(\frac{T_2}{T_1}\right)^{5/7}\right] \qquad \left[V_3 = R\frac{T_1}{p_1}\left(\frac{T_2}{T_1}\right)^{5/7}\right]$$

(f) ΔE, Q and W for the full cycle?

For the full cycle, the process is $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$

Since initial and final states are the same, we can directly get $\Delta E = 0$.

$$Q = Q_{12} + Q_{23} + Q_{31} = \frac{5}{2} R(T_2 - T_1) + 0 + \frac{7}{2} RT_1 \left[1 - \left(\frac{T_2}{T_1} \right)^{5/7} \right]$$

$$= \frac{5}{2} RT_2 + RT_1 \left[1 - \frac{7}{2} \left(\frac{T_2}{T_1} \right)^{5/7} \right]$$

$$W = W_{12} + W_{23} + W_{31} = 0 - \frac{5}{2} RT_2 \left[\left(\frac{T_1}{T_2} \right)^{2/7} - 1 \right] + RT_1 \left[1 - \left(\frac{T_2}{T_1} \right)^{5/7} \right]$$

$$\Rightarrow W = \frac{5}{2} RT_2 + RT_1 \left[1 - \frac{7}{2} \left(\frac{T_2}{T_1} \right)^{5/7} \right] = Q$$

Also, from the first law of thermaldynamics

$$W = Q - \Delta E = Q - 0 = Q$$

(g) What ΔE_{23}, Q_{23} and W_{23} if $2\rightarrow 3$ changes to be isothermal?

The process $2 \rightarrow 3$ is isothermal, $T_3 = T_2 \implies p_3 V_3 = p_2 V_2$

The change in the internal energy is $\Delta E_{23} = n C_V R(T_3 - T_2) = 0$

The work done by the gas is

$$W_{23} = \int_{V_2}^{V_3} p\, dV = \int_{V_2}^{V_3} \frac{RT_2}{V} dV = RT_2 ln\frac{V_3}{V_2} = RT_2 ln\frac{p_2}{p_3} = RT_2 ln\frac{p_2}{p_1}$$

$$\implies W_{23} = RT_2 ln\frac{T_2}{T_1} \qquad (p_2 = p_1 \frac{T_2}{T_1})$$

From the first law of thermaldynamics the increased heat is

$$Q_{23} = W_{23} = RT_2 ln\frac{T_2}{T_1}$$