## Problems sheet for the $1^{\text {st }}$ exam in "Physical Chemistry for Energy Engineering" (12:00-14:00, October 13, 2018)

*1: Please do not write answers in this problems sheet. What is written in the problems sheet is not evaluated.
*2: Please return both the problems sheet and the answer sheet to after the exam.
[Problem-I: 15 pt ( $3 \times 5$ pt)] 1 pt for each item. If all 4 items are correctly answered in each of problems (1), (2) and (3), 1 pt is added for each.
(1) Please choose all items that correctly explain about systems. Then, for the wrong statement(s), please explain why it is wrong.
(a) System is a part of space, matter, etc, that is encompassed by a boundary. The outside the system is called
"surroundings"

## Correct

(b) "Closed system" is a system which can exchange neither energy nor matter with its surroundings. Thus, in this system, both energy and mass are constant.

Wrong. The closed system can exchange the energy.
(c) "Open system" is a system which can exchange both energy and matter with its surroundings. In this system, neither the energy nor the mass are constant.

Correct.
(d) "Thermally isolated system" is a system which cannot exchange energy as a heat with surroundings. In this system, the energy is not constant.

Correct.
(2) Please choose all items that correctly explain about the laws of thermodynamics. Then, for the wrong statement(s), please explain why it is wrong.
(a) The first law is about energy, and the second law is about entropy and the third law is about enthalpy.

Wrong. The third law is about the entropy, not about the enthalpy.
(b) The third law defines the scale of enthalpy (e.g. the condition which makes enthalpy 0 ).

Wrong. 'enthalpy' should be replaced with 'entropy'.
(c) The second law has several versions of statement. For example, "Heat cannot spontaneously flow from cold regions to hot regions without external work being performed on the system" is one of them. Correct.
(d) If we know the value of energy transferred as heat in a process, we can definitely determine the value of energy transferred as work in the process using the $1^{\text {st }}$ law.

Wrong. As the energy conservation law is $\Delta \mathrm{U}=\mathrm{q}+\mathrm{w}$, we need to also know the energy change.
(3) Please choose all items that correctly explain about entropy. Then, for the wrong statement(s), please explain why it is wrong.
(a) The entropy change of a system in any irreversible process is positive, according to the $2^{\text {nd }}$ law of thermodynamics.

Wrong. "The entropy change is positive in any irreversible process" is correct only for an isolated system.
(b) [J K] is an appropriate unit for entropy.

Wrong. The unit of entropy should be [J/K]
(c) If a system goes through an adiabatic process, the entropy of the system is not changed.

Wrong. This is correct only for reversible adiabatic process.
*I also accept "correct" because I gave such a solution in 2014 exam that I uploaded on eTL. But, "wrong" is more appropriate here.
(d) Entropy is defined as " $d S=\frac{\delta q}{T}$,

Wrong. This equation is satisfied only for reversible processes.
[Problem-II: 15 pt ( $3 \times 5$ pt)] Answer the following questions about heat capacity.
(1) Please derive the definition of constant-pressure heat capacity ( $C_{P}$ ) of real gas, starting from the definition of heat capacity and the first-law of thermodynamics. The definition of heat capacity is given as $q=C \Delta T$, where $q$ is the heat required to increase the temperature of the system by $\Delta \mathrm{T}$ and $C$ (a heat capacity) is a coefficient to correlate $q$ and $\Delta \mathrm{T}$. Note that $C$ is usually dependent on the temperature for real gas.

The heat capacity is given as $q=C \Delta \mathrm{~T}$. The constant pressure heat capacity is the heat capacity for reversible constant-pressure system.

By the first law, $d U=\delta q+\delta w$. As the process is reversible, $d U=-P d V+\delta q$
When the pressure is constant, $\delta q=d U-P d V=d U-P d V+V d P=d(U+P V)=d H$. Thus, $q=\Delta H$
Then, the heat capacity is given as $C_{p}=\lim _{\Delta T \rightarrow 0}\left(\frac{\Delta H}{\Delta T}\right)_{P}=\left(\frac{\partial H}{\partial T}\right)_{P}$ or more exactly $\left(\frac{\partial H}{\partial T}\right)_{N, P}$
(2) If the system is of ideal gas, $C_{p}$ can be written total derivative form (not partial derivative form). Please derive the equation.

In the case of ideal gas, $\Delta H$ only depends on temperature as
$U \equiv U(T), P V=n R T$ and then $H=U+P V=U+n R T \equiv H(T)$
Thus, independent of the pressure, the constant-pressure heat capacity is given as $C_{p}=\frac{d H}{d T}$.
*Be sure this does not mean $\mathrm{dH} / \mathrm{dT}$ gives always $C_{p}$. $\mathrm{C}_{\mathrm{p}}$ is equal to $\mathrm{dH} / \mathrm{dT}$ of a constant pressure process.
(3) Answer $\mathrm{C}_{\mathrm{p}}$ of mono-atomic molecule (e.g. He ) and $\mathrm{C}_{\mathrm{p}}$ of di-atomic molecule (e.g. $\mathrm{H}_{2}$ ) assuming that they are ideal gasses. Explain why such difference occurs between mono-atomic molecule and di-atomic molecule.

In the case of mono-atomic molecule, the degree of freedom in the kinetic energy is 3 . Thus, the internal energy becomes $U=\frac{3}{2} n R T$. Then, adding $\mathrm{PV}=\mathrm{nRT}$ term, the constant pressure heat capacity is given as

$$
C_{p}=\frac{d H}{d T}=\frac{d(U+n R T)}{d T}=\frac{5}{2} n R
$$

In the case of di-atomic molecule, the degree of freedom in the kinetic energy of the center of mass is 3 , as the same with mono-atomic molecule. In addition, we have two rotational degrees of freedom for H -H molecule. Although there is additionally 1 vibrational mode, which causes additional $n R$ increase in the heat capacity at high temperatures because each vibration mode includes 2 degrees of freedom (kinetic and potential), it is not activated at low temperatures and thus is neglected in the ideal gas. Consequently, the internal energy becomes
$U=\frac{5}{2} n R T$. Then, adding $\mathrm{PV}=\mathrm{nRT}$ term, the constant pressure heat capacity is given as
$C_{p}=\frac{d H}{d T}=\frac{d(U+n R T)}{d T}=\frac{7}{2} n R$

## [Problem-III: $\mathbf{1 5}$ pt (3x5pt)]

(1) Using Redlich-Kwong equation as the equation of state, derive an equation to evaluate the work required for an isothermal reversible expansion from a molar volume of $\bar{V}_{1}$ to $\bar{V}_{2}$ ( $\bar{V}$ is a molar volume defined as " $\bar{V}=V / n$ " where $n$ is the amount of gas in mole). The Redlich-Kwong equation can be written as $P=\frac{R T}{\bar{V}-B}-\frac{A}{\bar{V}(\bar{V}+B) T^{1 / 2}}$ where $A$ and $B$ are constants and $A=3.2205 \mathrm{~m}^{6} \mathrm{~Pa} \mathrm{~mol}^{-2} \mathrm{~K}^{1 / 2}, B=2.985 \times 10^{-5} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$. Then, using the derived equation above, calculate the work involved in the isothermal reversible compression of 3 moles of $\mathrm{CH}_{4}$ gas from a volume of $2.00 \times 10^{-3} \mathrm{~m}^{3}$ to $1.00 \times 10^{-3}$ $\mathrm{m}^{3}$ at 400 K .

As the process is reversible ( $\delta w=-P d V$ )

$$
w=\int \delta w=-\int P d V=-\int\left(\frac{R T}{\bar{V}-B}-\frac{A}{\bar{V}(\bar{V}+B) T^{1 / 2}}\right) d V
$$

As $d \bar{V}=d(V / n)=\frac{d V}{n}$ thus $d V=n d \bar{V}$,

$$
\begin{aligned}
& w=-\int\left(\frac{R T}{\bar{V}-B}-\frac{A}{\bar{V}(\bar{V}+B) T^{1 / 2}}\right) n d \bar{V}=-n \int\left(\frac{R T}{\bar{V}-B}-\frac{A}{B T^{1 / 2}}\left(\frac{1}{\bar{V}}-\frac{1}{\bar{V}+B}\right)\right) d \bar{V} \\
& =-n R T \ln \left(\frac{\bar{V}_{2}-B}{\bar{V}_{1}-B}\right)+\frac{n A}{B T^{1 / 2}}\left\{\ln \left(\frac{\bar{V}_{2}}{\bar{V}_{1}}\right)-\ln \left(\frac{\bar{V}_{2}+B}{\bar{V}_{1}+B}\right)\right\}
\end{aligned}
$$

Applying $\bar{V}_{1}=\frac{2.00 \times 10^{-3}}{3}=0.667 \times 10^{-3}\left[\mathrm{~m}^{3}\right], \bar{V}_{2}=\frac{1.00 \times 10^{-3}}{3}=0.333 \times 10^{-3}\left[\mathrm{~m}^{3}\right], n=3[\mathrm{~mol}], T=400[\mathrm{~K}]$
we obtain 6.72 kJ .
(2) Assuming $\mathrm{CH}_{4}$ is an ideal gas, do the same with (1).

In the case of ideal gas, $\mathrm{PV}=$ const. is achieved for isothermal process. If it is reversible, we have

$$
w=\int \delta w=-\int P d V=-\int \frac{n R T}{V} d V=n R T \ln \left(\frac{V_{1}}{V_{2}}\right)
$$

This gives 6.91 kJ .
(3) If the compression is done from $2.00 \times 10^{-3} \mathrm{~m}^{3}$ to $3.5 \times 10^{-5} \mathrm{~m}^{3}$, the difference between the Redlich-Kwong equation and the ideal gas equation becomes significant. (You don't need to calculate the values.) Explain why the significant difference occurs in this case.

This is because $3.5 \times 10^{-5} \mathrm{~m}^{3}$ causes a high pressure, which cannot be nicely described by the ideal gas. Specifically, if the pressure is high, the average inter-molecule distance becomes short and the inter-molecular interaction becomes non-negligible. In addition, the collision probability of molecules increases. In the case of ideal gas, it is assumed that there is no interaction between molecules and there is no collision between molecules. This assumption becomes inaccurate for real gasses at high pressures.

## [Problem-IV: 12 pt (5 pt for (1) and 7 pt for (2))]

(1) We consider a general cycle (e.g. engine). By a sole operation of this cycle, the following energy transfers occur: $Q_{i n}$ $[J](>0)$, the energy transferred as heat to the system from the surroundings; $Q_{\text {out }}[J](>0)$, the energy transferred as heat to the surroundings from the system; and $W_{\text {out }}[J](>0)$, the net energy transferred as work from the system to the surroundings. Please give an equation to express the efficiency $(\eta)$ of this cycle using $Q_{i n}$ and $Q_{o u t}$, starting from the definition of cycle efficiency.

The efficiency of cycle is defined as

$$
\eta=\frac{W_{\text {system } \rightarrow \text { surroundings }}}{Q_{\text {surroundings } \rightarrow \text { system }}}
$$

By the first law, $\Delta U=-W_{\text {system } \rightarrow \text { surroundings }}+Q_{\text {surroundings } \rightarrow \text { system }}-Q_{\text {system } \rightarrow \text { surroundings }}$
As this is a cycle, $\Delta U=0$. Therefore, $W_{\text {system } \rightarrow \text { surroundings }}=Q_{\text {surroundings } \rightarrow \text { system }}-Q_{\text {system } \rightarrow \text { surroundings }}$

$$
\eta=\frac{W_{\text {system } \rightarrow \text { surroundings }}}{Q_{\text {surroundings } \rightarrow \text { system }}}=\frac{Q_{\text {surroundings } \rightarrow \text { system }}-Q_{\text {system } \rightarrow \text { surroundings }}}{Q_{\text {surroundings } \rightarrow \text { system }}}=\frac{Q_{\text {in }}-Q_{\text {out }}}{Q_{\text {in }}}=1-\frac{Q_{\text {out }}}{Q_{\text {in }}}
$$

(2) Carnot cycle is composed of 4 processes: (i) isothermal expansion using thermostat $\mathrm{T}_{1}$, (ii) adiabatic expansion, (iii) isothermal compression using thermostat $\mathrm{T}_{2}$, and (iv) adiabatic compression. Derive the expression of the efficiency using $\mathrm{T}_{1}$ and $\mathrm{T}_{2}$.
*As definition, "Carnot cycle" is a reversible cycle.

For simplicity, we derive the relation for ideal gas. (However, as shown below with van der Walls gas, the same result is also achieved for real gasses.)

The first law of reversible isothermal process $(d T=0)$ for ideal gas $(U=U(T))$ is:

$$
Q_{1}=q_{A \rightarrow B}=-w_{A \rightarrow B}=\int P d V=n R T_{H} \ln \frac{V_{B}}{V_{A^{\prime}}}, Q_{2}=-q_{B \rightarrow C}=n R T_{L} \ln \frac{V_{C}}{V_{D}}
$$

For reversible adiabatic processes, we can use the relationship between T and V as: $\left(\frac{T_{\text {fin }}}{T_{\text {ini }}}\right)^{\alpha}=\left(\frac{V_{\text {ini }}}{V_{\text {fin }}}\right)$ where $\alpha=$ const. (e.g. $\alpha=\frac{3}{2}$ for He). Using this equation gives $\left(\frac{T_{C}}{T_{B}}\right)^{\alpha}=\left(\frac{T_{L}}{T_{H}}\right)^{\alpha}=\left(\frac{V_{B}}{V_{C}}\right)$ and $\left(\frac{T_{A}}{T_{D}}\right)^{\alpha}=\left(\frac{T_{H}}{T_{L}}\right)^{\alpha}=\left(\frac{V_{D}}{V_{A}}\right)$. Comparing these 2 equations gives $\left(\frac{V_{B}}{V_{C}}\right)=\left(\frac{V_{A}}{V_{D}}\right)$ then $\left(\frac{V_{B}}{V_{A}}\right)=\left(\frac{V_{C}}{V_{D}}\right)$. Thus, $\frac{Q_{2}}{Q_{1}}=\frac{n R T_{L} \ln \frac{V_{C}}{V_{D}}}{n R T_{H} \ln \frac{V_{B}}{V_{A}}}=\frac{T_{L}}{T_{H}}$
Thus, for the Carnot cycle, the efficiency is expressed as
$\eta=\frac{W_{\text {system } \rightarrow \text { surroundings }}}{Q_{\text {surroundings } \rightarrow \text { system }}}=1-\frac{Q_{\text {out }}}{Q_{\text {in }}}=1-\frac{T_{L}}{T_{H}}$
<Appendix> in the case of van der Waals gas, whose equation of state is $P=\frac{R T}{\bar{V}-b}-\frac{a}{\bar{V}^{2}}=\frac{n R T}{V-b}-\frac{a n^{2}}{V^{2}}$ First, derive the formula for the internal energy (U) of van der Waals gas. For this, we use the following differential equation:
$d U=\left(\frac{\partial U}{\partial T}\right)_{V} d T+\left(\frac{\partial U}{\partial V}\right)_{T} d V$
Here we do not consider there is mass exchange with the surroundings,
as it is often assumed so in the case of thermodynamic cycle.
For the first term, we assume that the constant volume heat capacity is expressed as $c_{V}=c n R T$, where $c$ is a constant.
(This is a part of the definition of van der Waals gas).
For the second term, the partial derivative is the constant-volume heat capacity, $\left(\frac{\partial U}{\partial T}\right)_{V} \equiv c_{V}=c n R T$.
Then, the second term is written down as follows:

$$
d S=\left(\frac{\partial S}{\partial T}\right)_{V} d T+\left(\frac{\partial S}{\partial V}\right)_{T} d V
$$

For a reversible process, the first and second laws give $d U=T d S-P d V$, then

$$
d U=T\left\{\left(\frac{\partial S}{\partial T}\right)_{V} d T+\left(\frac{\partial S}{\partial V}\right)_{T} d V\right\}-P d V=\left\{T\left(\frac{\partial S}{\partial T}\right)_{V}\right\} d T+\left\{T\left(\frac{\partial S}{\partial V}\right)_{T}-P\right\} d V \text {, and }
$$

$$
\text { Comparing this with } d U=\left(\frac{\partial U}{\partial T}\right)_{V} d T+\left(\frac{\partial U}{\partial V}\right)_{T} d V
$$

$$
\left(\frac{\partial U}{\partial V}\right)_{T}=T\left(\frac{\partial S}{\partial V}\right)_{T}-P=T\left(\frac{\partial P}{\partial T}\right)_{V}-P \text {, where we used one of Maxwell relations, }\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V} .
$$

Accordingly, for van der Waals gas, $\left(\frac{\partial U}{\partial T}\right)_{V}=T\left(\frac{\partial P}{\partial T}\right)_{V}-P=T\left\{\frac{\partial}{\partial T}\left(\frac{n R T}{V-b}-\frac{n^{2} a}{V^{2}}\right)_{V}\right\}-P=\frac{n R T}{V-b}-P=\frac{a n^{2}}{V^{2}}$
Therefore, $d U=\left(\frac{\partial U}{\partial T}\right)_{V} d T+\left(\frac{\partial U}{\partial V}\right)_{T} d V=c n R T d T+\frac{a n^{2}}{V^{2}} d V$
$\int d U=\frac{c n R}{2}\left(T_{2}^{2}-T_{1}^{2}\right)-a n^{2}\left(\frac{1}{V_{2}}-\frac{1}{V_{1}}\right)$

The work, heat, the internal energy change of the system by the isothermal expansion are given as
$w_{1}=-\int P d V=-n R T \ln \frac{\left(V_{2}-b\right)}{\left(V_{1}-b\right)}-a n^{2}\left(\frac{1}{V_{2}}-\frac{1}{V_{1}}\right)$
$\Delta U_{1}=\frac{c n R}{2}\left(T_{2}^{2}-T_{1}^{2}\right)-a n^{2}\left(\frac{1}{V_{2}}-\frac{1}{V_{1}}\right)=-a n^{2}\left(\frac{1}{V_{2}}-\frac{1}{V_{1}}\right)$
$\Delta U_{1}=q_{1}+w_{1}$ thus $q_{1}=n R T_{H} \ln \frac{\left(V_{2}-b\right)}{\left(V_{1}-b\right)}$
Likewise, the work, heat, the internal change of the system by the isothermal compression are given as
$w_{3}=-\int P d V=-n R T \ln \frac{\left(V_{4}-b\right)}{\left(V_{3}-b\right)}-a n^{2}\left(\frac{1}{V_{4}}-\frac{1}{V_{3}}\right)$
$\Delta U_{3}=\frac{c n R}{2}\left(T_{4}^{2}-T_{3}^{2}\right)-a n^{2}\left(\frac{1}{V_{4}}-\frac{1}{V_{3}}\right)=-a n^{2}\left(\frac{1}{V_{4}}-\frac{1}{V_{3}}\right)$
$\Delta U_{3}=q_{3}+w_{3}$ thus $q_{3}=n R T_{L} \ln \frac{\left(V_{4}-b\right)}{\left(V_{3}-b\right)}$
Because the other processes are adiabatic processes,
$Q_{\text {in }}=\left|q_{1}\right|=n R T_{H} \ln \frac{\left(V_{2}-b\right)}{\left(V_{1}-b\right)}, Q_{\text {out }}=\left|q_{3}\right|=-n R T_{L} \ln \frac{\left(V_{4}-b\right)}{\left(V_{3}-b\right)}$,
As a result, we have
$\eta=\frac{W_{\text {system } \rightarrow \text { surroundings }}}{Q_{\text {surroundings } \rightarrow \text { system }}}=1-\frac{Q_{\text {out }}}{Q_{\text {in }}}=1+\frac{T_{L} \ln \frac{\left(V_{4}-b\right)}{\left(V_{3}-b\right)}}{T_{H} \ln \frac{\left(V_{2}-b\right)}{\left(V_{1}-b\right)}}$
For adiabatic processes, we can derive the following relation (I skip the confirmation here): $\frac{\left(V_{4}-b\right)}{\left(V_{3}-b\right)}=\frac{\left(V_{1}-b\right)}{\left(V_{2}-b\right)}$
Using this, we confirm $\eta=1-\frac{T_{L}}{T_{H}}$ for Carnot cycle of van der Waals gas as well.
[Problem-V: $25 \rightarrow 29$ pt, (1)-(2): 4pt for each, (3): 6pt, (4)-(6): 5pt for each]
Otto cycle is composed of 4 processes: (i) adiabatic compression from $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$, (ii) constant volume heating with a thermostat, (iii) adiabatic expansion from $\mathrm{V}_{2}$ to $\mathrm{V}_{1}$, and (iv) constant volume cooling with another thermostat. Assuming the system is composed of ideal gas whose constant-volume heat capacity $\left(C_{v}\right)$ is given as $(5 / 2) n R$ and all processes are quasi-static (but not necessarily reversible), answer the following questions.
(1) Draw P-V diagram of this cycle ( $x$-axis is $V$ and $y$-axis is $P$ ).
*You don't need to draw a quantitatively correct figure; please draw a qualitatively correct one.
(2) Draw T-S diagram of this cycle ( $x$-axis is $S$ and $y$-axis is $T$ ).
*You don't need to draw a quantitatively correct figure; please draw a qualitatively correct one.

(from Wikipedia)
(3) Express the heat, work, internal energy change, entropy change for each process. You can use $T_{1}, T_{2}, T_{3}, T_{4}$ and $V_{1}$, and $V_{2}$ in the expressions, where $T_{1}, T_{2}, T_{3}$ and $T_{4}$ are the beginning temperatures of processes (i), (ii), (iii) and (iv), respectively.
<Process (i), from state 1 to state $2>$ adiabatic compression from $\mathrm{V}_{1}$ to $\mathrm{V}_{2}$
$q_{1}=0, \Delta S_{1}=0$,
$\Delta U_{1}=w_{1}=\int_{T_{1}}^{T_{2}} c_{v} d T=\frac{5}{2} n R\left(T_{2}-T_{1}\right)$
<Process (ii), from state 2 to state $3>$ constant volume heating with a thermostat ( $\mathrm{T}_{3}$ )
$w_{2}=0$
$\Delta U_{2}=q_{2}=c_{v} \Delta T=\frac{5}{2} n R\left(T_{3}-T_{2}\right)$
This process is not reversible because the heat flow occurs between the system and the surroundings while there are some temperature differences between them. To calculate the entropy change, we consider an imaginary reversible process, where the temperature of the system increases by one-by-one contacting to infinitely many thermostats, each of which holds the infinitesimally higher temperature than the system at each moment. With this imaginary reversible cycle, the entropy change is written as

$$
\Delta S_{2}=\int_{T_{2}}^{T_{3}} \frac{d q_{r e v}}{T}=\int_{T_{2}}^{T_{3}} \frac{\frac{5}{2} n R d T}{T}=\frac{5}{2} n R \ln \frac{T_{3}}{T_{2}}
$$

<Process (iii), from state 3 to state $4>$ adiabatic expansion from $V_{2}$ to $V_{1}$
$q_{3}=0, \Delta S_{3}=0$,
$\Delta U_{3}=w_{3}=\int_{T_{3}}^{T_{4}} c_{v} d T=\frac{5}{2} n R\left(T_{4}-T_{3}\right)$
<Process (iv), from state 4 to state $1>$ constant volume cooling with a thermostat ( $\mathrm{T}_{1}$ )
$w_{4}=0$
$\Delta U_{4}=q_{4}=c_{v} \Delta T=\frac{5}{2} n R\left(T_{1}-T_{4}\right)$
As the same with process (ii), the entropy change is written as

$$
\Delta S_{4}=\int_{T_{4}}^{T_{1}} \frac{d q_{r e v}}{T}=\int_{T_{4}}^{T_{1}} \frac{\frac{5}{2} n R d T}{T}=\frac{5}{2} n R \ln \frac{T_{1}}{T_{4}}
$$

(4) Express $T_{4}$ using $T_{1}, T_{2}$ and $T_{3}$.

As the entropy is a state function, its change through one cycle should be 0 . Thus,

$$
\Delta S_{1}+\Delta S_{2}+\Delta S_{3}+\Delta S_{4}=0+\frac{5}{2} n R \ln \frac{T_{3}}{T_{2}}+0+\frac{5}{2} n R \ln \frac{T_{1}}{T_{4}}=\frac{5}{2} n R \ln \left(\frac{T_{3}}{T_{2}} \frac{T_{1}}{T_{4}}\right)=0
$$

Therefore, $\frac{T_{3}}{T_{2}} \frac{T_{1}}{T_{4}}=1, T_{4}=\frac{T_{1} T_{3}}{T_{2}}$
(5) Express the efficiency using $V_{1}$ and $V_{2}$.
$Q_{\text {in }}=\left|q_{2}\right|=\frac{5}{2} n R\left(T_{3}-T_{2}\right), Q_{\text {out }}=\left|q_{4}\right|=\frac{5}{2} n R\left(T_{4}-T_{1}\right)$
Therefore,
$\eta=1-\frac{Q_{\text {out }}}{Q_{\text {in }}}=1-\frac{\left(T_{4}-T_{1}\right)}{\left(T_{3}-T_{2}\right)}=1-\frac{T_{1}}{T_{2}} \frac{\frac{T_{4}}{T_{1}}-1}{\frac{T_{3}}{T_{2}}-1}$
Here, for an adiabatic process (i), we have the following relation in the initial and final temperatures:
$d U=\frac{5}{2} n R d T=\delta w=-\frac{n R T}{V} d V$
$\frac{5}{2} \frac{d T}{T}=-\frac{d V}{V},\left(\frac{T_{2}}{T_{1}}\right)^{\frac{5}{2}}=\left(\frac{V_{1}}{V_{2}}\right)$
Using this relation and $\frac{T_{3}}{T_{2}}=\frac{T_{4}}{T_{1}}$, we have
$\eta=1-\frac{T_{1}}{T_{2}} \frac{\frac{T_{4}}{T_{1}}-1}{T_{3}}-1 \quad 1-\frac{T_{1}}{T_{2}}=1-\left(\frac{V_{2}}{V_{1}}\right)^{\frac{2}{5}}$
(6) Show the efficiency of this cycle is lower than Carnot cycle. And explain the reason of it.

In the case of Carnot cycle of two thermostats ( $\mathrm{T}_{\mathrm{H}}=\mathrm{T}_{3}, \mathrm{~T}_{\mathrm{L}}=\mathrm{T}_{1}$ ), the efficiency becomes
$\eta_{\text {carnot }}=1-\frac{T_{L}}{T_{H}}=1-\frac{T_{1}}{T_{3}}$
Here, because $T_{3}>T_{2}$ is achieved as the process (ii) is a constant-volume heating, Otto cycle's efficiency is always lower than Carnot cycle efficiency. This is natural because Otto cycle include irreversible cycle, namely constant-V heating/cooling, where a heat transfer occurs with a finite temperature difference between the system and the surrounding if only two thermostats. According to a version of the second law, "The efficiency of a quasi-static or reversible Carnot cycle depends only on the temperatures of the two heat reservoirs, and is independent of the working substance. A Carnot engine operated in this way is the most efficient possible heat engine using those two temperatures." and the related theorem, "The efficiency of a (general) cycle using 2 thermostats is less than the efficiency of Carnot cycle: $\eta \leq \eta_{\text {carnot }}=1-\frac{T_{L}}{T_{H}}$. The equal sign is achieved when the cycle is reversible.", the efficiency of Otto cycle must be lower than that of Carnot cycle.
[Problem-VI: 18 pt ( 6 pt each)] We consider a reactor that can generate 750 M [J] work per second (thus 750 MW output). The temperature of reactor is 600 K , which can be considered as the high-temperature thermostat, and the temperature of river, which is used as the low-temperature thermostat and to which we dispose some energy as heat, is 300 K. Answer the following question.
(1) Assuming this reactor uses a cycle (engine) of two thermostats, answer the largest possible efficiency of this reactor.

The best efficiency of two-thermostats cycle is achieved for Carnot cycle and reversible cycle, which is expressed as follows according to the result of Problem IV.

$$
\eta_{\text {best }}=\frac{W_{\text {out }}}{Q_{\text {in }}}=1-\frac{T_{L}}{T_{H}}=1-\frac{300}{600}=0.5
$$

(2) Assuming the real efficiency of this reactor is $60 \%$ of the largest possible efficiency, answer how much energy is released to the river as heat per second.

The real efficiency becomes $\eta_{\text {real }}=\eta_{\text {best }} \times 0.6=0.3$
In this case, to achieve $W_{\text {out }}=750 \mathrm{MW}$, we need to have $Q_{i n}=\frac{W_{\text {out }}}{0.3}=2500 \mathrm{MW}$. The internal energy change by one cycle is 0 as the internal energy is a state function and the initial and final states are the same in a cycle.
Thus,

$$
\begin{aligned}
& \Delta Y=-W_{\text {out }}+Q_{\text {in }}-Q_{\text {out }}=-750 M W+2500 M W-Q_{\text {out }}=0 \\
& Q_{\text {out }}=1750 M W
\end{aligned}
$$

(3) The flow rate of river is $165 \mathrm{~m}^{3} / \mathrm{s}$. The density of water is $1000 \mathrm{~kg} / \mathrm{m}^{3}$. The heat capacity of water is $4.2 \mathrm{~kJ} / \mathrm{kg} / \mathrm{K}$. Then, answer what is the expected temperature increase of this river due to the release of the heat from the reactor.

Every second, 1750 MJ energy is disposed to the river. Every second, the water of $165 \times 1000 \mathrm{~kg}$ flows in river.
Then, the heat absorbed by 1 kg of water is calculated as

$$
q=\frac{1750 \times 10^{6}}{165 \times 10^{3}}=\frac{1750 \times 10^{6}}{165 \times 10^{3}}=10.6[\mathrm{~kJ} / \mathrm{kg}]
$$

As the heat capacity is $4.2 \mathrm{~kJ} / \mathrm{kg} / \mathrm{K}$, the temperature increase is $10.6 / 4.2=2.53 \mathrm{~K}$.

