

Physical Chemistry (I)

Midterm / November 9, 2013

1. (10%) There are many ways of description to elucidate the physical meanings of the *second law* of thermodynamics. In the following statements, write only in one sentence for what's wrong of the statement in description, interpretation, or application of the 2nd law; if you think that the statement is correct, make a short comment for it. (2% each)
- (a) The reversible isothermal expansion of an ideal gas is spontaneous.
 - (b) In Kelvin-Planck statement, it states that heat obtained from the hot reservoir cannot transfer completely into work, therefore we can conclude that work cannot transfer completely into heat as well.
 - (c) Clausius stated that no process is possible in which the only transfer of energy is as heat transferred from a hotter to a colder system.
 - (d) Combine Clausius inequality ($TdS \geq dq$) with the 1st law of thermodynamics ($dU = dq + dw$, only PV -work is involved), we conclude that $dU \leq TdS - PdV$, where the equality holds only for a reversible process.
 - (e) The kitchen is so hot so you can open the door of your refrigerator to cool down the kitchen.
2. (10%) One mole of an ideal gas with $C_{v,m} = \frac{3}{2}R$ is expanded adiabatically against a constant external pressure of $P_{\text{ex}} = 1$ bar until $T = T_f$ and $P = P_f$. The initial temperature and pressure are T_i and P_i , respectively; answer the following questions.
- (a) Express the internal energy change (ΔU) in terms of temperature or pressure. (2%)
 - (b) What is the *maximum* amount of work that can be done by this system? (2%)
 - (c) If $P_i = 25$ bar, $P_f = 1$ bar, and $T_i = 300$ K, determine the value of T_f . (3%)
 - (d) Compare the adiabatic process with the reversible isothermal expansion process and explain why the indicator diagram (PV plot) shows that $P_{\text{adibatic}} < P_{\text{isothermal}}$ for all $P < P_i$ (expansion), whereas $P_{\text{adibatic}} > P_{\text{isothermal}}$ for all $P > P_i$ (compression). (3%)

3. (15%) In the first half of the 19th century, Joule tried to measure the temperature change when a gas is expanded into a vacuum. However, the experimental setup was not sensitive enough so that Joule found no temperature change within the limit of his error. Soon afterward, Joule and Thomson devised a much more sensitive method to measure the temperature change upon expansion. Answer the following questions accordingly.

- (a) According to the result of Joule's experiment, draw a conclusion based on the

following expression: $\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$. (2%)

- (b) The internal pressure of the system is defined as $\left(\frac{\partial U}{\partial V}\right)_T$, show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \quad (3\%)$$

- (c) In Joule-Thompson's experiment, a constant applied pressure P_1 causes a quantity of gas to flow slowly from one chamber to another through a porous plug of silk or cotton. If a volume, V_1 , of gas is pushed through the porous plug, and the pressure on the other side of the chamber is maintained at P_2 until the volume becomes V_2 , calculate the net work done by the isolated system. (2%)

- (d) Following (c) and starting with $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$, show that

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T. \quad (2\%)$$

- (e) Explain under what conditions the gas can be liquefied under isenthalpic expansion. (2%)

- (f) Show that $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$. (4%)

4. (10%) At 298 K, the thermal expansion coefficient and the isothermal compressibility of liquid water are $\beta = 2.04 \times 10^{-4} \text{ K}^{-1}$ and $\kappa = 45.9 \times 10^{-6} \text{ bar}^{-1}$. Now based on the equation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ to answer the following questions.

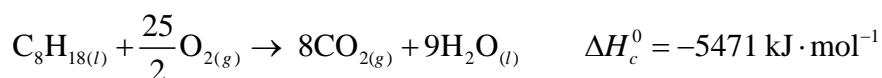
- (a) Calculate $\left(\frac{\partial U}{\partial V}\right)_T$ for water at 320 K and 1.0 bar. (2%)

- (b) If an external pressure equal to $\left(\frac{\partial U}{\partial V}\right)_T$ were applied to liquid water at 320 K, how much would its volume change in percentage? (3%)
- (c) Calculate $\left(\frac{\partial U}{\partial V}\right)_T$ for N_2 at 320 K and 1.0 bar, assuming that van der Waals equation can be applied with parameters $a = 1.37 \text{ dm}^6 \text{ bar mol}^{-2}$ and $b = 0.0387 \text{ dm}^3 \text{ mol}^{-1}$; note that at the relatively low pressure condition ($P = 1 \text{ bar}$), it might be safe to use the ideal gas law to determine V_m . (3%)
- (d) Compare the results obtained from (a) and (c) and make a comment for it. (2%)
5. (20%) The first law states that the energy of the universe is a constant while the second law states that the entropy of the universe tends always towards a maximum. Answer the following questions *only* based on the conditions it is provided.
- (a) If only PV -work is considered, prove that the inequality of work ($dw_{\text{rev}} < dw_{\text{irr}}$) is always valid (e.g., expansion or compression). (2%)
- (b) Prove that $dq_{\text{rev}} > dq_{\text{irr}}$ based on the conclusion made from (b). (2%)
- (c) Prove the Clausius inequality based on the conclusion of (c), i.e., $dS \geq \frac{dq}{T_{\text{surr}}}$, where the equality holds only for reversible processes. (2%)
- (d) Following (d), prove that the entropy change of any irreversible process is always greater than zero in an isolated system. (2%)
- (e) Assuming that the system is no longer isolated, i.e., the surroundings are a reservoir of energy and the heat entering the system is equal to the heat leaving the surroundings. Show that the Clausius inequality can be deduced to a more general expression for the 2nd law, i.e., $dS_{\text{tot}} = dS + dS_{\text{surr}} \geq 0$. (2%)
- (f) Show that the Gibbs energy change is always less than or equal to zero at the conditions of constant T and P , i.e., $(dG)_{T,P} \leq 0$ when only PV -work is involved. (2%)
- (g) Following (g), if non-expansion (non- PV) work is also considered here, i.e., $w = w_{\text{PV}} + w_{\text{non-PV}}$, with a short derivation to explain what is the physical meaning of ΔA at constant T . (2%)
- (h) A box contains two identical parts with a removable partition. One part of the box contains n moles of ideal gas A while the other part contains n moles of ideal gas B with the same P , V , and T for both A and B. Now the partition is removed and the gases spontaneously mix. What is the *maximum amount of work* that could be obtained from this spontaneous process? (4%)

6. (20%) Consider a reversible Carnot cycle for a sample of an ideal gas working substance (heat capacity C_v) running as a heat engine between two temperature reservoirs (T_H and T_C); the heat of q_H is transferred from the hot reservoir ($T = T_H$) to the engine, the engine does mechanical work w and the heat of q_C is transferred from the engine to the cold reservoir ($T = T_C$).

- Draw qualitatively the corresponding indicator diagram (PV plot) with the following sequence, $a \xrightarrow{(1)} b \xrightarrow{(2)} c \xrightarrow{(3)} d \xrightarrow{(4)} a$, and state the names for each process in segments (1)–(4). (3%)
- Give the physical meaning for the area inside the P - V plot. (2%)
- Draw qualitatively the corresponding diagram for the same Carnot cycle on a T vs. S plot with the same label as in (a). (3%)
- Derive an expression for the area inside the T - S plot and give the physical meaning of it. (3%)
- Now combine the results obtained from (b) and (d) to prove that $q_H = -w - q_C$. (2%)
- Make a derivation from (c) to prove that $\frac{q_H}{-q_C} = \frac{T_H}{T_C}$. (2%)
- Prove that the efficiency (ε) of a heat engine is $\varepsilon = 1 - \frac{T_C}{T_H}$. (2%)
- When the heat engine runs in the reverse direction, it can be used either as a heat pump or a refrigerator (or air conditioner). Relate the coefficients of performance of heat pump (η_{hp}) and refrigerator (η_r) with respect to T_H and T_C . (3%)

7. (10%) Octane (C_8H_{18}) can be used to construct a fuel cell based on the oxidation of the compound with the energy (enthalpy) released by the following reaction:



- Given that $\Delta G_{\text{octane}}^0 = -5296 \text{ kJ} \cdot \text{mol}^{-1}$, calculate the *maximum* work that is available through the combustion of the hydrocarbon at 298.15 K and 1 bar; note that the work includes both expansion and non-expansion types. (2%)
- Following (a), calculate the *minimum* heat that must be released into the surroundings at 298.15 K. (2%)
- Following (a) and (b), calculate the internal energy change of the system at the standard state. (2%)

- (d) Consider a heat engine with $T_H = 600$ K and $T_C = 300$ K. The engine is running with the combustion of octane as a heat source. Calculate the ratio for the *maximum* work available from the heat engine to that available in an ideal electrochemical fuel cell using octane as a fuel. (4%)

8. (10%) We define a general chemical reaction as $aA + bB + \dots \rightarrow cC + dD + \dots$, which for convenience we express the above reaction as $cC + dD + \dots - aA - bB - \dots = 0$, or equivalently $\sum_i \nu_i X_i = 0$, where ν_i stands for the stoichiometric coefficient of species X_i (now simplified as species i). Answer the following questions.

- (a) Define the extent of the reaction as ξ and the initial mole number of species i as n_i^0 to satisfy $n_i = n_i^0 + \nu_i \xi$, derive an expression for the reaction of Gibbs energy (ΔG_r) in terms of ξ at constant T and P . (2%)

- (b) Following (a), determine the criterion in terms of G vs. ξ for the forward reaction to be spontaneous at constant T and P . What is the criterion for the reaction reaching equilibrium? (2%)

- (c) Considering the reaction occurring in the gas phase, derive the expression for the thermodynamic equilibrium constant (K_p) as a function of standard state thermodynamic functions, ΔH_r° and ΔS_r° . (2%)

- (d) Derive an expression for the temperature variation of K_p in terms of ΔH_r° based on Gibbs-Helmholtz equation. What is the assumption you need to make for the derivation? (2%)

- (e) Express the mole-fraction equilibrium constant (K_x) in terms of K_p and $\Delta \nu$, where the mole fraction of species i (x_i) and the partial pressure of species i (P_i) are related by $P_i = x_i P$ and $\Delta \nu = c + d + \dots - a - b - \dots = \sum_i \nu_i$. (2%)

參考解答

1. (a) The reversible process is not spontaneous process because the system and the surrounding are in equilibrium.
- (b) Work can transfer into heat completely!
- (c) Heat transferred only from a colder to a hotter system is not possible.
- (d) “ $dU = TdS - PdV$ ” holds for both reversible and irreversible processes since U , T , S , P , and V are all state variables.
- (e) It does not work if the refrigerator is located inside the kitchen room because the heat released by the refrigerator is always larger than the heat taken from the refrigerator according to the 2nd law.

2. (a) For adiabatic processes $\Rightarrow q = 0$, $\Delta U = w = -P_{ex}(V_f - V_i)$

$$\Delta U = n \times C_{V,m}(T_f - T_i) = -P_{ex}(V_f - V_i)$$

- (b) Maximum work can be done when the final temperature reaches 0 K., i.e.,

$$-w_{max} = -\Delta U_{max} = 1 \times \frac{3}{2} R(T_i - 0) = \frac{3}{2} RT_i$$

$$(c) \quad \frac{3}{2} R(T_f - 300) = -1 \times \left(\frac{1 \cdot R T_f}{P_f} - \frac{1 \cdot R T_i}{P_i} \right)$$

$$\Rightarrow \frac{3}{2}(T_f - 300) = \frac{300}{25} - \frac{T_f}{1}$$

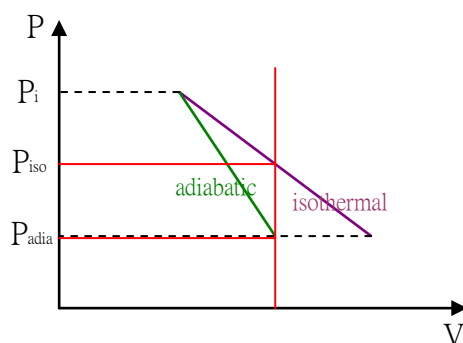
$$\Rightarrow T_f - 300 = 8 - \frac{2}{3} T_f$$

$$\Rightarrow \frac{5}{3} T_f = 308 \quad , \quad T_f = 184.8 \text{ K} \sim 185 \text{ K}$$

- (d) ① For $P < P_i \Rightarrow$ expansion

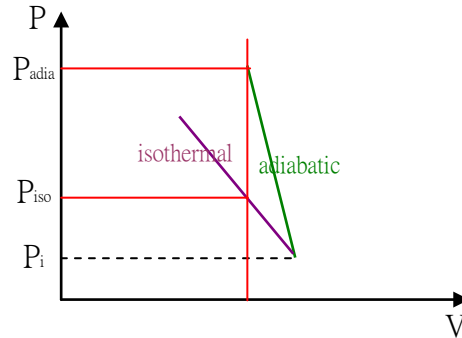
對外做功，等溫過程有外援但絕熱過程要消耗自己的內能而使 $T \downarrow$ ，

故 $P_{adia} < P_{iso}$ ($\because PV = nRT$, $P \propto T$ if V is constant)



② For $P > P_i \Rightarrow$ compression

對系統做功，等溫過程環境吸收此熱量，但絕熱過程此熱能轉變為系統之內能而使 $T \uparrow$ ，故 $P_{\text{adia}} > P_{\text{iso}}$ ($\because PV = nRT, P \propto T$ if V is constant)



3. (a) Joule's experiment shows $\Delta T = 0 \Rightarrow \left(\frac{\partial T}{\partial V} \right)_U = 0$, which implies

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

(b) $dU = TdS - PdV$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

$$(c) \quad w = - \int P_{\text{ex}} dV = -P_1(0 - V_1) - P_2(V_2 - 0) = P_1 V_1 - P_2 V_2$$

$$(d) \quad \because 0 = dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$\Rightarrow \left(\frac{\partial H}{\partial P} \right)_P dT = - \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$\Rightarrow \left(\frac{\partial T}{\partial P} \right)_H = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

$$\therefore \mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

$$\text{or } \mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = - \frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_P} = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T \Rightarrow \left(\frac{\partial H}{\partial P} \right)_T = -C_p \cdot \mu_{JT}$$

(e) In the condition of isenthalpic expansion, gas can only be liquefied in a cooling process when $\mu_{JT} > 0$; because when gas expansion occurs, $\Delta P < 0$, the condition for $\Delta T < 0$ (cooling process) being valid requires

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H > 0.$$

$$(f) \left(\frac{\partial C_p}{\partial P} \right)_T = \left[\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T} \right)_P \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P} \right)_T \right]_P$$

$$\text{由 } dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V = -T \left(\frac{\partial V}{\partial T} \right)_P + V$$

$$\text{故 } \left(\frac{\partial C_p}{\partial P} \right)_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P} \right)_T \right]_P = - \cancel{\left(\frac{\partial V}{\partial T} \right)_P} - T \left(\frac{\partial^2 V}{\partial T^2} \right)_P + \cancel{\left(\frac{\partial V}{\partial T} \right)_P} = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$

$$4. (a) \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = T \frac{\beta}{\kappa} - P = 320 \times \frac{2.04 \times 10^{-4}}{45.9 \times 10^{-6}} - 1.0 = 1421 \text{ bar}$$

$$(b) dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

$$\frac{dV}{V} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P dT + \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T dP = \beta dT - \kappa dP$$

$$\left(\frac{\Delta V}{V} \right)_T = -\kappa \Delta P = -45.9 \times 10^{-6} \times (1421 - 1) = -0.065 = -6.5\%$$

體積將減少 6.5%

$$(c) P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\therefore \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - b}$$

$$\therefore \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = \frac{RT}{V_m - b} - P = \frac{a}{V_m^2}$$

$$\cong a \cdot \left(\frac{P}{RT} \right)^2 = 1.37 \times \left(\frac{1.0}{8.314 \times 10^{-2} \times 320} \right)^2 = 1.94 \times 10^{-3} \text{ bar}$$

$$(d) \text{ For liquid water, } \left(\frac{\partial U}{\partial V} \right)_T = 1421 \text{ bar}$$

$$\text{For N}_2 \text{ gas, } \left(\frac{\partial U}{\partial V} \right)_T = 1.94 \times 10^{-3} \text{ bar}$$

由於液態水中分子與分子間的引力遠大於氣態 N₂，故前者的 internal pressure 大於後者高達 6 個數量級之多。

$$5. (a) \left. \begin{aligned} \delta W_{rev} &= -P dV \\ \delta W_{irr} &= -P_{ex} dV \end{aligned} \right\} \delta W_{irr} - \delta W_{rev} = (P - P_{ex}) dV$$

① If expansion, $P > P_{ex}$ and $dV > 0$

$$\text{故 } (P - P_{ex})dV > 0$$

② If compression, $P < P_{ex}$ and $dV < 0$

$$\text{故 } (P - P_{ex})dV > 0$$

In any case, $(P - P_{ex})dV > 0$

$$\text{故 } \delta W_{irr} - \delta W_{rev} > 0$$

$$\text{亦即 } \delta W_{rev} < \delta W_{irr}$$

$$(b) \quad dU = \delta q_{rev} + \delta W_{rev} = \delta q_{irr} + \delta W_{irr}$$

$$\therefore \delta q_{rev} - \delta q_{irr} = \delta W_{irr} - \delta W_{rev} > 0$$

$$\therefore \delta q_{rev} > \delta q_{irr}$$

$$(c) \quad \delta q_{rev} = T dS = T_{surr} dS$$

$$\left. \begin{array}{l} \text{故 } T_{surr} dS > \delta q_{irr} \\ \text{and } T_{surr} dS = \delta q_{rev} \end{array} \right\} T_{surr} dS \geq \delta q$$

$$\Rightarrow dS \geq \frac{\delta q}{T_{surr}}$$

$$(d) \quad dS > \frac{\delta q_{irr}}{T_{surr}} = 0 \quad (\delta q_{irr} = 0 \text{ for isolated system}) \Rightarrow dS(\text{isolated system}) > 0$$

$$(e) \quad dS_{surr} = \frac{\delta q_{surr}}{T_{surr}} = \frac{-\delta q}{T_{surr}}$$

$$dS_{tot} = dS + dS_{surr} \geq \frac{\delta q}{T_{surr}} + \frac{-\delta q}{T_{surr}} = 0 \Rightarrow dS_{tot} \geq 0$$

$$(f) \quad dU = \delta q + \delta w = \delta q - P_{ex} dV$$

$$dU + P_{ex} dV = \delta q \leq T_{surr} dS$$

$$\text{at constant } P \text{ and } T, P_{ex} = P, T_{surr} = T$$

$$\Rightarrow dU + P dV - T dS \leq 0$$

$$\Rightarrow d(U + PV - TS)_{T,P} \leq 0$$

$$\Rightarrow (dG)_{T,P} \leq 0$$

$$(g) \quad A = U - TS$$

$$dA = dU - TdS - SdT$$

$$= \cancel{TdS} - PdV + dW_{non-PV} - \cancel{TdS} - SdT = -SdT - PdV + dW_{non-PV}$$

$$\text{at constant } T, dA = -P dV + dW_{non-PV} = dW_{PV} + dW_{non-PV}$$

$$-(\Delta A)_T = -W_{PV} - W_{non-PV}$$

故定溫下之 $-\Delta A$ 即為系統對外所能做的最大功(包括 PV 及 non-PV 功)

另解

$$T_{surr} dS - dU \geq -dw = -dw_{PV} - dw_{non-PV}$$

at constant T , $T_{surr} = T$ and $TdS = d(TS)$

$$-d(U-TS)_T \geq -dw_{PV} - dw_{non-PV}$$

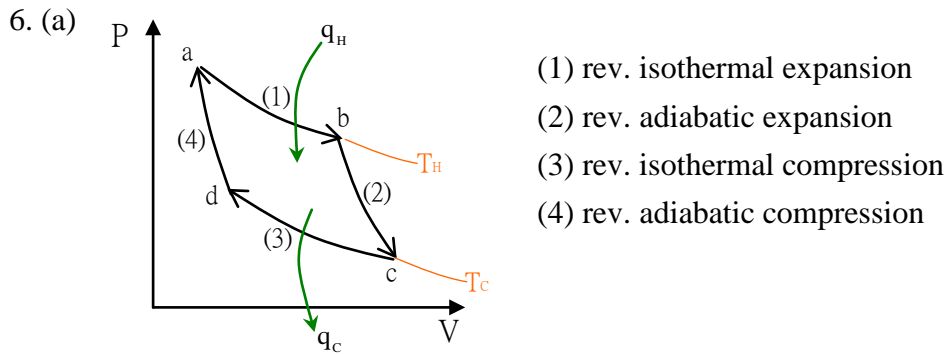
$$-(dA)_T \geq -dw \text{ or } -(\Delta A)_T = -w_{max}$$

(h)

PVT	PVT
n	n
A	B

 $\Delta S = \Delta S_A + \Delta S_B = nR \ln \frac{2V}{V} + nR \ln \frac{2V}{V} = 2nR \ln 2$

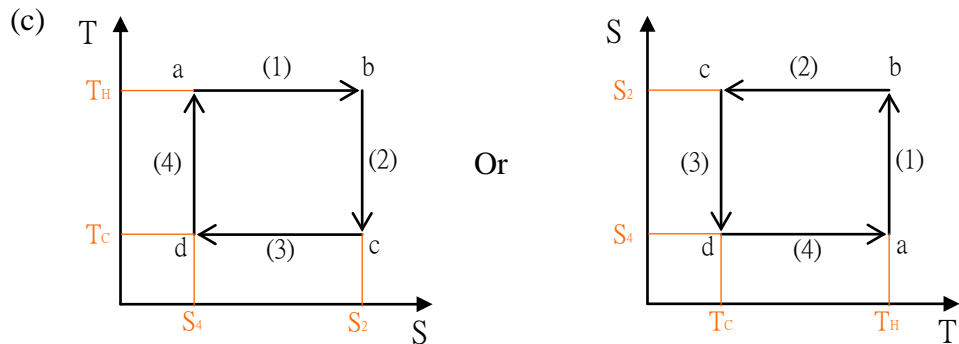
$$w'_{max} = \Delta G_{T,P} = \Delta H - T\Delta S = 0 - T \times 2nR \ln 2 = -2nRT \ln 2$$



(b) $Area = w = w_1 + w_2 + w_3 + w_4$

$$= -nRT_H \ln \frac{V_b}{V_a} - nRT_C \ln \frac{V_d}{V_c}$$

⇒ 系統對外所做的功



(d) $Area = (T_H - T_C) \cdot (S_2 - S_4) = T_H \Delta S - T_C \Delta S = q_H + q_C \Rightarrow$ 系統所吸收的熱

(e) $-w = q_H + q_C \Rightarrow q_H = -w - q_C$

(f) Because S is a state function,

$$0 = \oint dS = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = \frac{q_H}{T_H} + 0 + \frac{q_C}{T_C} + 0$$

$$\Rightarrow \frac{q_H}{T_H} + \frac{q_C}{T_C} = 0 \quad \text{or} \quad \frac{q_H}{-q_C} = \frac{T_H}{T_C}$$

$$(g) \quad \varepsilon = \frac{-w}{q_H} = \frac{q_H + q_C}{q_H} = 1 + \frac{q_C}{q_H} = 1 - \frac{T_C}{T_H}$$

$$(h) \quad \eta_{hp} = \frac{-q_H}{w} = \frac{-q_H}{-q_H - q_C} = \frac{q_H}{q_H + q_C} = \frac{T_H}{T_H - T_C} = \frac{T_H}{\Delta T}$$

$$\eta_r = \frac{q_C}{w} = \frac{q_C}{-q_H - q_C} = \frac{-q_C}{q_H + q_C} = \frac{T_C}{T_H - T_C} = \frac{T_C}{\Delta T}$$

$$7. (a) \quad G = U + PV - TS = H - TS = A + PV$$

$$\Delta G^\circ = \Delta A^\circ + \Delta(PV) = \Delta A^\circ + \Delta nRT$$

$$w_{max} = \Delta A^\circ = \Delta G^\circ - \Delta nRT = -5296 - \frac{\left(8 - \frac{25}{2}\right) \times 8.314 \times 298.15}{1000} = -5285 \text{ kJmol}^{-1}$$

$$(b) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$q_{rev} = T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ = -5471 - (-5296) = -175 \text{ kJmol}^{-1}$$

$$(c) \quad \Delta U^\circ = \Delta A^\circ - T\Delta S^\circ = -5285 - 175 = -5460 \text{ kJmol}^{-1}$$

$$(d) \quad \varepsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{300}{600} = 0.5$$

$$w_{he} = -q_H \times \varepsilon = \Delta H^\circ \times \varepsilon = -5471 \times 0.5 = -2735.5 \text{ kJmol}^{-1}$$

$$\frac{w_{he}}{w_{fc}} = \frac{-2735.5}{-5296} = 52\%$$

$$\text{We can define: } \varepsilon_{fc} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}$$

系統無法利用的熱
反應熱

$$8. (a)$$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

$$n_i = n_i^\circ + v_i \xi$$

$$dn_i = v_i d\xi$$

$$\sum_i \mu_i dn_i = \sum_i \mu_i v_i d\xi = \Delta G_r d\xi$$

$$dG = -SdT + VdP + \Delta G_r d\xi$$

$$\Rightarrow \Delta G_r = \left(\frac{\partial G}{\partial \xi} \right)_{T,P}$$

(b)

$$\text{Spontaneous: } \Delta G_r = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} < 0$$

$$\text{Equilibrium: } \Delta G_r = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$$

(c)

$$\begin{aligned} \Delta G_r &= \sum_i \nu_i \mu_i = c\mu_C + d\mu_D + \dots - a\mu_A - b\mu_B - \dots \\ &= c \left(\mu_C^\circ + RT \ln \frac{P_C}{P^\circ} \right) + d \left(\mu_D^\circ + RT \ln \frac{P_D}{P^\circ} \right) + \dots \\ &\quad - a \left(\mu_A^\circ + RT \ln \frac{P_A}{P^\circ} \right) - b \left(\mu_B^\circ + RT \ln \frac{P_B}{P^\circ} \right) \\ &= \left(c\mu_C^\circ + d\mu_D^\circ + \dots - a\mu_A^\circ - b\mu_B^\circ - \dots \right) + RT \ln \frac{\left(\frac{P_C}{P^\circ} \right)^c \left(\frac{P_D}{P^\circ} \right)^d \dots}{\left(\frac{P_A}{P^\circ} \right)^a \left(\frac{P_B}{P^\circ} \right)^b \dots} \\ &= \sum_i \nu_i \mu_i^\circ + RT \ln Q_p \\ &= \Delta G_r^\circ + RT \ln Q_p \\ &\text{at equilibrium, } \Delta G_r = 0 \text{ and } Q_p = K_p \\ &\Rightarrow RT \ln K_p = -\Delta G_r^\circ = -\Delta H_r^\circ + T \Delta S_r^\circ \\ &\Rightarrow K_p = \exp \left(-\frac{\Delta H_r^\circ}{RT} + \frac{\Delta S_r^\circ}{R} \right) \end{aligned}$$

(d)

$$\begin{aligned} \text{Gibbs-Helmholtz equation: } \left[\frac{\partial (G/T)}{\partial T} \right]_p &= -\frac{H}{T^2} \\ \Rightarrow \left[\frac{\partial (\Delta G_r^\circ / T)}{\partial T} \right]_p &= -\frac{\Delta H_r^\circ}{T^2} \\ \Rightarrow \left[\frac{\partial \ln K_p}{\partial T} \right]_p &= \frac{\Delta H_r^\circ}{RT^2} \Rightarrow \text{no assumption} \\ \int_{T_1}^{T_2} d \ln K_p &= \int_{T_1}^{T_2} \frac{\Delta H_r^\circ}{RT^2} dT \cong \frac{\Delta H_r^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \\ \ln \frac{K_p(T_2)}{K_p(T_1)} &= \frac{\Delta H_r^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \Rightarrow \Delta H_r^\circ &\text{ is independent of } T \end{aligned}$$

(e)

$$\begin{aligned}
K_p &= \frac{\left(\frac{P_C}{P^\circ}\right)^c \left(\frac{P_D}{P^\circ}\right)^d \cdots \left(\frac{x_C P}{P^\circ}\right)^c \left(\frac{x_D P}{P^\circ}\right)^d \cdots}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b \cdots \left(\frac{x_A P}{P^\circ}\right)^a \left(\frac{x_B P}{P^\circ}\right)^b \cdots} = \left(\frac{x_C^c x_D^d \cdots}{x_A^a x_B^b \cdots}\right) \left(\frac{P}{P^\circ}\right)^{c+d+\cdots-a-b-\cdots} \\
&= K_x \left(\frac{P}{P^\circ}\right)^{\Delta v}
\end{aligned}$$