Chapter 5   The Second Law of Thermodynamics

§5-1.The Carnot Cycle and Efficiency

1. Carnot engine is one of the heat engines.

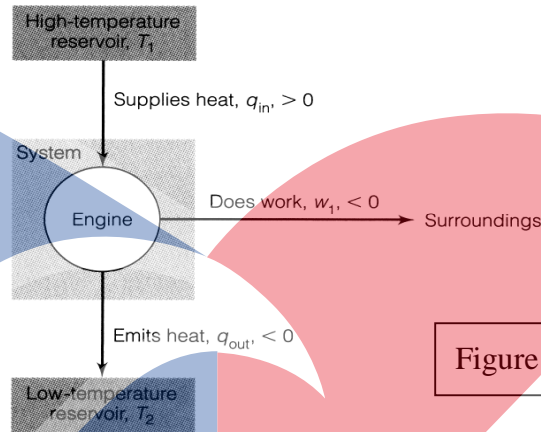 ●heat engine: An engine which can convert heat to work.

Figure 5-1

2. Figure 5.1 shows a modern diagram of how Carnot defined an engine.

  (1)The engine gets heat, q_{in} (or q_h), from some high-temperature reservoir (called heat source or heat reservoir).

  (2)The engine performed some work, W, on the surroundings.

  (3)The engine then disposed of the leftover heat (q_{out} or q_c) in a reservoir (called heat tank) that has some lower temperature.

3. The steps of Carnot cycle:

  (1)A→B: Reversible isothermal expansion:

    ●從 high-temperature 的 heat source 吸收 q_h 的熱量，在 T_{high} 下，進行 isothermal, rev., expansion. → $P_A V_A = P_B V_B$

    ●The amount of work performed by the system was W_1.

 (2) B→C: Reversible adiabatic expansion:

    ●進行 reversible adiabatic expansion 對 surroundings 做 work W_2

      ↦ $P_B V_B^\gamma = P_C V_C^\gamma$

    ●溫度由 T_{high} 降至 T_{low}。

  (3)C→D: Reversible isothermal compression:

    ●release q_c 的 heat 到 low-temperature 的 heat tank。在 T_{low} 下，進行 reversible isothermal compression → $P_C V_C = P_D V_D$

    ●The amount of work in this step will be called W_3.

(4)D→A: Reversible adiabatic compression:
- ●藉由絕熱壓縮使溫度由 T_{low} 昇溫至 T_{high}。➔ $P_D V_D^{\gamma} = P_A V_A^{\gamma}$
- ●Work is done on the system. This amount of work is termed W_4.
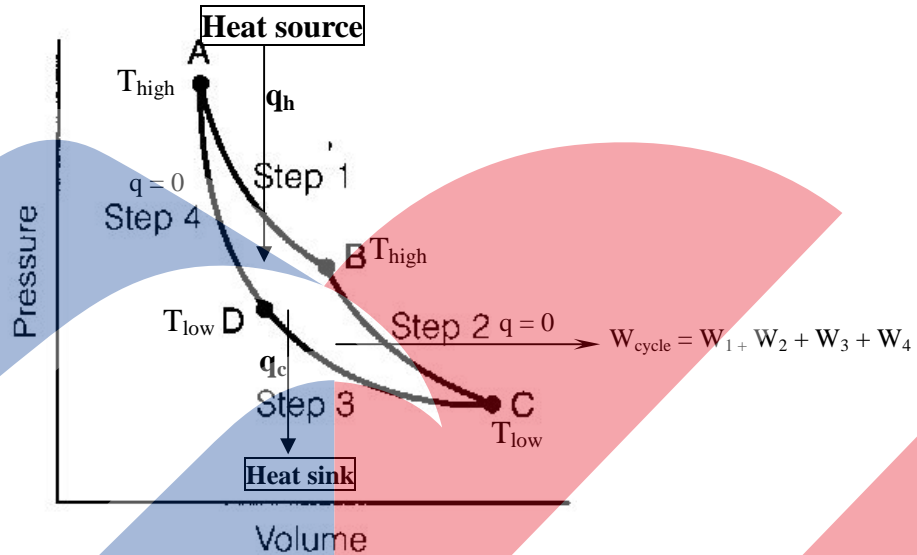
4.Cyclic process:

(1)Since the system has returned to the original conditions, by definition of a state fnnction, $\Delta U = 0$, for the overall process.

$$\therefore \quad \Delta U = 0 = q_h + W_1 + W_2 + q_c + W_3 + W_4$$

(2)The entire work performed by the cycle:

$$W_{cycle} = W_1 + W_2 + W_3 + W_4$$

The entire heat flow of the cycle:

$$q_{cycle} = q_h + q_c$$

$$\therefore \quad \Delta U = 0 = q_{cycle} + W_{cycle} \text{ or } q_{cycle} = -W_{cycle}$$

(3)Define: efficiency (η) of a heat engine as the negative ratio of the work of the cycle to the heat that comes from the high-temperature reservoir.

η= (work performed)/(heat absorbed)

$$= \frac{-W_{cycle}}{q_h} = \frac{q_{cycle}}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

(4)Define efficiency in terms of the temperatures of high- and low-temperature reservoirs.

❶Steps A→B and C→D are Reversible isothermal process:

$\therefore \Delta U_{A \to B} = 0$ and $\Delta U_{C \to D} = 0$

$\therefore \Delta U_{A \to B} = 0 = q_h + W_1 \rightarrow q_h = -W_1 = -(-nRT_{high}\ln(\frac{V_B}{V_A})) = nRT_{high}\ln(\frac{V_B}{V_A})$

$\Delta U_{C \to D} = 0 = q_c + W_3 \rightarrow q_c = -W_3 = -(-nRT_{low}\ln(\frac{V_D}{V_C})) = nRT_{low}\ln(\frac{V_D}{V_C})$

❷Steps B→C and D→C are Reversible adiabatic process:

$$\bullet\ \frac{T_2}{T_1} = (\frac{V_2}{V_1})^{(1-\gamma)}$$

$\therefore$ Step B→C $\rightarrow$ $\dfrac{T_{high}}{T_{low}} = (\dfrac{V_B}{V_C})^{(1-\gamma)}$

Step C→A $\rightarrow$ $\dfrac{T_{high}}{T_{low}} = (\dfrac{V_A}{V_D})^{(1-\gamma)}$

$$\bullet\ \frac{V_B}{V_C} = \frac{V_A}{V_D} \ \text{ or } \ \frac{V_D}{V_C} = \frac{V_A}{V_B}$$

❸$\therefore q_h = nRT_{high}\ln(\frac{V_B}{V_A}) = -nRT_{high}\ln(\frac{V_A}{V_B})$

$q_c = nRT_{low}\ln(\frac{V_D}{V_C}) = nRT_{low}\ln(\frac{V_A}{V_B})$

$\therefore\ \dfrac{q_c}{q_h} = -\dfrac{T_{low}}{T_{high}}$

$$\therefore \eta = \frac{-W_{cycle}}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h} = 1 - \frac{T_{low}}{T_{high}} \quad \text{重要！}$$

since $1 + \dfrac{q_c}{q_h} = 1 - \dfrac{T_{low}}{T_{high}}$

$\rightarrow \dfrac{q_c}{q_h} + \dfrac{T_{low}}{T_{high}} = 0 \rightarrow \dfrac{q_c}{T_{low}} + \dfrac{q_h}{T_{high}} = 0$

(5)The thermal efficiency of a Carnot engine can approach unity only when T_h approaches infinity or Tc (T_{low}) approaches zero. Neither of these conditions is attainable.

●The cold reservoirs

  ↳① atmosphere, lakes and rivers, and the oceans.

   ② Tc $\fallingdotseq$ 300 K.

●The hot reservoirs

  ↳① combustion of fossil fuels and fission of radioactive elements in
    nuclear reactors.

5-3

② $T_h \doteqdot 600$ K.

$$\therefore \eta \equiv 1 - \frac{T_C}{T_h} = 1 - (300/600) = 0.5$$

- A rough practical limit for a Carnot engine.
- Actual heat engines are irreversible, and their thermal efficiencies rarely exceed 0.35.

- heat source(或 step A→B) 的 T_{high} 越高，則 η 越高；當然，T_{low} 越低則排放出去的廢熱越少，η 越高。但無論如何，η < 1
- $T_{low} = 0$ (or $q_c = 0$) ➔ $e = 1$。但此為不可能的。

※The second law of thermodynamics in terms of heat engine:
  ↳ It is impossible to construct an engine, operating in cycles, that isothermally converts heat to work.

Example 5-1:

A central power plant, rated at 800,000 kW, generates steam at 585 K and discards heat to a river at 295 K. If the thermal efficiency of the plant is 70% of the maximum possible value, how much heat is discarded to the river at rated power?

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Example 5-2:

A reversible Carnot cycle engine operates between 500℃ and 60℃ and releases 2500 cal to the heat tank. Find the net work produced per cycle?

※※※若 heat source 和 heat sink 的大小有限，則 T_h 和 T_{low} (T_c)不是定值，此時，

$\dfrac{q_c}{T_{low}} + \dfrac{q_h}{T_{high}} = 0$ 不成立，但改為 $\dfrac{dq_C}{T_C} + \dfrac{dq_h}{T_h} = 0$ 則是成立的。

Example 5-3:

一 heat engine 自 10 kg、90℃ 水的 heat source 吸進熱量至水溫降為 60℃，經做功後，向含有 5 kg 水的 heat sink 放出熱量，已知 heat sink 的水初溫為 5℃，請計算所做的功。

T_{c2} = 331 K

q_h = 300000

q_c = 265000

※※※The thermodynamics of refrigeration (heat pump)

　1. heat pump: an outside power source supplies work that forces heat from a low-
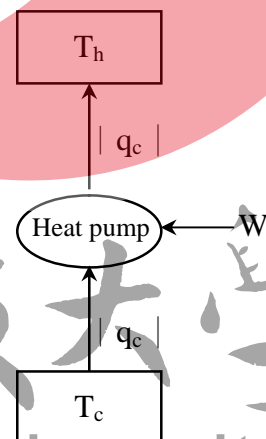　　　to high-temperature region.

　2. An energy $|q_c|$ is removed from a cool source

　　at temperature Tc and then deposited in a warmer

　　sink at a temperature T_h, then

$$\Delta S = -\dfrac{|q_c|}{T_c} + \dfrac{|q_c|}{T_h} < 0$$

　　　　∴不是 spontaneous process

　　　　S 與 spontaneous process 將在後面說明。

　●Define: coefficient of performance, C:

　C = (heat transferred)/(worked done)

$$= \dfrac{|q_c|}{|W|} = \dfrac{T_c}{T_h - T_c} \qquad\qquad \therefore\ T_h - T_c \downarrow \rightarrow C \uparrow$$

Example 5-4:

一屋子內有空氣 10 kg，假設其 $\hat{C}_p$ 為 7 cal/mol·K，而室外的溫度為 35℃，今欲利用冷氣機將室內的溫度降到 28 及 27℃，則各需提供多少 work 給冷氣機？

§5-2. Entropy

1. For a Carnot engine:

$$\because \frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \quad \rightarrow \quad 微量時：\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0$$

∴一個完整的 Carnot cycle，其工作流體因吸熱或放熱所得的 Q/T 之總和為零。

可以表示為：$\oint \frac{dQ_{rev}}{T} = 0$

2. Define entropy S:

$$dS = \frac{dQ_{rev}}{T} \quad \text{or} \quad dQ_{rev} = TdS \quad \text{or} \quad \Delta S = \int \frac{dQ_{rev}}{T}$$

❶entropy 是衡量一個 system 中，disorder 的程度。

❷entropy change ΔS：指系統內，任何一變化所引起的亂度改變。

❸系統的 entropy 增加 (即 ΔS > 0)，有可能是：

　①氣體擴張。

　②phase change (汽化、熔融、昇華)。

　③系統的溫度上升。

　④物質混合 (溶解、-----)。

❹ $dS = \dfrac{dQ_{irrev}}{T}$ 是錯的！ 事實上，$dS > \dfrac{dQ_{irrev}}{T}$
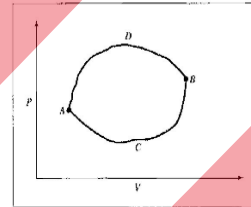
∴一般寫成 $dS \geqq \dfrac{dq}{T}$

❶For irreversible, spontaneous processes → 取 ">" → 即 $dS > \dfrac{dq_{irrev}}{T}$

❷ For reversible processes → 取 "=" → 即 $dS = \dfrac{dq_{rev}}{T}$

※※ $dS < \dfrac{dq}{T}$ 是不存在的

(2)如右圖所示：(參閱課本 5-5)

❶Points A and B represent two equilibrium states of a particular fluid.

❷Paths ACB and ADB show two arbitrary reversible processes connecting A and B:

∵ $\Delta S = \displaystyle\int_{ACB} \dfrac{dQ_{rev}}{T}$ and $\Delta S = \displaystyle\int_{ADB} \dfrac{dQ_{rev}}{T}$

∴①ΔS is independent of path and is a property change given by $S_B - S_A$.

②If a process is reversible and adiabatic, $dQ_{rev} = 0$;

↳ $dS = \dfrac{dQ_{rev}}{T} = 0$ ---------------- isentropic process

③若 A → B 是 irreversible process，則求 $\Delta S_{A \to B}$ 時，需選定一樣是 A 到 B 的可逆程序(可能是 A → C → B)，再利用 $dS = \dfrac{dQ_{rev}}{T}$ ($\Delta S = \displaystyle\int \dfrac{dQ_{rev}}{T}$) 求得 $\Delta S_{A \to B}$。不可直接用不可逆程序的數據代入 $dS = \dfrac{dQ_{rev}}{T}$ 來求 $\Delta S_{A \to B}$。
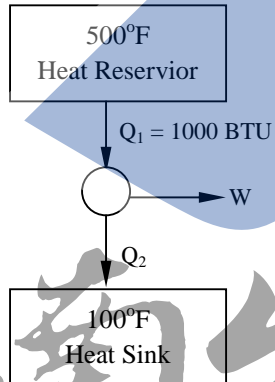
Example 5-5:

A Carnot cycle heat engine receives 500 kJ from a reservoir at 500℃, and rejects heat at 25℃.

(A)Show the cycle on a T-S diagram, considering the working fluid as the system.

(B)Calculate the work and efficiency of the cycle.

(C)Calculate the change in entropy of the high-temperature and low-temperature reservoirs.

Example 5-6:

```
┌──────────────┐
│   500ºF      │
│ Heat Reservoir│
└──────────────┘
       │ Q₁ = 1000 BTU
       ▼
      ( ) ────► W
       │ Q₂
       ▼
┌──────────────┐
│   100ºF      │
│  Heat Sink   │
└──────────────┘
```

Find: (A)W   (B)reservoir ΔS_1 (C)sink ΔS_2 (D)ΔS_{total}

§5-3. The Second Law of Thermodynamics

1. The Second Law of Thermodynamics 無理論的依據，是歸納許多事實經驗而成，故早已被公認其正確性。迄今為止，仍未見到違反此定律的任何現象發生。

2. 除了前面已介紹的熱力學第二定律的敘述外，尚有以下幾種常見或少見(但也

被認爲是)的敘述：

❶宇宙的 entropy 傾向於增加。

❷A spontaneous process is an irreversible process.

❸由磨擦而產生的熱是不可逆的。

❹理想氣體的 free expansion 是不可逆的。

❺dS $\geq \dfrac{dq}{T}$　　irrev.➔ ">" ; rev.➔ "="

§5-4. Entropy change of ideal gases in closed systems

1. Phase change at constant T, P:

$$\Delta S = \int \frac{dq_{rev}}{T_{trs}} = \frac{1}{T_{trs}} \int dq_{rev.} = \frac{q_{rev}}{T_{trs}} = \frac{n \times \Delta \hat{H}_{trs}}{T_{trs}}$$

2. Isothermal and reversible expansion (or compression) of an ideal gas:

$$\Delta S = \int \frac{dq}{T} = \int \frac{PdV}{T} = \int \frac{\left(\frac{nRT}{V}\right)dV}{T} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

3.(1) isometric 下，由 $T_1 \to T_2$ (reversible process)

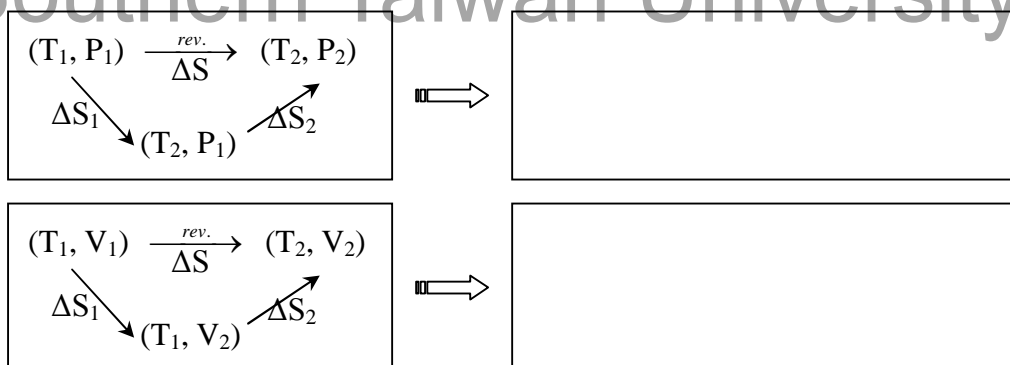$$\Delta S = \int \frac{dq}{T} = \int_{T_1}^{T2} \frac{n\hat{C}_v}{T} dT = n \hat{C}_v \int_{T_1}^{T2} \frac{1}{T} dT = n \hat{C}_v \ln \frac{T_2}{T_1} \text{ (} \hat{C}_v \text{ is constant)}$$

(2) isobaric processs, $T_1 \to T_2$(reversible process)

$$\Delta S = \int \frac{dq}{T} = \int_{T_1}^{T2} \frac{n\hat{C}_p}{T} dT = n \hat{C}_p \int_{T_1}^{T2} \frac{1}{T} dT = n \hat{C}_p \ln \frac{T_2}{T_1} \text{ (} \hat{C}_p \text{ is constant)}$$

4.$(T_1, P_1) \xrightarrow{rev.} (T_2, P_2)$　　or　$(T_1, V_1) \xrightarrow{rev.} (T_2, V_2)$

把原來的 process 拆開時，需保持一次只變化一個變數。

$(T_1, P_1) \xrightarrow[\Delta S]{rev.} (T_2, P_2)$

$\Delta S_1 \searrow (T_2, P_1) \nearrow \Delta S_2$

⟹

$(T_1, V_1) \xrightarrow[\Delta S]{rev.} (T_2, V_2)$

$\Delta S_1 \searrow (T_1, V_2) \nearrow \Delta S_2$

⟹

5. isothermal 下，ideal gas 的 mixing:

$$\Delta S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

※※基本例題：

Example 5-7:

Calculate ΔS_{vap} for 3 moles of benzene are evaporated under 1 atm, 80℃.

Given: At 1 atm, 80℃, the $\Delta \hat{H}_{vap}$ of benzene is 395 J/g.

Example 5-8:

At 1 atm pressure, the molar heat capacity of solid A is given by the formula (in units of $JK^{-1}mol^{-1}$)

$$\hat{C}_p = 21 + 4.0 \times 10^{-3} \, T$$

Find the entropy change if 3 moles of solid A are heated from 27℃ to 157℃?

Example 5-9:

An ideal gas is initially at 1 atm, 500 ml, 27℃. Then it expands reversibly to 1000 ml and 120℃. Calculate ΔS for the process if $\hat{C}_V = 12.5$ J/(mole K)
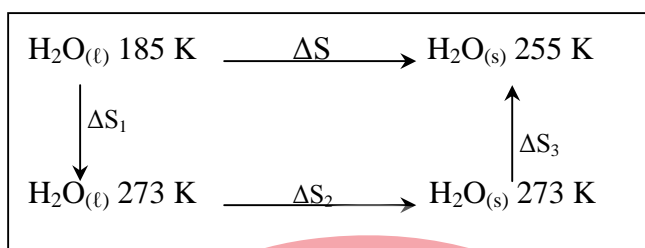
Example 5-10:

Find ΔS for the mixing 6 g of He, 4 g of H_2 and 14 g of N_2 at 27℃ & 1 bar?

Example 5-11:

求 1 mol、185 K、1 atm 的水變成 1 atm、255 K 的冰之 ΔS。　　　4.9　J/K

H_2O 的 $\hat{C}_{p(\ell)}$ = 75 Jmole^{-1} K^{-1}；$\hat{C}_{p(s)}$ = 34 Jmole^{-1} K^{-1}；$\Delta\hat{H}_{fus}$ = 6.01kJ/mol。

$$\begin{array}{ccc}
H_2O_{(\ell)}\ 185\ K & \xrightarrow{\quad\Delta S\quad} & H_2O_{(s)}\ 255\ K \\
\Big\downarrow \Delta S_1 & & \Big\uparrow \Delta S_3 \\
H_2O_{(\ell)}\ 273\ K & \xrightarrow{\quad\Delta S_2\quad} & H_2O_{(s)}\ 273\ K
\end{array}$$

Example 5-12:

一莫耳理想氣體自 10 atm，27℃ 的初狀態絕熱可逆膨脹至 1 atm。求該氣體在此過程產生之功和熵(entropy)之改變。　$\hat{C}_p$ = 7 cal/(mol·K)；$\hat{C}_v$ = 5 cal/(mol·K)

Example 5-13:

敘述導致一系統"entropy"增加的各種因素。

Example 5-14:

When 3 mole of liquid water at 25℃ is cooled to ice at -10℃, calculate the changes in enthalpy and entropy of the system, and those of the surroundings, respectively by taking the heat capacities as constant to be 18 calK^{-1}mol^{-1} for water and 9 calK^{-1}mol^{-1} for ice.
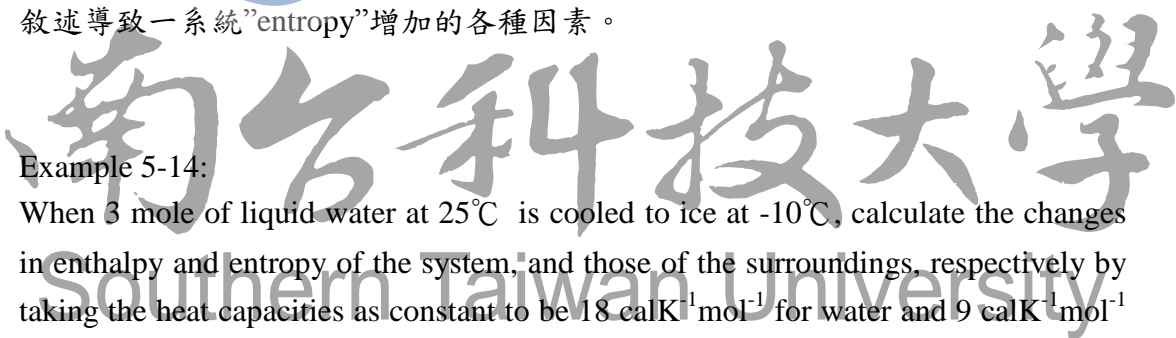
§5-5. Lost Work

1. Let heat q be transferred from a hotter system (T_h) to a cooler surrounding (T_C).

↳ ●The entropy change of the system at T_h: $\Delta S_h = \dfrac{-q}{T_h}$

●The entropy change of the reservoir at T_C: $\Delta S_C = \dfrac{q}{T_C}$

$\therefore \ \Delta S_{total} = \Delta S_h + \Delta S_C = \dfrac{-q}{T_h} + \dfrac{q}{T_C} = \dfrac{q(T_h - T_C)}{T_h T_C} > 0$

◆For an irreversible process ➔ $\Delta S_{total} > 0$

◆When T_h is only infinitesimally higher than T_C, the heat transfer is reversible, and ΔS_{total} approaching zero.

2.若此程序在 heat engine 內以 ”可逆” 的方式進行，在溫度 T_h 時吸熱 q_h，部分作 work 後，其餘熱量以 T_C 的方式排出。則所做的 work 為

$$\eta = \dfrac{-W_{cycle}}{q_h} = \dfrac{q_h + q_c}{q_h} = 1 + \dfrac{q_c}{q_h} = 1 - \dfrac{T_C}{T_h}$$

$$-W = q(1 - \dfrac{T_C}{T_h}) = q\dfrac{T_h - T_C}{T_h} = T_C\dfrac{q(T_h - T_C)}{T_h T_C} = T_C \Delta S_{total}$$

3.然而，實際的操作程序是不可逆的方式，所以，上式所表示的 work 完全損耗於不可逆程序上，成為損失掉而無法獲得的 work，稱為 lost work。

◆Lost work (W_{lost})：

(1)在不可逆程序中所耗費的 work。

(2) the difference between the actual work of a process and the ideal work for the process.

$W_{lost} \equiv W_s - W_{ideal}$

(3) $\therefore$ Lost work (W_{lost}) = $T_o\Delta S_{total}$ T_o:一般外界的溫度

Example 5-15:

A steel casting ($C_p = 0.12$ kcal/kgK) weighing 30 kg and at a temperature of 450℃ is quenched in 120 kg of oil ($C_p = 0.6$ kcal/kgK) at 20℃. There are no heat losses, find (A)the entropy change of the casting   (B)the entropy change of the oil (C)the entropy generated during the process and (D)the lost work?

Example 5-16:

A 50-kg block of iron casting at 500K is thrown into a large lake that is at a temperature of 285 K. The iron block eventually reaches thermal equilibrium with the lake water. Assuming an average specific heat of 0.45 kJ/(kgK) for the iron, determine (A)the entropy change of the iron block, (B)the entropy change of the lake water, and (C)the entropy generated during the process.
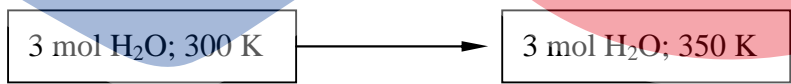
§5-6. Entropy Balance for open systems

1.由 fluid 進、出一個 system ➜ 亦可以寫出 entropy balance。
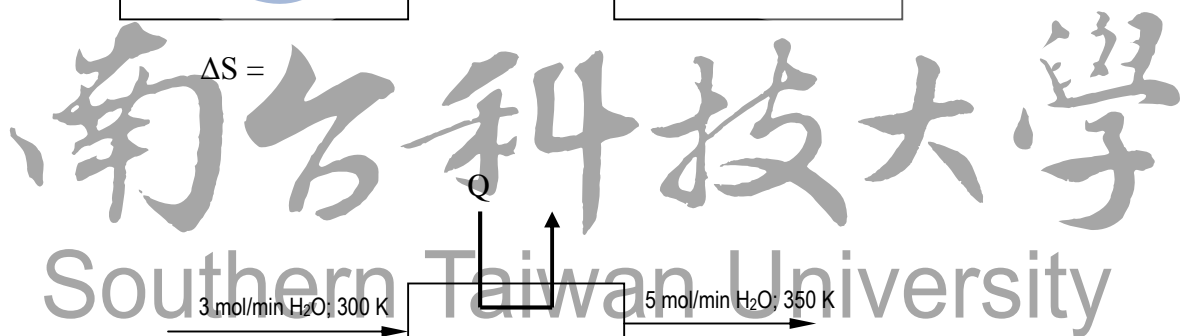
↳ However, entropy is not conserved.

❋2nd law:

☞The total entropy change associated with any process must be positive, with a limiting value of zero for a reversible process.

2.

| 3 mol H₂O; 300 K | ➜ | 3 mol H₂O; 350 K |

$\Delta S =$

Q

3 mol/min H₂O; 300 K ⟶ □ ⟶ 5 mol/min H₂O; 350 K

F mol/min H₂O; 290 K

$\Delta S =$

3. Writing the entropy balance:

  (1)Consider both the system and its surroundings.

  (2)Consider the entropy-generation term for the irreversibilities of the process.

    Including:

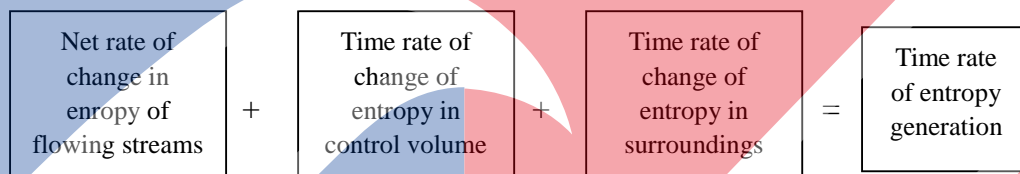   ❶The entropy changes in the streams flowing in and out of the control volume.

      ❷The entropy changes within the control volume.

      ❸The entropy changes in the surroundings.

         ❋Reversible process ➔ these three terms sum to zero ➔ $\Delta S_{total} = 0$.

         ❋Irreversible process ➔ ΔS_{total} = positive quantity.

         ∴The equation of entropy balance:

Net rate of change in enropy of flowing streams	+	Time rate of change of entropy in control volume	+	Time rate of change of entropy in surroundings	=	Time rate of entropy generation

or $\Delta(\hat{S}\dot{m})_{fs} + \dfrac{d(m\hat{S})_{cv}}{dt} + \dfrac{dS^t_{surr}}{dt} = \dot{S}_G \;\geqq\; 0$

                                         ┌──────────────────────────────┐
                      ●也許 surroundings 有很多個，下標 j 只是表示第 j 個 surroundings

  (3)若 surroundings 的溫度為 $T_{\sigma,j}$

    其 heat transfer rate = Q_j

    則 $\dfrac{dS^t_{surr}}{dt} = -\sum\limits_j \dfrac{\dot{Q}_j}{T_{\sigma,j}}$ ∴$\Delta(S\dot{m})_{fs} + \dfrac{d(m\hat{S})_{cv}}{dt} - \sum\limits_j \dfrac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \;\geqq\; 0$

    ❋❋$\dot{S}_G$ ➔ The rate of entropy generation,

      ①For irreversible processes ➔ positive

        ↳There are two sources of irreversibility:

          ◆Within the control volume ➔ internal irreversibilities

          ◆Resulting from heat transfer across finite temperature differences between system and surroundings ➔ external thermal irreversibilities.
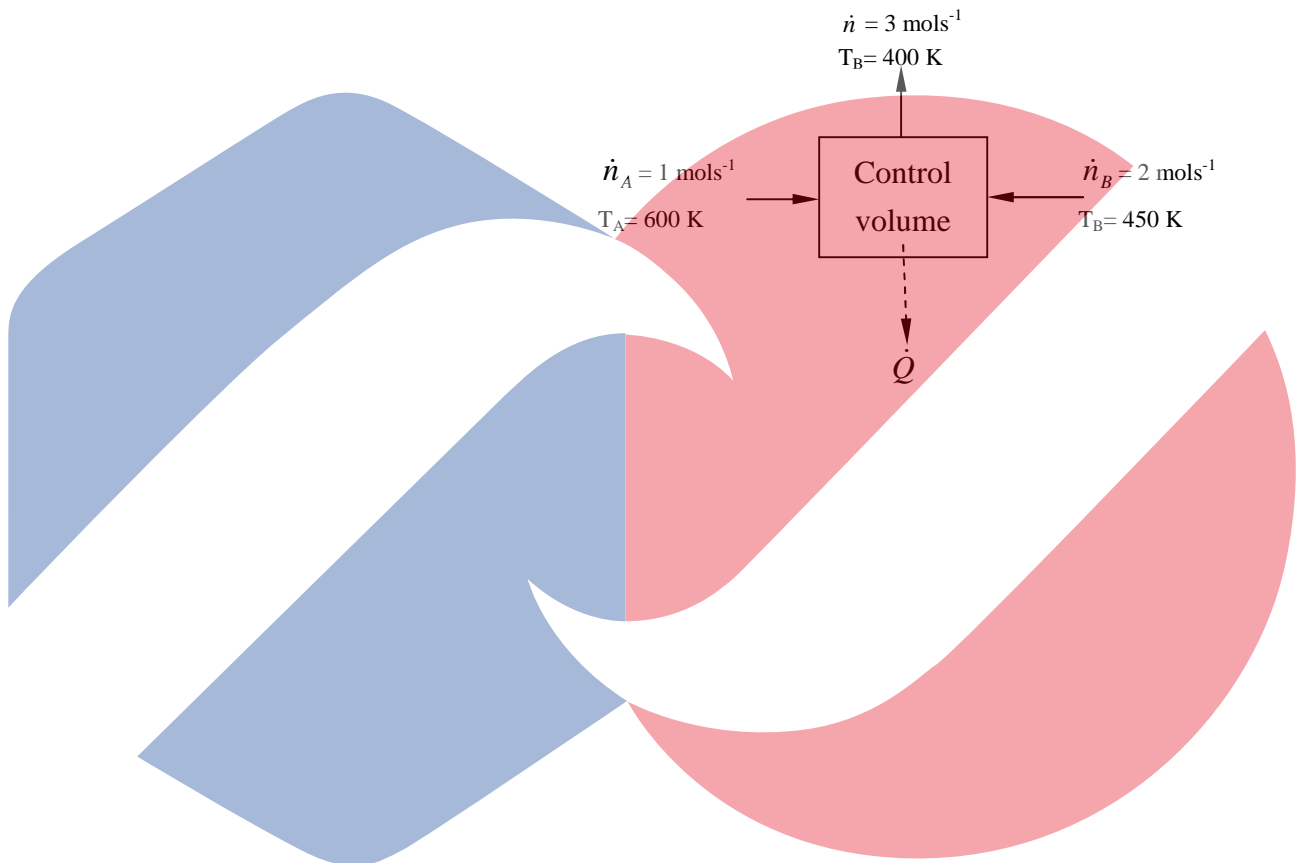
      ②For reversible processes ➔ 0

        ↳◆The process is internally reversible within the control volume.

          ◆Heat transfer between the control volume and its surroundings is reversible.

Example 5-17 :

In a steady-state flow process, 1 mols⁻¹ of air at 600 K and 1 atm is continuously mixed with 2 mols⁻¹ of air at 450 K and 1 atm. The product stream is at 400 K and 1 atm. Determine the rate of heat transfer and the rate of entropy generation for the process. Assume that air is an ideal gas with Cp = (7/2)R, that the surroundings are at 300 K, and that kinetic- and potential-energy changes are negligible.

$\dot{n}$ = 3 mols⁻¹
T_B= 400 K

$\dot{n}_A$ = 1 mols⁻¹   Control $\dot{n}_B$ = 2 mols⁻¹
T_A= 600 K   volume T_B= 450 K

$\dot{Q}$

Example 5-18:

An inventor claims to have devised a process which takes in only saturated steam at 100℃ and which by a complicated series of steps makes heat continuously available at a temperature level of 200℃. The inventor claims further that, for every kilogram of steam taken into the process, 2,000 kJ of energy as heat is liberated at the temperature level of 200℃. Show whether or net this process is possible. In order to give the inventor the benefit of any doubt, assume cooling water available in unlimited quantity at a temperature of 0℃.
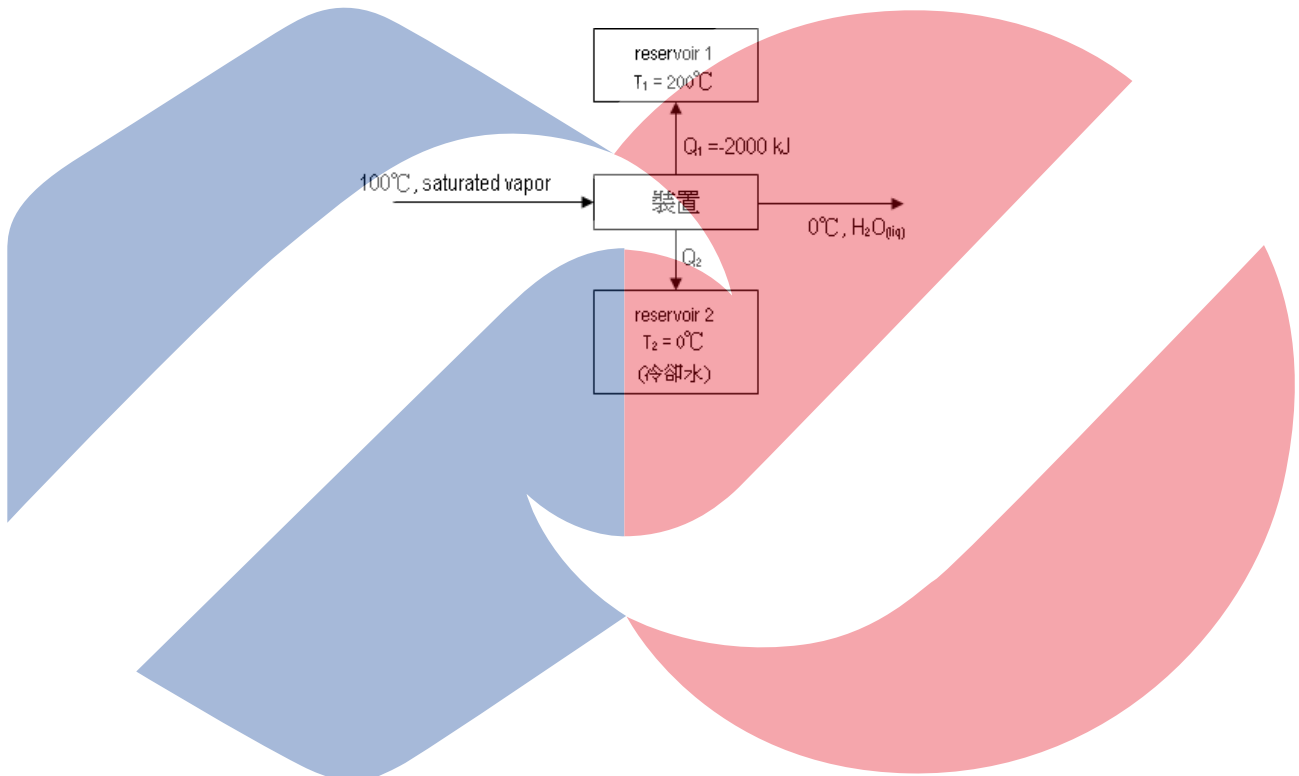
4. Lost work

(1) closed system: $W_{lost} \equiv W_s - W_{ideal}$

Open system: $\dot{W}_{lost} \equiv \dot{W}_s - \dot{W}_{ideal}$

(2) Steady state,

$$\Delta[(\hat{H} + (½)u^2 + gh)\dot{m}]_{fs} = \dot{Q} + \dot{W} \qquad \text{---- S.S.的能量平衡式}$$

∴the actual work rate: $\dot{W} = \Delta[(\hat{H} + (½)u^2 + gh)\dot{m}]_{fs} - \dot{Q}$

(3)The ideal work rate ➔ 發生在完全可逆的程序

$$\Delta(\hat{S}\dot{m})_{fs} + \frac{d(m\hat{S})_{cv}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geqq 0$$

● Steady state ➔ $\dfrac{d(m\hat{S})_{cv}}{dt} = 0$

●可逆程序 ➔ $\dot{S}_G = 0$ ●只考慮一個 Q ➔ $\sum_j \dfrac{\dot{Q}_j}{T_{\sigma,j}} = \dfrac{\dot{Q}}{T_\sigma}$

∴ $\Delta(\hat{S}\dot{m})_{fs} - \dfrac{\dot{Q}}{T_\sigma} = 0$ ➔ $\dot{Q} = T_\sigma \Delta(\hat{S}\dot{m})_{fs}$ 代入能量平衡式得

$$\Delta[(\hat{H} + (½)u^2 + gh)\dot{m}]_{fs} = T_\sigma \Delta(\hat{S}\dot{m})_{fs} + \dot{W}_{rev}$$

> 因為這裡是以可逆程序爲基準而得到的式子，此時的 work 自然是可逆程序的功($\dot{w}_{rev}$)。

另一方面，可逆程序是理想的程序，

所以，再以 $\dot{W}_{ideal}$ 來表示 $\dot{W}_{rev}$

因此，ideal work: $\dot{W}_{ideal} = \Delta[(\hat{H} + (½)u^2 + gh)\dot{m}]_{fs} - T_\sigma \Delta(\hat{S}\dot{m})_{fs}$

※若忽略 kinetic energy 與 potential energy

(大部分化學程序中，K.E.和 P.E.是可被忽略的！)

� $\dot{W}_{ideal} = \Delta(\hat{H}\dot{m})_{fs} - T_\sigma \Delta(\hat{S}\dot{m})_{fs}$

※若只有一進與一出

➢ $\dot{W}_{ideal} = \dot{m}(\Delta\hat{H} - T_\sigma \Delta\hat{S})$ ➔ $W_{deal} = \Delta\hat{H} - T_\sigma \Delta S$

(4) ideal work: $\dot{W}_{ideal} = \Delta[(\hat{H} + (½)u^2 + gh)\dot{m}]_{fs} - T_\sigma\Delta(\hat{S}\dot{m})_{fs}$

the actual work rate: $\dot{W} = \Delta[(\hat{H} + (½)u^2 + gh)\dot{m}]_{fs} - \dot{Q}$

$$\therefore \dot{W}_{lost} \equiv \dot{W}_s - \dot{W}_{ideal} = T_\sigma\Delta(\hat{S}\dot{m})_{fs} - \dot{Q}$$

◆For the case of a single surrounding temperature T_σ :

$$\therefore \quad \Delta(\hat{S}\dot{m})_{fs} + \frac{d(m\hat{S})_{cv}}{dt} - \sum_j\frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geqq 0$$

steady state ➔ $\Delta(\hat{S}\dot{m})_{fs} - \dfrac{\dot{Q}}{T_\sigma} = \dot{S}_G$

$$\therefore \quad T_\sigma\dot{S}_G = T_\sigma\Delta(\hat{S}\dot{m})_{fs} - \dot{Q} \quad \text{or} \quad T_\sigma\dot{S}_G + \dot{Q} = T_\sigma\Delta(\hat{S}\dot{m})_{fs}$$

$$\therefore \quad \dot{W}_{lost} \equiv \dot{W}_s - \dot{W}_{ideal} = T_\sigma\Delta(S\dot{m})_{fs} - \dot{Q} = T_\sigma\dot{S}_G$$

or $W_{lost} = T_\sigma S_G$

Example 5-19

The two basic types of steady-flow heat exchanger are characterized by their flow patterns: cocurrent and countercurrent. The two types are indicated in Fig. A. In cocurrent flow, heat is transferred from a hot stream, flowing from left to right, to a cold stream flowing in the same direction, as indicated by arrows. In countercurrent flow, the cold stream, again flowing from left to right, receives heat from the hot stream flowing in the opposite direction. The lines relate the temperatures of the hot and cold streams, T_H and T_c respectively, to $\dot{Q}_C$, the accumulated rate of heat addition to the cold stream as it progresses through the exchanger from the left end to an arbitrary downstream location. Consider the two cases, for each of which the following specifications apply:

$T_{H1} = 400$ K $T_{H2} = 350$ K $T_{C1} = 300$ K $\dot{n}_H = 1$ mol s^{-1}

The minimum temperature difference between the flowing streams is 10 K. Assume that both streams are ideal gases with $C_p = (^7/_2)R$. Find the lost work for both cases. Take $T_\sigma = 300$ K.
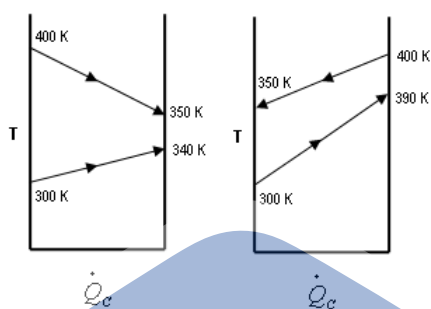
§5-7. The Third Law of Thermodynamics

1. H_2O (1 mol, 300 K, 1 atm) $\rightarrow$ H_2O (1 mol, 350 K, 1 atm)

   $\Delta S = S_2 - S_1 = n\,\hat{C}_p \ln(T_2/T_1) = 1 \times 18 \times \ln(350/300) = 2.775$ cal/K

   ●本計算可求得程序的 entropy change ΔS，但 H_2O (1 mol, 300 K, 1 atm) 與 H_2O (1 mol, 350 K, 1 atm)的 entropy(或稱之為 absolute entropy，即 S_2 與 S_1) 是多少便不得而知了。

2. The third Law of Thermodynamics:

   (1)Absolute entropy approaches zero as the absolute temperature approaches zero.

   (2)The entropy of all perfect crystalline substances is zero at T = 0 K.

   or $\lim\limits_{T \to 0} S(T) = 0$　for a perfectly crystalline material

   or $\left.\begin{array}{l} S_{(T = 0\,K)} = 0 \\ S_{(T > 0\,K)} > 0 \end{array}\right\}$　for perfect crystal

   ●在 T＝0 K 時，有的物質不遵守 S＝0 $\rightarrow$ 稱之為 imperfect crystal。 如：CO、H_2、N_2O、H_2O。

3. 由於 $S_{(T = 0\,K)} = 0$，所以，以 T＝0 K 為基礎便可以得到某一溫度時的 entropy， 此稱之為 Third-Law entropy。

   如：$S^o_{Ag}(298) = 42.55$ J/mol·K

   $S^o_{AgBr}(298) = 107.11$ J/mol·K

   $S^o_{NaCl}(298) = 95.06$ J/mol·K

Substance	$\Delta\bar{H}_f°$, kJ mol^{-1}	$\Delta\bar{G}_f°$, kJ mol^{-1}	$\bar{S}°$, J K^{-1} mol^{-1}	$\bar{C}_P°$, J K^{-1} mol^{-1}
H(g)	218.00	203.28	114.72	20.79
H$_2$(g)	0	0	130.68	28.84
D$_2$(g)	0	0	144.96	29.19
HD(g)	0.32	−1.46	143.80	29.20
Group 0				
He(g)	0	0	126.15	20.79
Ne(g)	0	0	146.33	20.79
Ar(g)	0	0	154.84	20.79
Kr(g)	0	0	164.08	20.79
Xe(g)	0	0	169.68	20.79
Rn(g)	0	0	176.23	20.79
Group I				
Li(c)	0	0	29.08	24.62
Li(g)	159.30	126.59	138.78	20.79
Na(c)	0	0	51.46	28.15
Na(g)	107.30	76.82	153.67	20.79
NaO$_2$(c)	−260.66	−218.71	115.90	72.14
Na$_2$O(c)	−417.98	−379.09	75.04	69.10
Na$_2$O$_2$(c)	−513.21	−449.63	94.80	89.27
NaOH(c)	−425.93	−379.74	64.44	59.53
NaCl(c)	−411.12	−384.00	72.10	50.50
NaCl(g)	−176.65	−196.66	229.81	35.77
Na$_2$SO$_4$(c)	−1387.82	−1269.85	149.60	128.14
Na$_2$SO$_4$·10H$_2$O(c)	−4327.26	−3646.85	592.00	587.40
Na$_2$CO$_3$(c)	−1130.77	−1048.01	138.80	111.00
NaHCO$_3$(c)	−950.81	−851.00	101.70	87.61
K(c)	0	0	64.67	29.50
K(g)	89.00	60.48	160.34	20.79
KOH(c)	−424.70	−37.00	78.90	64.00
KCl(c)	−436.68	−408.76	82.55	51.29

4. Entropies of Chemical Reactions

(1) The change in entropy of a chemical reaction equals the combined entropies of the products minus the combined entropies of the reactants. Thus,

$\Delta\hat{S}°_{rxn} = \sum \gamma_j \times \hat{S}°(\text{products}) - \sum \gamma_i \times \hat{S}°(\text{reactants})$ ------------standard condition

(2) When ΔS needs to be determined for a process that occurs at different temperatures and pressure.

◆先找出標準狀態的反應物與產物之 S^o。

◆依條件利用(A)或(B)求出不同溫度或不同壓力之反應物與產物之 S。

◆再利用$\Delta_{rxn}S = \sum \gamma_j \times S(products) - \sum \gamma_i \times S(reactants)$ 即可。
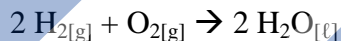
● 反應 aA + bB → cC + dD

(A)單一物質：$\Delta S = n\hat{C}\ln\dfrac{T_2}{T_1}$ → $\Delta\hat{S}_{rxn}(T_2) = \Delta\hat{S}_{rxn}(T_1) + \Delta\hat{C}\ln\dfrac{T_2}{T_1}$

(B)ideal gas：$\Delta S = nR\ln\dfrac{V_2}{V_1} = nR\ln\dfrac{P_1}{P_2}$

$\Rightarrow \Delta\hat{S}_{rxn}(P_2) = \Delta\hat{S}_{rxn}(P_1) + \Delta n \times R\ln\dfrac{P_1}{P_2}$ $\Delta n = (c+d)-(a+b)$ [gas 才能算]

Example 5-20:

Determine the change in entropy for the following chemical reaction occurring at the standard pressure and temperature.
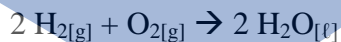
$2\,H_{2[g]} + O_{2[g]} \rightarrow 2\,H_2O_{[\ell]}$

Sol: From Appendix 2:

$S^o[H_{2[g]}] = 130.68$ J/mol·K; $S^o[O_{2[g]}] = 205.14$ J/mol·K

$S^o[H_2O_{[\ell]}] = 69.91$ J/mol·K

Example 5-21:

What is the entropy change of the reaction

$2\,H_{2[g]} + O_{2[g]} \rightarrow 2\,H_2O_{[\ell]}$

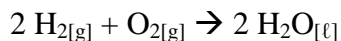at 80℃ and standard pressure? Treat the heat capacity of H_2, O_2, and H_2O as constant at 28.8, 29.4 and 75.3 J/mol·K, respectively.

Example 5-22:

What is the entropy change of the reaction

$2\,H_{2[g]} + O_{2[g]} \rightarrow 2\,H_2O_{[\ell]}$

at 25℃ and 300 atm?