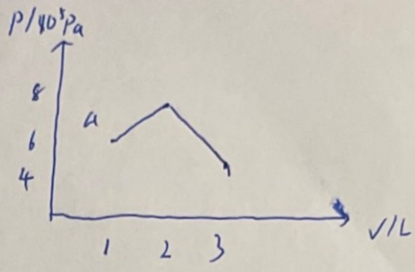
11.1 解 $A = \frac{1}{2}(p_a + p_b)(V_b - V_a) + \frac{1}{2}(p_b + p_c)(V_c - V_b)$

$= \frac{1}{2}(8+6)\times10^5 \times (2-1)\times10^{-3} + \frac{1}{2}(8+4)\times10^5\times(3-2)\times10^{-3}$

$= 1.3\times10^3 J.$



气体吸热为：

$Q = E_c - E_a + A$

$= C_{v.m}(T_c - T_a) + A$

$= \frac{i}{2}R(T_c - T_a) + A$

$= \frac{i}{2}(p_cV_c - p_aV_a) + A =$

$= \frac{5}{2}(4\times3 - 6\times1)\times10^5\times10^{-3} + 1.3\times10^3$

$= 2.79\times10^3 J$

熵变为：

$\Delta S = C_v \ln\frac{T_c}{T_a} + R\ln\frac{V_c}{V_a}$

$= \frac{i}{2}R\ln\frac{p_cV_c}{p_aV_a} + R\ln\frac{V_c}{V_a}$

$= R(\frac{i}{2}\ln\frac{p_c}{p_a} + \frac{i+2}{2}\ln\frac{V_c}{V_a})$

$= 8.31\times(\frac{5}{2}\times\ln\frac{4}{6} + \frac{5+2}{2}\times\ln\frac{3}{1})$

$= 23.5\ J/K$

11.2. 已知：$m=30g$, $T_1=-40°C$, $T_2=100°C$, $c_1=2.1\ J/(g.K)$, $c_2=4.2J/(g.K)$, $P=1.013\times10^5 Pa$, $\lambda=334J/g$, $L=2260J/$.

求：ΔS.

解：① -40°C的冰升温至0°C时ΔS_1

$\Delta S_1 = \int_{R\,T_1}^{T_2}\frac{dQ}{T} = \int_{R\,T_1}^{T_2}\frac{c_1 m dT}{T} = c_1 m\ln\frac{T_2}{T_1}$

② 冰等压等温熔成0°C的水时ΔS_2

$\Delta S_2 = {}_R\int_{T_2}\frac{dQ}{T_2} = \frac{Q_2}{T_2} = \frac{\lambda m}{T_2}$

③ 0°C的水等压升温至100°C时的ΔS_3

$\Delta S_3 = {}_R\int_{T_2}^{T_3}\frac{dQ}{T} = \int_{R\,T_2}^{T_3}\frac{c_2 m dT}{T} = c_2 m\ln\frac{T_3}{T_2}$

④ 100°C的水等压等温汽化为100°C的蒸气时的ΔS_4

$\Delta S_4 = \int_{R\,T_3}\frac{dQ}{T_3} = \frac{Q_4}{T_3} = \frac{Lm}{T_3}$

总熵变：

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = m(c_1\ln\frac{T_2}{T_1} + \frac{\lambda}{T_2} + c_2\ln\frac{T_3}{T_2} + \frac{L}{T_3})$

$= 30\times(2.1\times\ln\frac{273}{233} + \frac{334}{273} + 4.2\times\ln\frac{373}{273} + \frac{2260}{373})$

$= 268 (J/K).$

11.7. 解：(1) $\Delta S = \Delta S_{water} + \Delta S_{reservoir} = \int_{T_1}^{T_2}\frac{cmdT}{T} + \frac{Q}{T_2}$

$= cm\ln\frac{T_2}{T_1} + \frac{-cm(T_2-T_1)}{T_2}$

$= 4.18\times10^3\times1\times\ln\frac{373}{273} + \frac{-4.18\times10^3\times1\times(373-273)}{373}$

$= 184\ J/K > 0$

∴熵增加

(2) $\Delta S=\Delta S_{w_1}+\Delta S_{w_2}+\Delta S_{r_1}+\Delta S_{r_2}=\Delta S_w+\Delta S_{r_1}+\Delta S_{r_2}$

$$=cm\ln\frac{T_2}{T_1}+\frac{-cm(T'-T_1)}{T'}+\frac{-cm(T_2-T')}{T_2}$$

$$=4.18\times10^3\times1\times\ln\frac{373}{273}-\frac{4.18\times10^3\times1\times(323-373)}{323}-\frac{4.18\times10^3\times1\times(373-323)}{373}$$

$$=97\ J/K$$

熵也增加了，但比只用两个热库时增加得少。中间热库越多，熵增加得越少。如果中间热库"无限多"，过程就变得可逆，而系统熵将保持不变。

11.8. 解①要使水和冰质量相同，要有0.9kg水变成冰。

$$\Delta S_w=\frac{-Q}{T}=\frac{-334\times10^3\times0.9}{273}=-1.10\times10^3\ J/K$$

$$\Delta S_{en}=\frac{Q}{T}=1.10\times10^3\ J/K$$

总ΔS：

$$\Delta S_w+\Delta S_{en}=0.$$

②冰水混合物熵变：

$$\Delta S_w'=-\Delta S_w=1.10\times10^3\ J/K$$

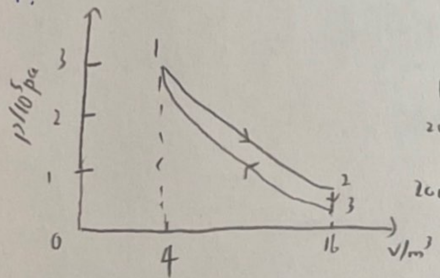
恒温箱放热的熵变：

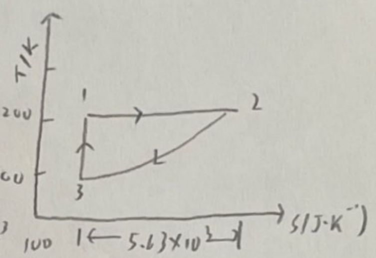
$$\Delta S_{em}'=-\frac{Q}{T'}=\frac{334\times10^3\times0.9}{373}=-0.81\times10^3\ J/K$$

总ΔS：

$$\Delta S_w'+\Delta S_{en}'=(1.10-0.81)\times10^3=0.29\times10^3\ J/K$$

11.9.





①等温过程：

$$A_T=\nu RT\ln\frac{V_2}{V_1}=p_1V_2\ln\frac{V_2}{V_1}=3.039\times10^5\times4\times\ln\frac{16}{4}=1.69\times10^6\ J.$$

$$\Delta S_T=\frac{Q}{T_1}=\nu R\ln\frac{V_2}{V_1}=\frac{p_1V_1}{T_1}\ln\frac{V_2}{V_1}=\frac{3.039\times10^5\times4}{300}\ln\frac{16}{4}=5.63\times10^3\ J/K$$

②等体过程

$A_v=0$

$$\Delta S_v=\int_{T_2}^{T_3}\frac{\nu C_{v,m}dT}{T}=\nu C_{v,m}\ln\frac{T_3}{T_2}$$

由于 $\frac{T_3}{T_2}=\frac{T_3}{T_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$

$$\Delta S_v=\nu(\gamma-1)C_{v,m}\ln\frac{V_1}{V_2}=\frac{p_1V_1}{T_1}\ln\frac{V_1}{V_2}=-5.63\times10^3\ J/K$$

③绝热过程

$$A_S=\frac{1}{\gamma-1}(p_2V_2-p_1V_1)=\frac{p_1V_1}{\gamma-1}\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1}-1\right]=\frac{3.039\times10^5\times4}{1.4-1}\left[\left(\frac{4}{16}\right)^{1.4-1}-1\right]=-1.30\times10^6\ J.$$

$\Delta S_S=0$、

④循环过程：

$$A=A_T+A_V+A_S=1.69\times10^6+0+(-1.3\times10^6)=0.39\times10^6\ J.$$

$$\Delta S=\Delta S_T+\Delta S_V+\Delta S_S=5.63\times10^3+(-5.63\times10^3)+0=0.$$

11.11. 以T和T'分别表示气体最初和最后温度，以V_1，和V_2表示原来容器内气体体积，有

$$\frac{1}{2}\nu C_{v,m}T+\frac{1}{2}\nu C_{v,m}T=\frac{1}{2}(\nu+\nu)C_{v,m}T'$$

即 $T'=T$.

$$p=\frac{2\nu RT}{V_1+V_2}=\frac{2\nu RT}{\frac{\nu RT}{p_1}+\frac{\nu RT}{p_2}}=\frac{2p_1p_2}{p_1+p_2}$$

设想两部分气体均可逆等温地变化到V'，则二者总熵变为

$$\Delta S=\Delta S_1+\Delta S_2=\nu R\ln\frac{V'}{V_1}+\nu R\ln\frac{V'}{V_2}$$

$$=\nu R\ln\frac{V_1+V_2}{2V_1}+\nu R\ln\frac{V_1+V_2}{2V_2}$$

$$=\nu R\ln\frac{(V_1+V_2)^2}{4V_1V_2}$$

$$=\nu R\ln\frac{(p_1+p_2)^2}{4p_1p_2}$$

由于$(p_1+p_2)^2>4p_1p_2$，所以$\Delta S>0$