ChE 141 Midterm 1
Fall 2006

1a) (5 points) First write the total differential for enthalpy in terms of T and P.

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

Since, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

1 point for total differential of H
1 point for putting in C_P definition
1 point for finding dH partial derivative from dH equation
1 point for Maxwell Relation
1 point for getting final answer

Now, let's find $\left(\frac{\partial H}{\partial P}\right)_T$

$$dH = TdS + VdP$$

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

$$dH = C_P dT + \left(V + T\left(\frac{\partial S}{\partial P}\right)_T\right)dP$$

From dG = -SdT + VdP, we can find the following Maxwell Relation:

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

Finally, $dH = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)dP$

b) (10 points)

Let's first find $\left(\frac{\partial V}{\partial P}\right)_T$ at 300 K.

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

1 point

Using the transition from state 1 to 2, the second term on the right-hand side is zero since dT = 0.

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP$$

1 point for eliminating term

$\Delta V = \left(\frac{\partial V}{\partial P}\right)_T \Delta P$ since $\left(\frac{\partial V}{\partial P}\right)_T$ is constant at a given temperature (given in problem statement)

$$V_2 - V_1 = \left(\frac{\partial V}{\partial P}\right)_T (P_2 - P_1)$$

1 point for equation
1 point for putting in values in equation

$$(0.9-1)\frac{cm^3}{mol} = \left(\frac{\partial V}{\partial P}\right)_T (100-1)bar$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -1.01*10^{-3}\,\frac{cm^3}{bar*mol}$$

2 point

Now for the equation of V as a function of P.

First, integrate $\left(\frac{\partial V}{\partial P}\right)_T$

2 point for work leading to equation
2 point for equation

$$\int_{V1}^{V} \partial V = \int_{P1}^{P} -1.01*10^{-3}\,\partial P$$

$$V - V_1 = -1.01*10^{-3}(P - P_1)$$

$$V = -1.01*10^{-3}(P-1)+1$$

where V is kept in cm^3/mol and P is in bar

note: equation is only valid for T = 300 K

c) (5 points)

Similar to the last part:

$$V_3 = \left(\frac{\partial V}{\partial T}\right)_{100bar}(T_3 - 300K) + 0.9\frac{cm^3}{mol} = 0.0005*(330-300) + 0.9 = 0.915\frac{cm^3}{mol}$$

$$V_4 = \left(\frac{\partial V}{\partial T}\right)_{100bar}(T_4 - 300K) + 0.9\frac{cm^3}{mol} = 0.0005*(350-300) + 0.9 = 0.925\frac{cm^3}{mol}$$

$$V_5 = \left(\frac{\partial V}{\partial P}\right)_{350}(P_5 - 100bar) + 0.925\frac{cm^3}{mol} = -0.002*(1-100) + 0.925 = 1.12\frac{cm^3}{mol}$$

1 point for V_3

1 point for V_4

1 point for V_5

1 point for equation for V_3, V_4

1 point for equation for V_5

d) (20 points)

$dH = C_P dT + VdP$ (given in problem)

$dH_{1\to2} = VdP$ because dT = 0

$$dH_{1\to2} = \left(-1.01*10^{-3}(P-P_1)+V_1\right)dP$$

$$\Delta H_{1\to2} = \left[-1.01*10^{-3}\,P^2\!\!\diagup_2 + 1.01*10^{-3}P_1P + V_1P\right]_{1bar}^{100bar}$$

$$= \left[-1.01*10^{-3}*\frac{100^2-1^2}{2}\right] + 1.01*10^{-3}(1bar)(100-1)+1*(100-1) = 94.05cm^3*bar$$

$dH_{2\to3} = C_P dT$ because pressure is constant

$$\Delta H_{2\to3} = 4\frac{J}{mol*K}\left(T_3-T_2\right) = 4*(330-300) = 120\frac{J}{mol}$$

$dH_{3\to4} = C_P dT$ because pressure is constant, again

$$\Delta H_{3\to4} = 4\frac{J}{mol*K}\left(T_4-T_3\right) = 4*(350-330) = 80\frac{J}{mol}$$

$dH_{4\to5} = VdP$ because Temperature is constant

$$dH_{4\to5} = \left(-.002*(P-P_4)+V_4\right)dP$$

$$\Delta H_{4\to5} = \left[-.002\,P^2\!\!\diagup_2 + .002P_4P + V_4P\right]_{100bar}^{1bar}$$

$$= \left[-.002*\frac{1^2-100^2}{2}\right] + .002(100bar)(1-100)+.925*(1-100) = -101.4cm^3*bar$$

For each enthalpy:
1 point for eliminating proper term
1 point for integration
1 point for putting in proper values
2 points for final answer

e) (20 points)

Let’s define a state 6 at T = 330 K and P = 1 bar.

We can find $\Delta H_{1\to5}$ because we have already found the other dH values for the other part of that cycle.

$$0.1\frac{J}{mol*K}=1\frac{cm^3bar}{mol*K}$$

$$\Delta H_{1\to5}=\Delta H_{1\to2}+\Delta H_{2\to3}+\Delta H_{3\to4}+\Delta H_{4\to5}=0.1*94.05+120+80+.1*(-101.4)$$
$$=199.3J$$

$$\Delta H_{1\to5}=C_P(T_5-T_1)$$
$$199.3J=C_P(350-300)$$
$$C_P(1bar)=3.99\frac{J}{mol*K}$$

$$\Delta H_{5\to6}=3.98*(T_6-T_5)=3.98*(330-350)$$
$$=-79.7\frac{J}{mol}$$

2 points for defining state 6
2.5 points for $\Delta H_{1\to5}$ equation from circle
2 points for $\Delta H_{1\to5}$ answer
2 points for C_P at 1 bar
2.5 points for second thermo. circle
2 points for $\Delta H_{6\to1}$ or $\Delta H_{5\to6}$
2 points for dH equation
2 points for integration
3 points for partial derivative value

Now, we can find $\Delta H_{3\to6}$ using a circle.

$$\Delta H_{3\to6}=\Delta H_{3\to4}+\Delta H_{4\to5}+\Delta H_{5\to6}$$
$$\Delta H_{3\to6}=80+0.1(-101.4)+(-79.7)=-9.84\frac{J}{mol}$$

$$dH_{3\to6}=VdP=\left[\left(\frac{\partial V}{\partial P}\right)_{330}*(P-P_3)+V_3\right]dP$$

$$\Delta H_{3\to6}=\left[\left(\frac{\partial V}{\partial P}\right)_{300}*\left(\frac{P^2}{2}\right)-\left(\frac{\partial V}{\partial P}\right)_{300}P_3P+V_3P\right]_{100bar}^{1bar}$$

$$\Delta H_{3\to6}=\left[\left(\frac{\partial V}{\partial P}\right)_{300}\left(\frac{1^2-100^2}{2}\right)-\left(\frac{\partial V}{\partial P}\right)_{300}(100bar)*(1-100)+0.915*(1-100)\right]$$
$$=-98.4cm^3*bar$$

$$\left(\frac{\partial V}{\partial P}\right)_{300}=-1.59*10^{-3}\frac{cm^3}{mol*bar}$$

1 Problem 2 (40 pts)

1.1 (a) (7 pts)

Given $dA = -SdT - PdV$, where A is Helmholtz free energy, S is entropy, P is pressure, and V is volume, show that $dS = \frac{C_V}{T}dT + (\frac{\partial P}{\partial T})_V dV$.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad \textbf{(2 pts)}$$

From the dA equation, we get the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ **(1 pt)**

$$\begin{aligned} dS &= \frac{dQ_{rev}}{T} \quad \textbf{(1 pt)} = \frac{dU}{T} \quad \text{(const V)} = \frac{C_V dT}{T} \quad \textbf{(1 pt)} \\ \left(\frac{\partial S}{\partial T}\right)_V &= \frac{C_V}{T} \quad \textbf{(1 pt)} \end{aligned}$$

Alternatively,

$$\begin{aligned} dU &= TdS - PdV \quad \textbf{(1 pt)} \\ dS &= \frac{dU}{T} - \frac{P}{T}dV \\ \left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \quad \textbf{(1 pt)} \\ &= \frac{C_V}{T} \quad \textbf{(1 pt)} \end{aligned}$$

Subbing these two relations into our initial dS expansion **(1 pt)** gives us the final result:

$$dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

1.2 (b) (7 pts)

After the diaphragm is broken, the temperature in the container quickly reaches a static value, please calculate this final temperature in the container after the diaphragm is broken.

An amount of heat Q is transferred from the gas formerly in the right half at $2T$ to the gas formerly in the left half at T, so that $|Q_L| = |Q_R|$. **(1 pt)** For each of the respective gases, $|Q| = NC_V\Delta T$. **(1 pt)**

$$\begin{aligned} NC_V\Delta T_L &= 1.5NC_V\Delta T_R \\ \Delta T_L &= 1.5\Delta T_R \quad \textbf{(1 pt)} \end{aligned}$$

Since they equilibrate, they must reach the same final temperature, so:

$$\begin{aligned} T + \Delta T_L &= 2T - \Delta T_R \quad \textbf{(1 pt)} \\ T + 1.5\Delta T_R &= 2T - \Delta T_R \\ \Delta T_R &= 0.4T \\ T_F &= 1.6T \quad \textbf{(3 pts)} \end{aligned}$$

Alternatively,

$$\begin{aligned} \Delta U &= Q + W \quad \textbf{(1 pt)} \\ &= 0 + 0 \quad \textbf{(1 pt)} \\ 0 &= \Delta U \\ &= (1.5N)C_V(T_F - 2T) + (N)C_V(T_F - T) \quad \textbf{(2 pts)} \\ &= 2.5NC_VT_F - 4NC_VT \\ T_F &= \frac{4}{2.5}T = 1.6T \quad \textbf{(3 pts)} \end{aligned}$$

A common error was to use the ideal gas law and equate $\left(\frac{PV}{NRT}\right)_i$ with $\left(\frac{PV}{NRT}\right)_f$. However, there is no single T_i, so this approach doesn't work. This approach was also tried for part c), but again there is no single T_i, so one needs to calculate quantities for each of the halves separately and then add them.

1.3 (c) (13 pts)

Calculate the change in internal energy and enthalpy in the container after the system reaches its final temperature.

$$\begin{aligned} \Delta U &= NC_V\Delta T \quad \textbf{(2.5 pts)} \\ &= \frac{3}{2}NR(0.6T) + \frac{3}{2}(1.5N)R(-0.4T) \\ &= 0 \quad \textbf{(4 pts)} \end{aligned}$$

Alternatively, $\Delta U = 0$ because was shown already in part b) or by same technique as in part b). **(6.5 pts)**

$$\begin{aligned} \Delta H &= NC_P\Delta T \quad \textbf{(2.5 pts)} \\ &= \frac{5}{2}NR(0.6T) + \frac{5}{2}R(1.5N)(-0.4T) \\ &= 0 \quad \textbf{(4 pts)} \end{aligned}$$

A common error was to not include the number of each half when calculating quantities.

1.4 (d) (13 pts)

Calculate the change of entropy in the container and the change of total entropy after the final temperature is reached.

$$\begin{aligned}
dS &= N\frac{C_V}{T}dT + N\left(\frac{\partial P}{\partial T}\right)_V dV \quad \textbf{(2 pts)} \\
&= N\frac{C_V}{T}dT + \frac{NR}{V}dV \quad \text{(ideal gas)} \quad \textbf{(3 pts)} \\
\Delta S &= NC_V \ln\frac{T_2}{T_1} + NR\ln\frac{V_2}{V_1} \quad \textbf{(2 pts)} \\
&= \frac{3}{2}NR\ln\frac{1.6T}{1T} + NR\ln\frac{2V}{V} + \frac{3}{2}(1.5N)R\ln\frac{1.6T}{2T} + (1.5N)R\ln\frac{2V}{V} \\
&= NR[1.5\ln 1.6 + 2.5\ln 2 + 2.25\ln 0.8] \\
&= 1.94NR \quad \textbf{(4 pts)}
\end{aligned}$$

The environment is unchanged, so the total entropy change is also $1.94NR$. **(2 pts)**

A common error was to start with $dS = \frac{dQ_{rev}}{T}$ and conclude that $dS = 0$ since there is no heat transfer to the container (it's well-insulated). But this is an *irreversible* process so that *actual* heat transfer Q is not the reversible heat transfer Q_rev.

Another common error was to immediately cancel the term $\left(\frac{\partial P}{\partial T}\right)_V dV$ because there was no volume change for the container as a whole. This is true, however, since there is no single T_i, one can't do this calculation for the container as a whole and thus must do the calculation for each of the halves, in which case $dV \neq 0$.