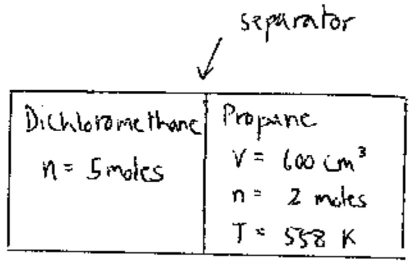
# Problem Set D

## Problem 13




At equilibrium - temperature on both sides are equal
- pressure on both sides are equal

because the separator is thermally conductive and freely moving.

For propane

Using Redlich - Kwong $$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$$

$$a = 0.42748\, R^2 T_c^{2.5} / P_c$$

$$b = 0.08664\, RT_c / P_c$$

with $T_c = 369.8\ K$ $P_c = 42.48$ bar

$$\therefore\ a = \frac{0.42748 \times 8.314^2 \times 369.8^{2.5}}{42.48 \times 10^5} = 18.3\ Nm^4K^{1/2}/mol^2$$

$$b = \frac{0.08664 \times 8.314 \times 369.8}{42.48 \times 10^5} = 6.27 \times 10^{-5}\ m^3/mol$$

$\therefore$ From Redlich Kwong EOS $V = \frac{600 \times 10^{-6}}{2} = 3 \times 10^{-4}\ m^3/mol$

$$P = \frac{8.314 \times 558}{3\times10^{-4} - 6.27\times10^{-5}} - \frac{18.3}{558^{1/2} \times 3\times10^{-4} \times (6\times10^{-4} + 6.27\times10^{-5})}$$

$$= 124.3 \times 10^{5} \text{ Pa}$$

$$= 124.3 \text{ bar}$$

now if we want to we could use the Redlich-Kwong EOS again

with $P = 124.3 \times 10^{5}$ Pa

$T = 558$ K

and a and b for dichloromethane

then solve for $V$ iteratively

But it is easier to make use of the generalized correlations

$$Z = Z^{0} + \omega Z^{1}$$

now that we know P and T of the gases

$$P_r = \frac{124.3}{60.80} = 2.045 \qquad T_r = \frac{558}{510} = 1.094$$

from tables E3, E4 $\qquad Z^{0} = 0.3953 \qquad Z^{1} = 0.0698$

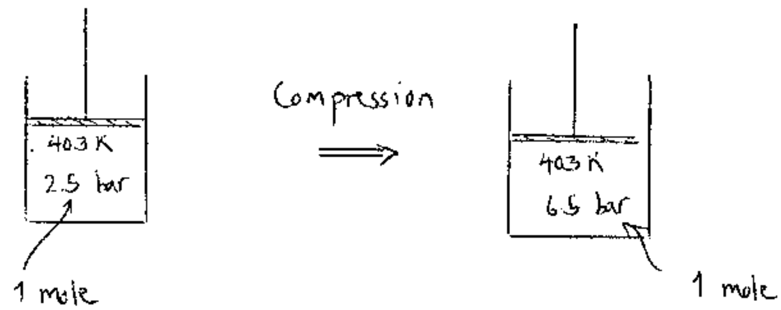
and $\omega = 0.199$

$$\therefore Z = 0.3953 + (0.199 \times 0.0698) = 0.4092$$

$$\therefore V = \frac{ZRT}{P} = \frac{0.4092 \times 8.314 \times 558}{124.3 \times 10^{5}} = 1.53 \times 10^{-4} \text{ m}^3/\text{mol}$$

$\therefore$ dichloromethane occupied $1.53 \times 10^{-4} \times 5 = \boxed{7.64 \times 10^{-4} \text{ m}^3}$

# Problem 14




If this compression is
- isothermal
- reversible

$$W = -\int n P \, dV$$

For an ideal gas $\quad P = \frac{RT}{V}$

since $T$ is constant

$$W = -nRT \int_{V_{initial}}^{V_{final}} \frac{dV}{V}$$

$$= -nRT \ln \frac{V_{final}}{V_{initial}}$$

From ideal gas EOS $\quad V_{initial} = \frac{RT}{P_{initial}} \qquad V_{final} = \frac{RT}{P_{final}}$

$$\therefore \frac{V_{final}}{V_{initial}} = \frac{P_{initial}}{P_{final}} = \frac{2.5}{6.5} = 0.385$$

$$\therefore W = -1 \times 8.314 \times 403 \times \ln 0.385$$

$$= 3201 \text{ J}$$ +ve since work is done on gas

So in the real compression $W_{real} = 1.30 \times 3201 = 4161\,J$

We can calculate the entropy changes of the gas using

$$\Delta S^{gas} = \frac{Q_{rev}}{T}$$

* Remember, S is a state function, so the changes in S of gas in cylinder that occurs as a result of a compression process is the same whether the process is reversible or irreversible

From 1st law $\Delta U = Q + W$

For ideal gas U is a function of T only

$\therefore \Delta U = 0$ since T is constant

$\therefore Q = -W$

$\therefore Q_{rev} = -W_{rev} = -3201\,J$

-ve as heat is transfer out of the process

$$\therefore \boxed{\Delta S^{gas} = \frac{Q_{rev}}{T} = \frac{-3201}{403} = -7.94\ J/mol\,K}$$

In effect, we calculate the change in entropy of a gas undergone irreversible isothermal compression by using the fact that S is a state function, and so $\Delta S$ can be calculated along any path we choose. So we end up choosing the most convenient path, ie. the isothermal reversible compression.

The entropy change of a heat reservoir is always given by $\frac{Q}{T}$ where Q is the quantity of heat transferred to or from the reservoir at temperature T.

$$\Delta S^{reservoir} = \frac{\overset{\swarrow \text{ actual } Q}{Q}}{T \leftarrow \text{reservoir temperature}}$$

$$= \frac{4161}{298}$$

$$\boxed{\Delta S^{reservoir} = 14.0 \text{ J/mol K}}$$

$$\Delta S_{total} = \Delta S_{gas} + \Delta S_{reservoir}$$

$$= -7.94 + 14$$

$$\boxed{\Delta S_{total} = 6.0 \text{ J/mol K}}$$

<u>Note</u> $\Delta S_{total} > 0$ as the process is irreversible as required by the 2nd law.

Another way to calculate $\Delta S^{gas}$ is to use

$$\Delta S = \int_{T_0}^{T} C_p^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}$$

that we derived in class for an ideal gas although this eqn. was derived for a reversible process, we can use it here as S is a state function

$$\therefore \quad \Delta S = \underset{\substack{\text{isothermal}\\\downarrow}}{0} - R \ln \frac{6.5}{2.5}$$

$$= -7.94 \text{ J/mol K}$$

**15.**

a) We want to write dS in terms of changes of P and V (dS = something dP + somethang dV)

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

$$= \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV \qquad \text{because } \left(\frac{\partial a}{\partial b}\right)_d \left(\frac{\partial b}{\partial c}\right)_d = \left(\frac{\partial a}{\partial c}\right)_d$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{Cv}{T} \text{ and } \left(\frac{\partial S}{\partial T}\right)_P = \frac{Cp}{T} \qquad \text{(derived in lecture)}$$

$$dS = \frac{Cv}{T}\left(\frac{\partial T}{\partial P}\right)_V dP + \frac{Cp}{T}\left(\frac{\partial T}{\partial V}\right)_P dV \qquad \textbf{(QED)}$$

b) For an ideal gas: PV = RT → T = PV/R. Therefore from part a):

$$dS = \frac{Cv}{T}\left(\frac{\partial T}{\partial P}\right)_V dP + \frac{Cp}{T}\left(\frac{\partial T}{\partial V}\right)_P dV = \frac{Cv}{T}\frac{V}{R}dP + \frac{Cp}{T}\frac{P}{R}dV$$

We have dT and dV terms whereas what we want is dP and dT.

$$V = \frac{RT}{P} \quad \Rightarrow \quad dV = \frac{\partial}{\partial P}\left(\frac{RT}{P}\right)dP + \frac{\partial}{\partial T}\left(\frac{RT}{P}\right)dT \quad \Rightarrow \quad dV = -\frac{RT}{P^2}dP + \frac{R}{P}dT$$

Substituting this expression for dV in the above equation gives us:

$$dS = \frac{Cv}{T}\frac{V}{R}dP + \frac{Cp}{T}\frac{P}{R}\left[-\frac{RT}{P^2}dP + \frac{R}{P}dT\right] \qquad \text{Now we collect terms for dP and dT:}$$

$$= \frac{Cp}{T}dT + \left[\frac{CvV}{RT} - \frac{Cp}{P}\right] = \frac{Cp}{T}dT + \left[\frac{Cv}{P} - \frac{Cp}{P}\right]dP$$

Finally, since Cp - Cv = R for ideal gas, we get:

$$dS = \frac{Cp}{T}dT - \frac{R}{P}dP \qquad \text{for ideal gas} \qquad \textbf{(QED)}$$

c) We want dU in terms of dT and dP.

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \qquad\qquad dU = TdS - PdV$$

$$= \left[T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

We have terms involving S, which we want to replace with P, V, T, and Cp.

We know from before that $\left(\frac{\partial S}{\partial T}\right)_P = \frac{Cp}{T}$. From Maxwell's, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ (see lecture for derivation)

$$dU = \left[T\frac{Cp}{T} - P\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left[-T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

$$dU = \left[Cp - P\left(\frac{\partial V}{\partial T}\right)_P\right]dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP \qquad \textbf{(QED)}$$

d) We want to use PV = ZRT in the expression in part c) – keeping in mind that Z = f(P,V,T)

$$V = \frac{ZRT}{P} \quad \Rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial Z}{\partial T}\right)_P \frac{RT}{P} + \frac{ZR}{P} \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial Z}{\partial P}\right)_T \frac{RT}{P} - \frac{ZRT}{P^2}$$

$$dU = \left[Cp - P\left(\frac{\partial V}{\partial T}\right)_P\right]dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP \qquad \text{Substituting the above expressions:}$$

$$dU = \left\{Cp - P\left[\left(\frac{\partial Z}{\partial T}\right)_P \frac{RT}{P} + \frac{ZR}{P}\right]\right\}dT - \left\{T\left[\left(\frac{\partial Z}{\partial T}\right)_P \frac{RT}{P} + \frac{ZR}{P}\right] + P\left[\left(\frac{\partial Z}{\partial P}\right)_T \frac{RT}{P} - \frac{ZRT}{P^2}\right]\right\}dP$$

Collecting and canceling out terms gives us:

$$\mathbf{dU} = \left[\mathbf{Cp} - \left(\frac{\partial \mathbf{Z}}{\partial \mathbf{T}}\right)_\mathbf{P} \mathbf{RT} - \mathbf{ZR}\right]\mathbf{dT} - \left[\left(\frac{\partial \mathbf{Z}}{\partial \mathbf{T}}\right)_\mathbf{P} \frac{\mathbf{RT^2}}{\mathbf{P}} + \left(\frac{\partial \mathbf{Z}}{\partial \mathbf{P}}\right)_\mathbf{T} \mathbf{RT}\right]\mathbf{dP} \qquad \text{(ans)}$$

e) For ideal gas, Z = 1 (and thus, all derivatives of Z = 0). Therefore

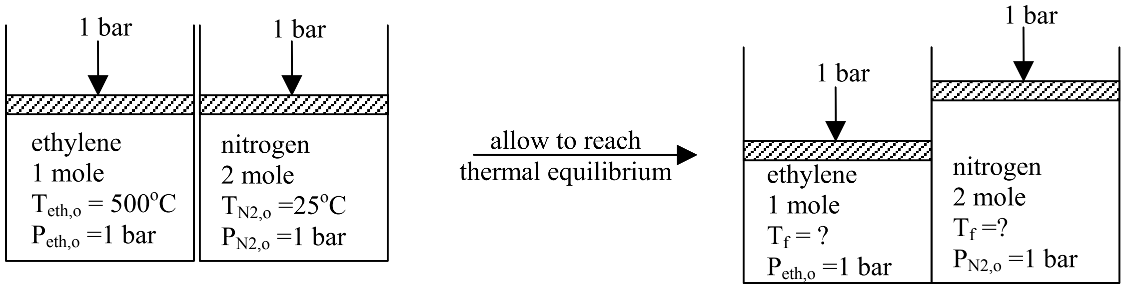
$$dU = [Cp - 0\cdot RT - 1\cdot R]dT - \left[0\cdot\frac{RT^2}{P} + 0\cdot RT\right]dP$$

$$dU = [Cp - R]dT$$

$$\mathbf{dU = Cv\,dT} \qquad \text{for ideal gas}$$

The expression is as we have seen it before. Performing a similar calculation will give you $dH^{ig}$ = Cp dT. Thus Maxwell's relationship shows that, for an ideal gas, the internal energy and enthalpy only depend on temperature.

**16.**




(Volumes are not drawn to scale ).

The gases are assumed to be ideal. We know the initial conditions. The process is isobaric. We know the final temperature of the two gases are equal (call it $T_f$) but we don't know what $T_f$ is. We want to know $\Delta S$.

Thinking process:

1) We can express $\Delta S$ – a state function – as a function of the final states ($T_f$, $P_f$) and initial states ($T_o$, $P_o$) of the two gases.
2) We can define all the states except that we don't know $T_f$.
3) We may be able to get $T_f$ through another equation we have: the 1st law.

Let's write the 1st law, taking both gases as our system:

$dU^t = \delta Q + \delta W$

We will assume that Q = 0, meaning that there is no heat transfer to the surrounding. The only heat transfer is between the two gases to allow them to reach thermal equilibrium.

Is W = 0? P is constant, T changes → V must change. So $-PdV \neq 0$. We will write out the work terms for both gases:

$$dU^t = dU^t_{eth} + dU^t_{N2} = \overbrace{\cancel{\delta Q}}^{=0} + \delta W_{eth} + \delta W_{N2} \quad \Rightarrow \quad dU^t_{eth} + dU^t_{N2} = \delta W_{eth} + \delta W_{N2}$$

For an ideal gas: $dU^t = nCvdT$.

As for W, we have our usual expression $\delta W = -nPdV$. Therefore we can expand the above to:

$$n_{eth}Cv_{eth}dT_{eth} + n_{N2}Cv_{N2}dT_{N2} = -n_{eth}P_{eth}dV_{eth} + -n_{N2}P_{N2}dV_{N2}$$

Since this is ideal gas (V = RT/P) and since the process is isobaric, dV = R/P dT. Then:

$$n_{eth}Cv_{eth}dT_{eth} + n_{N2}Cv_{N2}dT_{N2} = -n_{eth}P_{eth}\frac{R}{P_{eth}}dT_{eth} + -n_{N2}P_{N2}\frac{R}{P_{N2}}dT_{N2} = -n_{eth}RdT_{eth} + -n_{N2}RdT_{N2}$$

$$n_{eth}(Cv_{eth} + R)dT_{eth} + n_{N2}(Cv_{N2} + R)dT_{N2} = 0$$

$$n_{eth}Cp_{eth}dT_{eth} + n_{N2}Cp_{N2}dT_{N2} = 0$$

$$n_{eth}\int_{T_{eth,0}}^{T_f} Cp_{eth}dT_{eth} + n_{N2}\int_{T_{N2,0}}^{T_f} Cp_{N2}dT_{N2} = 0$$

Note: This result turns out to be equivalent to saying $\Delta H_{eth} + \Delta H_{N2} = \Delta H_{system} = 0$. This is true because the process is basically change of temperatures in constant pressure condition.

Using Cp information from Table C (we're not assuming Cp is constant), we know everything in the equation except $T_f$. We can solve for $T_f$. Writing it out:

$$n_{eth}\int_{T_{eth,0}}^{T_f} R(A_{eth}+B_{eth}T+C_{eth}T^2+D_{eth}T^{-2})dT + n_{N2}\int_{T_{N2,0}}^{T_f} R(A_{N2}+B_{N2}T+C_{N2}T^2+D_{N2}T^{-2})dT = 0$$

We can divide both sides of the equation with R, removing the R. From table C.1:

| | **A** | **B** | **C** | **D** |
|---|---|---|---|---|
| **ethylene** | 1.424 | $14.394 \times 10^{-3}$ | $-4.392 \times 10^{-6}$ | 0 |
| $\mathbf{N_2}$ | 3.280 | $0.593 \times 10^{-3}$ | 0 | $0.040 \times 10^{5}$ |

$$1\,\text{mol}\int_{773\,K}^{T_f}(1.424+14.394\cdot 10^{-3}T-4.392\cdot 10^{-6}T^2)dT + 2\,\text{mol}\int_{298\,K}^{T_f}(3.280+0.593\cdot 10^{-3}T+0.040\cdot 10^{5}T^{-2})dT = 0$$

$$\left[1.424(T_f-773)+\frac{14.394\cdot 10^{-3}}{2}(T_f^2-773^2)-\frac{4.392\cdot 10^{-6}}{3}(T_f^3-773^3)\right]$$

$$+2\left[3.280(T_f-298)+\frac{0.593\cdot 10^{-3}}{2}(T_f^2-298^2)-0.040\cdot 10^{5}(T_f^{-1}-298^{-1})\right]=0$$

Solving this gives us $T_f$ = <u>564 K</u>. (value in between 773 K and 298 K; makes sense)
Now we can find the value for ΔS:

$$dS=\frac{Cp}{T}dT-\frac{R}{P}\underbrace{\cancel{dP}}_{=0 \text{ isobaric}}$$

Writing out the <u>total</u> change in entropy as a combination of the two gases, we integrate from the initial temperatures to the final temperature:

$$\Delta S^t = n_{eth}\int_{T_{eth,0}}^{T_f}\frac{Cp_{eth}}{T}dT + n_{N2}\int_{T_{N2,0}}^{T_f}\frac{Cp_{N2}}{T}dT$$

Using the same Cp expressions as above we get:

$$\Delta S^t = n_{eth}\int_{T_{eth,0}}^{T_f} R(\frac{A_{eth}}{T}+B_{eth}+C_{eth}T+D_{eth}T^{-3})dT + n_{N2}\int_{T_{N2,0}}^{T_f} R(\frac{A_{N2}}{T}+B_{N2}+C_{N2}T+D_{N2}T^{-3})dT$$

Integrating (with $T_f$ = 564 K) and putting in the values, we get:

$$\Delta S = 1\,\text{mol}\cdot 8.314\,\text{J/mol K}\left[1.424\ln(\frac{564}{773})+14.394\cdot 10^{-3}(564-773)-\frac{4.392\cdot 10^{-6}}{2}(564^2-773^2)\right]$$

$$+2\,\text{mol}\cdot 8.314\,\text{J/mol K}\left[3.280\ln(\frac{564}{298})+\frac{0.593\cdot 10^{-3}}{2}(564-773)-\frac{0.040\cdot 10^{5}}{2}(564^{-2}-773^{-2})\right]$$

ΔS = -23.6 J/K + 37.7 J/K = **<u>14.1 J/K</u>**

Note: $\Delta S_{eth} < 0$ but $\Delta S_{N2} > 0$ and $\Delta S_{universe} > 0$.
(In this case $\Delta S_{surrounding} = 0$ because there is no interaction with surrounding).