# ChemE 2200 - Physical Chemistry II for Engineers
## Solutions to Exercises for Calculation Session 6

1. The formation reaction for $B_2H_6$(g) is

$$2\mathrm{B}(s) + 3\mathrm{H}_2(g) \rightarrow \mathrm{B}_2\mathrm{H}_6(g)$$

This reaction obtains from adding the second reaction, plus three times the third reaction, plus the reverse of the first reaction, as follows:

$$\begin{aligned} 2\mathrm{B}(s) + \tfrac{3}{2}\mathrm{O}_2(g) &\rightarrow \mathrm{B}_2\mathrm{O}_3(s) \\ 3\mathrm{H}_2(g) + \tfrac{3}{2}\mathrm{O}_2(g) &\rightarrow 3\mathrm{H}_2\mathrm{O}(g) \\ \mathrm{B}_2\mathrm{O}_3(s) + 3\mathrm{H}_2\mathrm{O}(g) &\rightarrow \mathrm{B}_2\mathrm{H}_6(g) + 3\mathrm{O}_2(g) \\ \text{sum}: \quad 2\mathrm{B}(s) + 3\mathrm{H}_2(g) &\rightarrow \mathrm{B}_2\mathrm{H}_6(g) \end{aligned}$$

Thus the heat of formation is

$$\begin{aligned} \Delta H_\mathrm{f} &= \Delta H_{\mathrm{rxn}\,2} + 3\Delta H_{\mathrm{rxn}\,3} - \Delta H_{\mathrm{rxn}\,1} \\ &= -2368 + 3\times(-241.8) - (-1941) = -1152 \text{ kJ/mol} \end{aligned}$$

Adapted from P. Atkins, *Physical Chemistry*, 6th edition, 1997.

2.(A) Tabulate the heat and work for each step.

| | $q$ | $w$ |
|---|---|---|
| step 1 | 220 | –300 |
| step 2 | –110 | 0 |
| step 3 | 60 | 110 |
| step 4 | –160 | 0 |
| step 5 | 290 | –220 |
| cycle: | +300 | –410 |

Because the system returns to the same temperature, pressure and volume, and gas identity (X) the state function $U$ must return to its initial value. That is, $\Delta U = 0$. However, from the table above, $\Delta U = q + w = +300 - 410 = -110$ kJ. Thus your assistant's report is not correct; the $T$, $P$, and $V$ after step 5 cannot be the same as before step1.

(B) We now have the possibility that X converted to Y and released energy in the process (the reaction is exothermic). The 1st law analysis of part (A) revealed that the system needed an additional 110 kJ. That is, the system did 410 kJ of work but absorbed only 300 kJ of heat. The system needs a source for an additional 110 kJ of energy. Because the reaction is exothermic, the reaction releases heat. The heat from the reaction stays in the system and therefore less heat needs to be absorbed from the surroundings. This could explain why $q$ was less than it should be to balance $w$. This possibility may account for the error in the assistant's report.

(C) If $2X \rightarrow X_2$, then the number of moles in the volume decreased. Yet the temperature, pressure, and volume are the same and both are ideal gases. This possibility cannot account for the error in the assistant's report.

From B.G. Kyle, *Chemical and Process Thermodynamics*, 3rd edition, 1999.

3.(A) True: This is the definition of a state function and a cyclic process.

(B) False: Consider the entropy of the surroundings in a cyclic process such as the Carnot Cycle. Although $\Delta S_{\text{system}} = 0$ for a cycle, $\Delta S_{\text{surroundings}}$ must be greater than 0 for the overall process to be spontaneous.

(C) False: $\Delta S$ is calculated by devising a reversible path between the initial state and the final state. Consider an irreversible adiabatic process. Although $q = 0$ for the actual process, it is possible that $q_{\text{rev}} \neq 0$ for the reversible path. An example is the expansion of a gas into a vacuum, as discussed in lecture T8.

(D) False. If the temperature dependence of $q_{\text{rev}}$ could be expressed as a constant times temperature, $q_{\text{rev}} = aT$, then this would be true. However, the temperature dependence of $q_{\text{rev}}$ cannot be expressed as a constant times temperature in general. Or, consider the consequences of $q_{\text{rev}}$ absorbed by a gas; temperature increases and entropy increases.

(E) False. The entropy of an isolated system will increase spontaneously if the entropy is not at its maximum. For example, a gas in the left side of an isolated container will spontaneously expand to fill the container and the entropy will increase; $\Delta S = R \ln 2$.

(F) False. Entropy is not conserved.

(G) True. In the sense that 'conserved' means neither created nor destroyed, because the system returns to the same state, $\Delta S = 0$.

(H) False. Although $\Delta S = 0$ for the cycling system, $\Delta S > 0$ for the surroundings. The total entropy in the universe (system + surroundings) increases.

4. $q$ and $w$ depend on the path. Because the path is not specified $q$ and $w$ cannot be calculated. Because the expansion is isothermal and for an ideal gas $U$ and $H$ depend on temperature only, $\Delta U = \Delta H = 0$. $S$ is a state function, so we need only devise a reversible path between the initial and final states. Calculate $\Delta S$ for an isothermal reversible expansion from 35 L to 90 L.

$$\Delta S \;=\; nR\ln\frac{V_2}{V_1} \;=\; (2\text{ mol})(8.314\text{ J/(K}\cdot\text{mol))}\ln\frac{90\text{ L}}{35\text{ L}} \;=\; 15.7\text{ J/K}$$

5. To calculate $\Delta S$ we use a reversible process. For a reversible constant-pressure process,

$$\delta q_{\text{rev}} \;=\; dH \;=\; C_{\text{P}}\,dT$$

Divide by $T$ to obtain an expression for entropy.

$$\frac{\delta q_{\text{rev}}}{T} \;=\; \frac{C_{\text{P}}}{T}\,dT$$

$$\Delta S \;=\; \int \frac{\delta q_{\text{rev}}}{T} \;=\; \int_{T_1}^{T_2} \frac{C_{\text{P}}}{T}\,dT \;=\; C_{\text{P}}\ln\frac{T_2}{T_1} \;=\; n\overline{C}_{\text{P}}\ln\frac{T_2}{T_1}$$

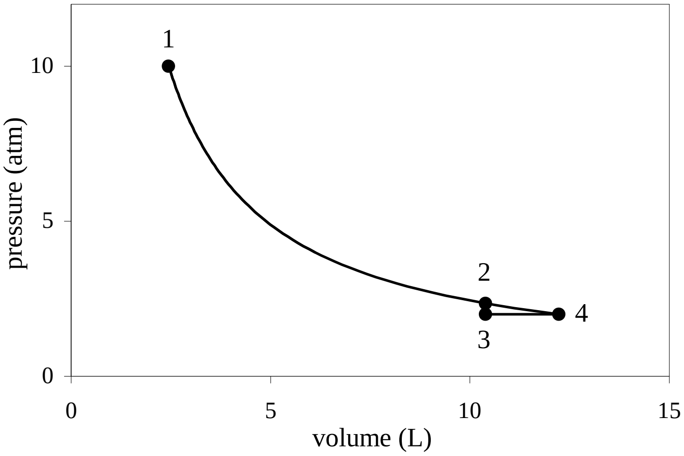
For 2 moles of $H_2O(l)$,

$$\Delta S \;=\; (2.0\text{ mol})\left(\frac{75.2\text{ J}}{\text{K}\cdot\text{mol}}\right)\ln\frac{363\text{ K}}{283\text{ K}} \;=\; 37.4\text{ J/K}$$

Adapted from *Problems & Solutions to Accompany McQuarrie - Simon Physical Chemistry: A Molecular Approach*, Heather Cox (University Science Books, 1997), exercise 20-13.

6. Because $U$, $H$ and $S$ are all state functions, we may devise any path between the initial and final states. To calculate $\Delta S$ we must devise a series of reversible paths.

The natural variables for $U$ are $T$ and $V$. Use the following paths: An isothermal expansion to the final volume (path 1 to 2 on the figure below), then isochoric cooling to the final temperature (path 2 to 3). This path is shown below.



Because this is an ideal gas, $\Delta U = 0$ for the isothermal expansion. The change in internal energy for the isochoric cooling is

$$\Delta U = n\overline{C}_V(T_{\text{final}} - T_{\text{initial}}) = n\frac{3}{2}R(T_{\text{final}} - T_{\text{initial}})$$

$$= (1\text{ mol})\frac{3}{2}(8.314\text{ J/K}\cdot\text{mol})(253.2\text{ K} - 298\text{ K}) = -559\text{ J}$$

To calculate $\Delta H$ use a path of isothermal expansion to the final pressure (path 1 to 4 on the figure above), then isobaric cooling to the final temperature (path 4 to 3). Because this is an ideal gas, $\Delta H = 0$ for the isothermal expansion. The change in enthalpy for the isobaric cooling is

$$\Delta H = n\overline{C}_P(T_{\text{final}} - T_{\text{initial}}) = n\frac{5}{2}R(T_{\text{final}} - T_{\text{initial}})$$

$$= (1\text{ mol})\frac{5}{2}(8.314\text{ J/K}\cdot\text{mol})(253.2\text{ K} - 298\text{ K}) = -931\text{ J}$$

Another method to calculate $\Delta H$ is to start with $\Delta U$ and add the $PV$ term. Use two paths - first decrease the pressure isochoricly from 10 atm to 2 atm, then increase the volume from 2.45 L to 10.39 L:

$$\begin{aligned}\Delta H &= \Delta U + \Delta(PV)\\ &= \Delta U + V\Delta P + P\Delta V\\ &= -559\text{ J} + (2.45\text{ L})(2\text{ atm} - 10\text{ atm})\frac{101.3\text{ J}}{\text{L}\cdot\text{atm}} + (2\text{ atm})(10.39\text{ L} - 2.45\text{ L})\frac{101.3\text{ J}}{\text{L}\cdot\text{atm}}\\ &= -936\text{ J}\end{aligned}$$

Or one may evaluate as the change in the product PV from the initial state (10 atm and 2.45 L) to the final state (2 atm and 10.39 L):

$$\begin{aligned}\Delta H &= \Delta U + \Delta(PV)\\ &= \Delta U + (PV)_{\text{final}} - (PV)_{\text{initial}}\\ &= -559\text{ J} + (2\text{ atm})(10.39\text{ L})\frac{101.3\text{ J}}{\text{L}\cdot\text{atm}} - (10\text{ atm})(2.45\text{ L})\frac{101.3\text{ J}}{\text{L}\cdot\text{atm}}\\ &= -936\text{ J}\end{aligned}$$

To calculate $\Delta S$ we could use either the paths we used for $\Delta U$ or the paths we used for $\Delta H$. But to use the paths for $\Delta U$ we would need to calculate the final volume. (This assumes we did not use the alternate method to calculate $\Delta H$). The $\Delta H$ path (isothermal state 1 to state 4 and then isobaric state 4 to state 3) is easier because we already know the pressures and temperatures.

$$\begin{aligned}\Delta S &= -nR\ln\frac{P_{\text{final}}}{P_{\text{initial}}} + n\overline{C}_{\text{P}}\ln\frac{T_{\text{final}}}{T_{\text{initial}}}\\ &= -(1\text{ mol})(8.314\text{ J/K}\cdot\text{mol})\ln\frac{2\text{ atm}}{10\text{ atm}} + (1\text{ mol})\frac{5}{2}(8.314\text{ J/K}\cdot\text{mol})\ln\frac{253.2\text{ K}}{298\text{ K}}\\ &= +9.99\text{ J/K}\end{aligned}$$

Adapted from K. J. Laidler and J. H. Meiser, *Physical Chemistry*, 3rd edition, 1999.

7.(A) Use the definition of the Joule-Thomson coefficient to calculate the temperature decrease during the expansion.

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu$$

$$dT = \mu dP \qquad \text{at constant } H$$

Assuming μ is constant, we have

$$\int_{T_1}^{T_2} dT = \mu\int_{P_1}^{P_2} dP$$

$$T_2 - T_1 = \mu(P_2 - P_1)$$

$$T_2 = T_1 + \mu(P_2 - P_1) = 290\text{ K} + 1.11\text{ K/atm}\times(1-120\text{ atm}) = 290\text{ K} - 132\text{ K} = 158\text{ K}$$

158K is below the sublimation temperature, 195K. Because the predicted temperature is below the sublimation temperature, we predict some $CO_2$ will sublime. This means the discharged $CO_2$ will be a mixture of $CO_2$ gas and $CO_2$ solid at 195K.

(B) Analyze the isenthalpic Joule-Thomson by a series of steps, such that the overall change in enthalpy is zero. Start with an isothermal expansion to 1 atm from 120 atm. The enthalpy increase during the isothermal expansion must equal the enthalpy decrease during the isobaric cooling to the sublimation point (195 K) plus the enthalpy decrease by sublimation of a portion of the $CO_2$ at 195 K.

First calculate the change in enthalpy for an isothermal expansion. Calculate on a molar basis.

$$\left(\frac{\partial \overline{H}}{\partial P}\right)_T = -\mu\overline{C}_{\text{P}}$$

$$d\overline{H} = -\mu\overline{C}_{\text{P}}\,dP \qquad \text{at constant } T.$$

$$\int_{\overline{H}_1}^{\overline{H}_2} d\overline{H} = -\mu\int_{P_1}^{P_2}\overline{C}_{\text{P}}\,dP$$

Assume both μ and $\overline{C}_{\text{P}}$ are independent of pressure.

$$\overline{H}_2 - \overline{H}_1 = q = -\mu\overline{C}_{\text{P}}(P_2 - P_1) = -(1.11\text{ K/atm})(36\text{ J/(K}\cdot\text{mol)})(1-120\text{ atm}) = 4.76\text{ kJ/mol}$$

Calculate how much heat is needed to cool to 195 K from 290 K.

$$q = \overline{C}_{\text{P}}(T_3 - T_2) = 36\text{ J/(K}\cdot\text{mol)}(195\text{ K} - 290\text{ K}) = -3.42\text{ kJ/mol}$$

Thus for 1 mol of $CO_2$, 3.42 kJ is withdrawn from the $CO_2$ to cool to 195 K. We have 4.76 – (–3.42) = 8.18 kJ remaining to sublime some of the $CO_2$. Calculate how much $CO_2$ can be sublimed with 8.18 kJ.

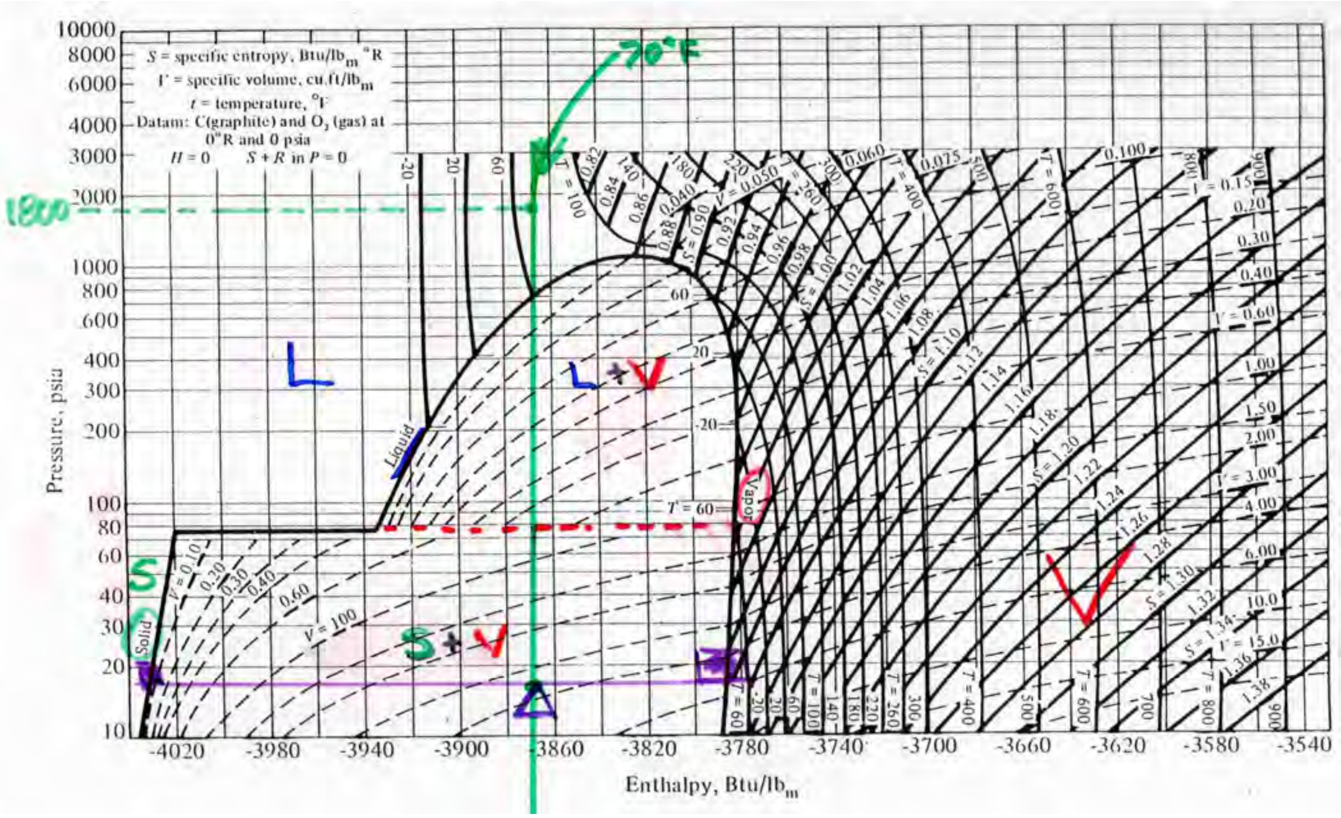
$$\frac{q}{\Delta\overline{H}_{\text{subl}}} = \frac{8.18\text{ kJ}}{25\text{ kJ/mol}} = 0.33\text{ mol}$$

About 33% of the $CO_2$ sublimes in this approximation.

(C) For a graphical solution we recall that a Joule-Thomson expansion is isenthalpic. We start at $P$ = 120 atm = 1800 psi and $T$ = 290 K = 63 F and move vertically down the chart to $P$ = 14.7 psi, which is in the solid+vapor two-phase region. Use the Lever Rule to determine the relative amount of each phase. The total length of the lever is about

112 mm. The arm to the vapor border is 40 mm, so the fraction of solid is 40/112 = 0.36. The graphical analysis is probably more accurate than the calculation, which required a lot of approximations. However, the agreement is reassuring.

The graphical solution is shown below.



In summary, the discharge from a typical $CO_2$ fire extinguisher is at 195 K (–108 F) and about 36% of the discharge is dry ice.

The Team Competition Champions for Calculation Session 6:

# Michelle Nguyen, Lizzy Frazier, and Megan Cheng

“How Well Do You Know
the Chemical Engineering Faculty Members?”

Score = 6/10 and 3rd of 20 team solutions submitted.