ChemE 2200 – Physical Chemistry II for Engineers

Solutions to Calculation Session 7 Exercises

1.(A) True. This is postulated to be true; the second law of thermodynamics states that the entropy of an isolated system increases for a spontaneous process.

(B) False. A closed system is one that does not exchange matter with its surroundings, however, it may exchange heat. If the reversible heat is negative, then the entropy of the system will be negative. Consider the reversible, isothermal compression of an ideal gas.

(C) True. For example, if the Carnot cycle is run in the opposite direction, the +/– signs on q and w change. Work is done on the system (the engine) and heat is extracted from the cold reservoir. This is known as a heat pump. Air conditioners and refrigerators are examples of heat pumps.

(D) False. The third law of thermodynamics also requires that the substance be a perfect crystal. If the substance is amorphous (like glass compared to quartz) or the crystal contains defects (such as vacancies or dislocations) then there are multiple arrangements even at 0 K. Thus the entropy is not precisely zero at 0 K. The entropy will be very, very close to zero, but not zero.

(E) True. No heat will transfer across the piston because $\Delta T = 0$ and the piston will not move because $\Delta P = 0$.

(F) False. Although the two different gases have the same molar entropy, it is possible the two gases have different temperatures and pressures.

(G) False. Although the He (an ideal gas) in the two different compartments have the same molar entropy, it is possible the He gases have different temperatures and pressures. Consider an adiabatic, reversible path on a P-V map. (Recall the molar entropy is constant for an ideal gas on an adiabatic path.) For an ideal gas, every point on this path has the same molar entropy, yet the points have different molar volumes and pressures. To guarantee that two He gases have the same temperature and pressure, at least two parameters must be equal. For example, $\overline{S}_\mathrm{A} = \overline{S}_\mathrm{B}$ and $\overline{V}_\mathrm{A} = \overline{V}_\mathrm{B}$.

(H) True. U and S are the state functions of the first and second law respectively, which when combined encapsulate the whole of thermodynamics. They tell us if a process will happen, and if so, place constraints on how it will happen.

(I) False. The first law tells us that internal energy is a state function; therefore it is independent of path. However, the first law does not tell us if a given path is forbidden. For example, consider a hot and cold block of metal in an isolated system in thermal contact (see figure 20.4 McQuarrie &Simon). Common experience predicts that heat flows from the hot block to the cold block. The first law, however, allows heat to flow from the cold block to the hot block. The first law only requires that $q_\mathrm{hot} = -q_\mathrm{cold}$.

(J) True. By definition A and G combine both statements of the first and second law. Look at how A and G are derived. Start with some form of the first law, with the appropriate constraints (e.g. constant T), write an equivalent statement of the first law using $TdS \geq \delta q$, and subtract the first from the second.

2.(A) CO_2: more atoms and larger mass.

(B) D_2O: larger mass.

(C) $CH_3CH_2CH_2CH_2NH_2$: more flexibility; more configurations possible.

Adapted from *Problems & Solutions to Accompany McQuarrie - Simon Physical Chemistry: A Molecular Approach*, Heather Cox (University Science Books, 1997), exercises 21-40 and 21-41.

3. Because the molar entropy of a solid or liquid is much smaller than the molar entropy of a gas, we need only consider the change in the number of gas molecules for each reaction; $\Delta S_{rxn} \propto \Delta n_{gas}$.

(A) $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta n_{gas} = 1 - 1 = 0$

(B) $H_2(g) + O_2(g) \rightarrow H_2O_2(g)$ $\Delta n_{gas} = 1 - 2 = -1$

(C) $CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O\,(\ell)$ $\Delta n_{gas} = 1 - 4 = -3$

(D) $C(s) + H_2O\,(\ell) \rightarrow CO(g) + H_2(g)$ $\Delta n_{gas} = 2 - 0 = +2$

(E) $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ $\Delta n_{gas} = 2 - 1 = +1$

The ranking is therefore (D) > (E) > (A) > (B) > (C).

Adapted from *Problems & Solutions to Accompany McQuarrie - Simon Physical Chemistry: A Molecular Approach*, Heather Cox (University Science Books, 1997), exercise 21-42.

4. To calculate the change in entropy – a state function – we need to devise a series of reversible paths between the initial and final states. The first path is reversible isobaric heating from 300 K to 930K. The second path is isothermal compression from 1 atm to 17 atm.

Path 1. Because argon is an ideal monatomic gas, $\overline{C}_P = (5/2)R$.

$$\Delta S_1 = n\overline{C}_P \ln\frac{T_2}{T_1} = (1\,\text{mol})\frac{5}{2}(8.314\text{ J/(K}\cdot\text{mol))}\ln\frac{930\text{ K}}{300\text{ K}} = +23.52\text{ J/K}$$

Path 2.

$$\Delta S_2 = -nR\ln\frac{P_2}{P_1} = (1\,\text{mol})(8.314\text{ J/(K}\cdot\text{mol))}\ln\frac{17\text{ atm}}{1\text{ atm}} = -23.56\text{ J/K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = +23.52\text{ J/K} - 23.56\text{ J/K} = -0.06\text{ J/K}$$

The total entropy change is almost zero. This is nearly an adiabatic compression.

Adapted from J. H. Noggle, *Physical Chemistry*, 3rd edition, 1996.

5. We used U to derive an equation in terms of T and V because the natural variables of U are T and V. T and P are the natural variables of H. Start with the fundamental equation for dH.

$$dH = TdS + VdP \qquad (1)$$

Write the total differential for dH in terms of T and P.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (2)$$

Substitute equation (2) into equation (1) and solve for dS.

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

$$dS = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP \qquad (3)$$

Write the total differential for dS in terms of T and P.

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad (4)$$

The terms preceding dT in both equations (3) and (4) must be equal.

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{C_P}{T} \qquad (5)$$

Likewise, the terms preceding dP in both equations (3) and (4) must be equal.

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \qquad (6)$$

For an ideal gas, H depends on temperature only; $(\partial H/\partial P)_T = 0$. Also for an ideal gas, $V = nRT/P$. Thus equation (6) becomes

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[0 - \frac{nRT}{P}\right] = -\frac{nR}{P} \qquad (7)$$

Substitute equations (5) and (7) into equation (4) and integrate. Note also for an ideal gas, $(\partial C_\mathrm{P}/\partial T)_P = 0$.

$$\int dS = \int_{T_1}^{T_2} \frac{C_\mathrm{P}}{T}\,dT - \int_{P_1}^{P_2} \frac{nR}{P}\,dP$$

$$\Delta S = C_\mathrm{P} \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$$

$$\Delta\overline{S} = \overline{C}_\mathrm{P} \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

6. Here are two approaches. One approach starts with the differential expression for H in terms of S and P.

$$dH = TdS - VdP$$

At constant P this expression becomes

$$dH = TdS$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

Another approach is to apply the product rule to the initial expression.

$$\left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P$$

Use the definition of heat capacity and the Useful Relationship from the handout.

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

From the reciprocal rule for partial derivatives,

$$\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial S}{\partial T}\right)_P = 1$$

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{1}{\frac{C_P}{T}} = \frac{T}{C_P}$$

Substitute into the product rule expression.

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

Adapted from J. H. Noggle, *Physical Chemistry*, 3rd edition, 1996.

7.(A) This is a Joule-Thomson expansion of an ideal diatomic gas. We applied the 1st law of thermodynamics to a Joule-Thomson expansion in lecture and calculated that the expansion does not cool an ideal gas and the expansion is isenthalpic, $\Delta H = 0$. So there is no enthalpy change between the inlet stream and the outlet stream.

Define n_cold as the mols of cold output and n_hot as the mols of hot output. Assume a basis of 1 mol total, so $n_\mathrm{hot} = 1 - n_\mathrm{cold}$.

Calculate the enthalpy change.

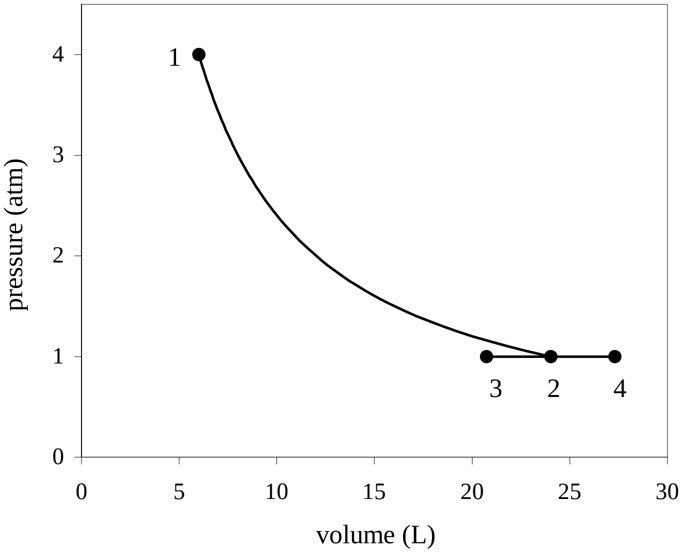
$$\begin{aligned}\Delta H &= 0 = H_{\text{in}} - n_{\text{cold}}H_{\text{cold out}} - n_{\text{hot}}H_{\text{hot out}}\\ &= (n_{\text{cold}}+n_{\text{hot}})H_{\text{in}} - n_{\text{cold}}H_{\text{cold out}} - n_{\text{hot}}H_{\text{hot out}}\\ &= n_{\text{cold}}(H_{\text{in}}-H_{\text{cold out}})+n_{\text{hot}}(H_{\text{in}}-H_{\text{hot out}})\\ &= n_{\text{cold}}(H_{\text{in}}-H_{\text{cold out}})+(1-n_{\text{cold}})(H_{\text{in}}-H_{\text{hot out}})\end{aligned}$$

For this example calculation, assume $T_{\text{cold}} = -4.$ºC (269 K) and $T_{\text{hot}} = 25.$ºC (298 K).

$$\begin{aligned}0 &= n_{\text{cold}}\int_{293\text{ K}}^{269\text{ K}} \overline{C}_{\text{P, N}_2}\,dT + (1-n_{\text{cold}})\int_{293\text{ K}}^{298\text{ K}} \overline{C}_{\text{P, N}_2}\,dT\\ &= n_{\text{cold}}\overline{C}_{\text{P, N}_2}(269\text{ K}-293\text{ K}) + (1-n_{\text{cold}})\overline{C}_{\text{P, N}_2}(298\text{ K}-293\text{ K})\\ &= -24n_{\text{cold}} + (1-n_{\text{cold}})5\\ -5 &= -29n_{\text{cold}}\\ n_{\text{cold}} &= 0.17\text{ mol}\end{aligned}$$

Thus $n_{\text{hot}} = 1 - n_{\text{cold}} = 0.83$ mol. And $n_{\text{cold}}/n_{\text{hot}} = 0.17/0.83 = 0.20$.

(B) To verify that the 2nd law of thermodynamics is satisfied we must show that $\Delta S > 0$. The actual process is irreversible. To calculate ΔS we must devise a reversible path from the initial condition (1 mol at 4 atm and 293 K) to the final conditions: a cold stream (0.17 mol at 1 atm and 269 K) and a hot stream (0.83 mol at 1 atm and 298 K.) Use two reversible processes: (1) path 1→2: a reversible isothermal expansion to 1 atm and 293 K and (2) an isobaric cooling - path 2→3 (or heating - path 2→4) for the two outputs.



Calculate the change in entropy for the cold stream.

$$\Delta S = \Delta S_{\text{isothermal}} + \Delta S_{\text{isobaric}}$$

For the isothermal path, use the expression derived in class.

$$\Delta S_{\text{isothermal}} = nR\ln\frac{V_2}{V_1}$$

For the isobaric path, use the expression given in the exercise statement.

$$\Delta S_{\text{isobaric}} = n\overline{C}_{\text{P}}\ln\frac{T_2}{T_1}$$

Substitute these expressions into the equation for the total entropy. Write an expression for the cold stream and use the ideal gas law relation $V_2/V_1 = P_1/P_2$ for an isothermal process.

$$\begin{aligned}\Delta S_{\text{cold}} &= n_{\text{cold}} R \ln \frac{V_2}{V_1} + n_{\text{cold}} \overline{C}_{\text{P}} \ln \frac{T_{\text{cold}}}{T_1} \\ &= n_{\text{cold}} R \ln \frac{P_1}{P_2} + n_{\text{cold}} \overline{C}_{\text{P}} \ln \frac{T_{\text{cold}}}{T_1}\end{aligned}$$

Substitute the pressures and temperatures into the above expression.

$$\begin{aligned}\Delta S_{\text{cold}} &= (0.17\text{ mol})(8.314\text{ J}/(\text{K}\cdot\text{mol}))\ln\frac{4}{1} + (0.17\text{ mol})(29\text{ J}/(\text{K}\cdot\text{mol})\ln\frac{269}{293} \\ &= +1.96\text{ J}/\text{K} - 0.42\text{ J}/\text{K} = +1.54\text{ J}/\text{K}\end{aligned}$$

The calculation for the hot stream is similar and the result is

$$\Delta S_{\text{hot}} = n_{\text{hot}} R \ln \frac{P_1}{P_2} + n_{\text{hot}} \overline{C}_{\text{P}} \ln \frac{T_{\text{hot}}}{T_1}$$

Substitute the pressures and temperatures into the above expression.

$$\begin{aligned}\Delta S_{\text{hot}} &= (0.83\text{ mol})(8.314\text{ J}/(\text{K}\cdot\text{mol}))\ln\frac{4}{1} + (0.83\text{ mol})(29\text{ J}/(\text{K}\cdot\text{mol})\ln\frac{298}{293} \\ &= +9.57\text{ J}/\text{K} + 0.41\text{ J}/\text{K} = +9.97\text{ J}/\text{K}\end{aligned}$$

Calculate the total entropy change.

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{cold}} + \Delta S_{\text{hot}} \\ &= 1.54\text{ J}/\text{K} + 9.97\text{ J}/\text{K} = +11.5\text{ J}/\text{K}\end{aligned}$$

Because $\Delta S > 0$, the separation into hot and cold streams is spontaneous. The key to spontaneity is the pressure drop to 1 atm from 4 atm, which is strongly spontaneous.

The Team Competition Champions for Calculation Session 7:

Team Losers II

Christina Boehm, Mahika Arora, Liam Chelkowski, Noyonima Masud, and Shani Abeyakoon

Score =91/96 and the 3rd of 20 team submissions!

The 2nd Law Table of Truths

formula	isolated system	ideal gas	spontaneous process	reversible process	adiabatic process	isothermal process	isobaric process	isochoric process
$TdS = PdV$		X		X		X		
$\Delta S = 0$				X	X			
$\Delta S > 0$	X		X					
$\Delta A < 0$			X			X		X
$\Delta A = w_{\text{max}}$				X		X		
$d\overline{S} = \dfrac{\overline{C}_{\text{P}}}{T}dT$							X	
$d\overline{S} = \dfrac{R}{\overline{V}}d\overline{V}$		X				X		
$d\overline{S} = \dfrac{\overline{C}_{\text{V}}}{T}dT$								X
$d\overline{S} = -\dfrac{R}{P}dP$		X				X		
$\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$				X			X	
$\Delta S_{\text{mix}} = -R\sum y_i \ln y_i$		X						
$\Delta S = C_V \ln\dfrac{T_2}{T_1} + R\ln\dfrac{V_2}{V_1}$		X		X				

Notes on some items from the 2nd Law Table of Truths.

$TdS = PdV$

This equation obtains from the fundamental equation $dU = TdS - PdV$ when $dU = 0$. The internal energy is constant for an isothermal process and an ideal gas. Note that $dU = TdS - PdV$ was derived from the 1st law of thermodynamics, $dU = \delta q + \delta w$, by substituting $TdS = \delta q_{\text{rev}}$. Thus it is true only when applied to reversible processes. See McQuarrie and Simon, p. 853, eqn (21.1).

$\Delta S > 0$

This is the condition for spontaneity for an isolated system only; $q = 0$ and $w = 0$. For a closed system, one may do work on the system and decrease its entropy. Or one may extract heat from the system and decrease its entropy.

$\Delta A < 0$

See McQuarrie and Simon, pp. 881-2, eqn (22.5).

$\Delta G < 0$

See McQuarrie and Simon, pp. 884, eqn (22.12).

$\Delta A = w_{\text{max}}$

See McQuarrie and Simon, pp. 883, eqn (22.9).

$\Delta G = w_{\text{max non PV}}$

See McQuarrie and Simon, pp. 886, eqn (22.16).

$$d\bar{S} = \frac{\bar{C}_{\mathrm{P}}}{T}\,dT$$

This obtains from the useful relation

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_{\mathrm{P}}}{T}$$

so it requires that P is constant.

$$d\bar{S} = \frac{R}{\bar{V}}\,d\bar{V}$$

This is derived from the Maxwell relation, assuming an ideal gas.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\frac{nRT}{V}\right)_V = \frac{nR}{V}$$

so it also requires that T is constant.

$$d\bar{S} = \frac{\bar{C}_{\mathrm{V}}}{T}\,dT$$

This obtains from the useful relation

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_{\mathrm{V}}}{T}$$

so it requires that V is constant.

$$d\bar{S} = -\frac{R}{P}\,dP$$

This is derived from the Maxwell relation, assuming an ideal gas.

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

so it also requires that T is constant.

$$\Delta S_{\mathrm{vap}} = \Delta H_{\mathrm{vap}}/T$$

See McQuarrie and Simon, pp. 857, section 21-3.

$$\Delta S_{\mathrm{mix}} = -R\sum y_i \ln y_i$$

See McQuarrie and Simon, pp. 836, equation (20.30).

$$\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$

See Slide 6 of Lecture T7.