

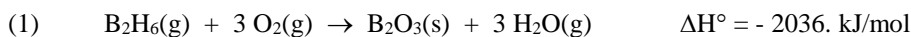
CHM 3400 – Problem Set 3

Due date: Wednesday, February 5th.

Do all of the following problems. Show your work.

“Scientists do not believe; they check.” – John Cornforth

1) Using only the data given below, find the value for ΔH°_f for diborane, $B_2H_6(g)$, at 298. K.



2) One mole of argon gas ($C_{p,m} = 20.79 \text{ J/mol}\cdot\text{K}$) at an initial temperature $T_i = 450.0 \text{ K}$ is expanded adiabatically and irreversibly against an unknown constant external pressure. The value for work for the process is $w = - 1098. \text{ J}$. Based on this information find the final temperature of the gas. You may assume that argon is an ideal gas.

3) Gasoline consists of a mixture of hydrocarbons and other compounds. One of these hydrocarbons is n-decane ($C_{10}H_{22}(\ell)$).

a) Give the correctly balanced combustion reaction for n-decane.

b) The enthalpy of combustion for n-decane is $\Delta H^\circ_{\text{comb}}(C_{10}H_{22}(\ell)) = - 6777.9 \text{ kJ/mol}$. Based on this information, find the numerical value for $\Delta H^\circ_f(C_{10}H_{22}(\ell))$, the enthalpy of formation for n-decane. Note that $\Delta H^\circ_f(CO_2(g)) = - 393.51 \text{ kJ/mol}$, $\Delta H^\circ_f(H_2O(\ell)) = - 285.83 \text{ kJ/mol}$.

4) Consider the following gas phase chemical reaction



a) Using the table of average bond enthalpies in Handout 2, estimate the value for ΔH_{rxn} for reaction 4.1

b) Using the thermochemical data in the table below (given at $T = 25.0 \text{ }^\circ\text{C}$), find the value for $\Delta H^\circ_{\text{rxn}}$ for reaction 4.1

c) Which value for reaction enthalpy is better? Why?

d) Using the thermochemical data in the table below, find the value for $\Delta S^\circ_{\text{rxn}}$ for reaction 4.1

e) Using your values for $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ for reaction 4.1, find the values for $\Delta S^\circ_{\text{sys}}$, $\Delta S^\circ_{\text{surr}}$, and $\Delta S^\circ_{\text{univ}}$ when one mole of reaction 4.1 is carried out under standard conditions and $T = 25.0 \text{ }^\circ\text{C}$.

f) Will reaction 4.1 occur spontaneously at standard conditions and $T = 25.0 \text{ }^\circ\text{C}$? Why or why not?

Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)	ΔG°_f (kJ/mol)	$C_{p,m}$ (J/mol·K)
$C_2H_4(g)$	52.26	219.56	68.15	43.56
$C_2H_6(g)$	- 84.68	229.60	- 32.82	52.63
$NH_3(g)$	- 46.11	192.45	- 16.45	35.06
$N_2(g)$	0.0	205.2	0.0	29.12

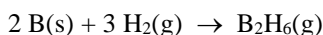
5) 60.00 g of $H_2O(\ell)$ ($M = 18.02 \text{ g/mol}$) at $T = 40.00 \text{ }^\circ\text{C}$ is added to 40.00 g of $H_2O(\ell)$ at $T = 20.00 \text{ }^\circ\text{C}$ in an insulated container.

a) What is T_f , the final temperature of the water when equilibrium is reached? Note that the constant pressure molar heat capacity for water is $C_{p,m} = 75.29 \text{ J/mol}\cdot\text{K}$, and is constant over the temperature range of the problem.

b) What is ΔS for the above process? (HINT: Since entropy is a state function, you can find the change in entropy separately for the 60.00 g of water and the 40.00 g of water, and then combine the results to obtain ΔS .)

Solutions.

1) The formation reaction is



We need some combination of processes that sum to this reaction.



In the above we have used the fact that reversing the direction of a reaction changes the sign of ΔH° , and multiplying a reaction by a constant value means that ΔH° must also be multiplied by the same constant. Both of these are consequences of enthalpy being a state function.

2) From the first law

$$\Delta U = q + w$$

The process is adiabatic, and so $q = 0$; therefore $\Delta U = w = -1098. \text{ J}$

For any process on an ideal gas, we can find the change in internal energy using

$$\Delta U = \int_{T_i}^{T_f} n C_{V,m} dT$$

It is also true for an ideal gas that $C_{p,m} - C_{v,m} = R$

$$\text{So } C_{v,m} = C_{p,m} - R = 20.79 \text{ J/mol}\cdot\text{K} - 8.3145 \text{ J/mol}\cdot\text{K} = 12.48 \text{ J/mol}\cdot\text{K}$$

Since the value for $C_{v,m}$ in this problem is independent of temperature, we may say

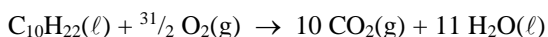
$$\Delta U = \int_{T_i}^{T_f} n C_{v,m} dT = n C_{v,m} \int_{T_i}^{T_f} dT = n C_{v,m} (T_f - T_i) = n C_{v,m} \Delta T$$

$$\text{So } n C_{v,m} \Delta T = \Delta U$$

$$\Delta T = \frac{\Delta U}{n C_{v,m}} = \frac{-1098 \text{ J}}{(1.000 \text{ mol})(12.48 \text{ J/mol}\cdot\text{K})} = -88.0 \text{ K}$$

$$\text{And so } \Delta T = T_f - T_i ; T_f = T_i + \Delta T = 450.0 \text{ K} + (-88.0 \text{ K}) = 362.0 \text{ K}$$

3) a) Based on the definition of the combustion reaction, the reaction is



Note that, as is the case for formation reactions, we sometimes will have fractional coefficients in the balanced combustion reaction (as we must satisfy the requirement that it is one mole of a single reactant that is involved).

b) From the general expression for the enthalpy change for a chemical reaction, we may say

$$\begin{aligned}\Delta H^{\circ}_{\text{rxn}} &= \Delta H^{\circ}_{\text{comb}}(\text{C}_{10}\text{H}_{22}(\ell)) = [\sum \Delta H^{\circ}_{\text{f}}(\text{products})] - [\sum \Delta H^{\circ}_{\text{f}}(\text{reactants})] \\ &= [10 \Delta H^{\circ}_{\text{f}}(\text{CO}_2(\text{g})) + 11 \Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}(\ell))] - [\Delta H^{\circ}_{\text{f}}(\text{C}_{10}\text{H}_{22}(\ell)) + {}^{31/2} \Delta H^{\circ}_{\text{f}}(\text{O}_2(\text{g}))]\end{aligned}$$

Solving for $\Delta H^{\circ}_{\text{f}}(\text{C}_{10}\text{H}_{22}(\ell))$ gives

$$\begin{aligned}\Delta H^{\circ}_{\text{f}}(\text{C}_{10}\text{H}_{22}(\ell)) &= [10 \Delta H^{\circ}_{\text{f}}(\text{CO}_2(\text{g})) + 11 \Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}(\ell))] - [\Delta H^{\circ}_{\text{comb}}(\text{C}_{10}\text{H}_{22}(\ell)) + {}^{31/2} \Delta H^{\circ}_{\text{f}}(\text{O}_2(\text{g}))] \\ &= [10 (- 393.51 \text{ kJ/mol}) + 11 (- 285.83 \text{ kJ/mol})] - [(-6777.9 \text{ kJ/mol}) + {}^{31/2} (0 \text{ kJ/mol})] \\ &= - 301.3 \text{ kJ/mol}\end{aligned}$$

4) a) We can estimate the enthalpy change for the reaction as

$$\Delta H \cong [\sum (\text{bonds for reactants})] - [\sum (\text{bonds for products})]$$

where we use average values for bond strengths.

Reactant bonds	Product bonds
6 N-H 6 (388 kJ/mol)	1 N≡N 1 (945 kJ/mol)
12 C-H 12 (412 kJ/mol)	18 C-H 18 (412 kJ/mol)
3 C=C 3 (612 kJ/mol)	3 C-C 3 (348 kJ/mol)
TOTAL = 9108 kJ/mol	TOTAL = 9405 kJ/mol

So $\Delta H \cong (9108 \text{ kJ/mol}) - (9405 \text{ kJ/mol}) = - 297 \text{ kJ/mol}$

$$\begin{aligned}\text{b) } \Delta H^{\circ}_{\text{rxn}} &= [\sum \Delta H^{\circ}_{\text{f}}(\text{products})] - [\sum \Delta H^{\circ}_{\text{f}}(\text{reactants})] \\ &= [\Delta H^{\circ}_{\text{f}}(\text{N}_2(\text{g})) + 3 \Delta H^{\circ}_{\text{f}}(\text{C}_2\text{H}_6(\text{g}))] - [2 \Delta H^{\circ}_{\text{f}}(\text{NH}_3(\text{g})) + 3 \Delta H^{\circ}_{\text{f}}(\text{C}_2\text{H}_4(\text{g}))] \\ &= [(0 \text{ kJ/mol}) + 3 (- 84.68 \text{ kJ/mol})] - [2 (-46.11 \text{ kJ/mol}) + 3 (52.26 \text{ kJ/mol})] \\ &= (- 254.04 \text{ kJ/mol}) - (64.56 \text{ kJ/mol}) = - 318.60 \text{ kJ/mol}\end{aligned}$$

c) The value calculated from the formation enthalpies is better, as it is based on precise experimental data, rather than average bond strengths.

$$\begin{aligned}\text{d) } \Delta S^{\circ}_{\text{rxn}} &= [\sum S^{\circ}(\text{products})] - [\sum S^{\circ}(\text{reactants})] \\ &= [S^{\circ}(\text{N}_2(\text{g})) + 3 S^{\circ}(\text{C}_2\text{H}_6(\text{g}))] - [2 S^{\circ}(\text{NH}_3(\text{g})) + 3 S^{\circ}(\text{C}_2\text{H}_4(\text{g}))] \\ &= [(205.2 \text{ J/mol}\cdot\text{K}) + 3 (229.60 \text{ J/mol}\cdot\text{K})] - [2 (192.45 \text{ J/mol}\cdot\text{K}) + 3 (219.56 \text{ J/mol}\cdot\text{K})] \\ &= (894.0 \text{ J/mol}\cdot\text{K}) - (1043.58 \text{ J/mol}\cdot\text{K}) = - 149.6 \text{ J/mol}\cdot\text{K}\end{aligned}$$

$$\text{e) } \Delta S^{\circ}_{\text{syst}} = \Delta S^{\circ}_{\text{rxn}} = - 149.6 \text{ J/mol}\cdot\text{K}$$

$$\Delta S^{\circ}_{\text{surr}} = - \frac{\Delta H^{\circ}_{\text{rxn}}}{T} = - \frac{(- 318600. \text{ J/mol})}{(298.15 \text{ K})} = + 1068.6 \text{ J/mol}\cdot\text{K}$$

So $\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{sys}} + \Delta S^\circ_{\text{surr}} = (-149.6 \text{ J/mol}\cdot\text{K}) + (1068.6 \text{ J/mol}\cdot\text{K}) = +919.0 \text{ J/mol}\cdot\text{K}$

f) Since $\Delta S^\circ_{\text{univ}} > 0$, the reaction will be spontaneous for standard conditions and $T = 25.0 \text{ }^\circ\text{C}$. Notice that the reaction is spontaneous even though $\Delta S^\circ_{\text{rxn}}$ is less than zero. The only thing that matters when using entropy and the Second Law to decide if a reaction is spontaneous is the sign for the entropy change for the universe.

5) a) Because we are mixing hot and cold water, and because the heat capacity is constant over the temperature range of the problem, it is relatively easy to find the final temperature for the system.

If we define $\Delta T_{\text{hot}} = T_{\text{hot}} - T_f = \text{change of temperature of the hot water}$ $m_{\text{hot}} = \text{mass of hot water}$
 $\Delta T_{\text{cold}} = T_f - T_{\text{cold}} = \text{change of temperature of the cold water}$ $m_{\text{cold}} = \text{mass of cold water}$

Then $\Delta T_{\text{hot}} m_{\text{hot}} = \Delta T_{\text{cold}} m_{\text{cold}}$

$$\Delta T_{\text{hot}} = (m_{\text{cold}}/m_{\text{hot}}) \Delta T_{\text{cold}}$$

But $\Delta T_{\text{hot}} + \Delta T_{\text{cold}} = (T_{\text{hot}} - T_{\text{cold}})$

So $(m_{\text{cold}}/m_{\text{hot}}) \Delta T_{\text{cold}} + \Delta T_{\text{cold}} = (T_{\text{hot}} - T_{\text{cold}})$

$$\Delta T_{\text{cold}} [1 + (m_{\text{cold}}/m_{\text{hot}})] = (T_{\text{hot}} - T_{\text{cold}})$$

$$\Delta T_{\text{cold}} = \frac{(T_{\text{hot}} - T_{\text{cold}})}{[1 + (m_{\text{cold}}/m_{\text{hot}})]} = \frac{(40.00 \text{ }^\circ\text{C} - 20.00 \text{ }^\circ\text{C})}{[1 + (40.00 \text{ g}/60.00 \text{ g})]} = 12.00 \text{ }^\circ\text{C}$$

And so $T_f = T_{\text{cold}} + \Delta T = 20.00 \text{ }^\circ\text{C} + 12.00 \text{ }^\circ\text{C} = 32.00 \text{ }^\circ\text{C}$

b) It is easiest to find the entropy change for the hot water and the cold water separately, and then combine the results to find ΔS .

moles hot water = $60.00 \text{ g} \frac{1 \text{ mol}}{18.02 \text{ g}} = 3.330 \text{ mol}$ moles cold water = $40.00 \text{ g} \frac{1 \text{ mol}}{18.02 \text{ g}} = 2.220 \text{ mol}$

$T_{\text{hot, initial}} = 40.00 \text{ }^\circ\text{C} = 313.15 \text{ K}$

$T_{\text{cold, initial}} = 20.00 \text{ }^\circ\text{C} = 293.15 \text{ K}$

$T_f = 32.00 \text{ }^\circ\text{C} = 305.15 \text{ K}$

For heating at constant pressure, $\Delta S = \int_{T_i}^{T_f} \frac{n C_{p,m}}{T} dT$

and if $C_{p,m}$ is constant $\Delta S = n C_{p,m} \int_{T_i}^{T_f} dT/T = n C_{p,m} \ln(T_f/T_i)$

So $\Delta S_{\text{hot}} = (3.330 \text{ mol}) (75.29 \text{ J/mol}\cdot\text{K}) \ln(305.15 \text{ K}/313.15 \text{ K}) = -6.488 \text{ J/K}$

$\Delta S_{\text{cold}} = (2.220 \text{ mol}) (75.29 \text{ J/mol}\cdot\text{K}) \ln(305.15 \text{ K}/293.15 \text{ K}) = +6.706 \text{ J/K}$

Combining, we get $\Delta S = \Delta S_{\text{hot}} + \Delta S_{\text{cold}} = (-6.488 \text{ J/K}) + (6.706 \text{ J/K}) = +0.218 \text{ J/K}$

Since the container is insulated, the process is adiabatic, and so $\Delta S_{\text{surr}} = 0$, and so $\Delta S_{\text{univ}} = \Delta S = 0.218 \text{ J/K}$. Since $\Delta S_{\text{univ}} > 0$, the process is spontaneous, as expected.