"Fun with Thermodynamics!"

(#1) ~~1.~~ Answer the following questions about thermodynamics. AP 2005 Form B

	Substance	Combustion Reaction	Enthalpy of Combustion, ΔH°_{comb}, at 298 K (kJ mol^{-1})
Rxn ①	$H_2(g)$	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	−290
Rxn ②	$C(s)$	$C(s) + O_2(g) \rightarrow CO_2(g)$	−390
Rxn ③	$CH_3OH(l)$		−730

(a) In the ~~empty box in the table above,~~ space below write a balanced chemical equation for the complete combustion of one mole of $CH_3OH(l)$. Assume products are in their standard states at 298 K. Coefficients do not need to be whole numbers. (so $H_2O(l)$ since 25°C)

$$CH_3OH_{(l)} + \frac{3}{2} O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O_{(l)} \quad (\Delta H = -730\text{ kJ})$$

(b) On the basis of your answer to part (a) and the information in the table, determine the enthalpy change for the reaction $C(s) + H_2(g) + H_2O(l) \rightarrow CH_3OH(l)$.

Rxn ① $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ $\quad \Delta H = -290$ kJ

Rxn ② $C_{(s)} + O_2 \rightarrow CO_2$ $\quad \Delta H = -390$ kJ

Reverse of Rxn ③ $CO_2 + 2H_2O \rightarrow CH_3OH + \frac{3}{2} O_2$ $\quad \Delta H = +730$ kJ

$H_2 + C + H_2O \rightarrow CH_3OH$ $\quad \Delta H = -290 + -390 + 730$

$\Delta H = 50$ kJ

(c) Write the balanced chemical equation that shows the reaction that is used to determine the enthalpy of formation for one mole of $CH_3OH(l)$.

$$C_{(s)} + 2\,H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CH_3OH_{(l)}$$

(d) Predict the sign of ΔS° for the combustion of $H_2(g)$. Explain your reasoning.

ΔS° will be negative since $1\frac{1}{2}$ moles gas $(1\,H_2 + \frac{1}{2} O_2)$ become 1 mole of liquid; $\Delta n_{gas} = -1.5$. Since the number of gas molecules decreases, entropy decreases.

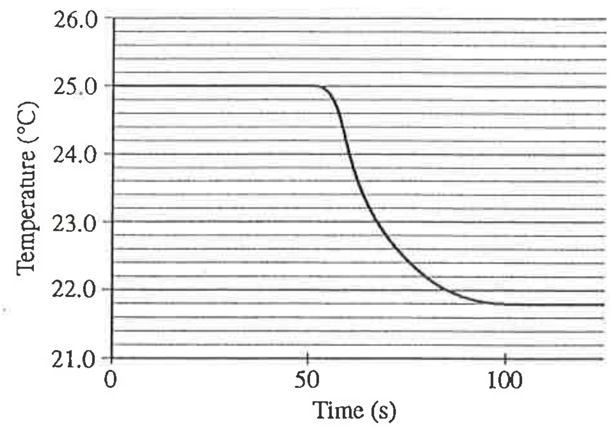
(e) On the basis of bond energies, explain why the combustion of $H_2(g)$ is exothermic.

H–H + ½ (O=O) ⟶ (H–O–H)

The energy required to break 1 mole of (H–H) bonds and ½ mole of (O=O) bonds must be less than the amount of energy released when 2 moles of (H–O) bonds.

② A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2. The student places 91.95 g of water at 25°C into a coffee-cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25°C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.

2010 AP



$\Delta T = 21.8°C - 25.0°C$

$\Delta T = -3.2\ °C$

(a) Determine the change in temperature of the solution that results from the dissolution of the urea.

(b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

The dissolution must be endothermic. Since the water decreased temperature (ΔT_{H_2O} was negative), the urea must have absorbed energy from the H_2O as it dissolved.

(c) Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J g^{-1} $°C^{-1}$ throughout the experiment.

(i) Calculate the heat of dissolution of the urea in joules.

(ii) Calculate the molar enthalpy of solution, ΔH°_{soln}, of urea in kJ mol^{-1}.

include both masses since the specific heat is for both.

i) $|q| = |mc\Delta T| = (91.95\,g + 5.13\,g)(4.2\,J/g°C)(3.2\,°C) = 1304.76\,J$

1300 J (i)

H_2NCONH_2

ii) $(5.13\,g\ \text{urea})\left(\frac{1\,\text{mole}}{60.0554\,g}\right) = 0.08542$ moles urea

$\frac{(1304.76\,J)\left(\frac{1\,kJ}{1000\,J}\right)}{0.08542\ \text{moles}} = \Delta H = 15.27 \rightarrow$ 15 kJ/mole (ii)

(d) Using the information in the table below, calculate the value of the molar entropy of solution, ΔS°_{soln}, of urea at 298 K. Include units with your answer.

	Accepted Value
ΔH°_{soln} of urea	14.0 kJ mol^{-1}
ΔG°_{soln} of urea	−6.9 kJ mol^{-1}

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$-6.9\ kJ/mole = 14.0\ \frac{kJ}{mole} - 298K(\Delta S^\circ)$

$\Delta S^\circ = 0.070134\ kJ/mol\cdot K$

$\Delta S^\circ = 0.0701\ \frac{kJ}{mol\cdot K}$ or $70.1\ J/mol\cdot K$

(#2 cont'd) (2010, cont'd)

(e) The student repeats the experiment and this time obtains a result for ΔH°_{soln} of urea that is 11 percent below the accepted value. Calculate the value of ΔH°_{soln} that the student obtained in this second trial.

(14.0 KJ/mol)(0.11) = 1.54 KJ/mole (or do 14.0(.89) = 12.5)

↑ accepted value

14.0 KJ/mole − 1.54 KJ/mole = 12.46 → **12.5 KJ/mole**

(f) The student performs a third trial of the experiment but this time adds urea that has been taken directly from a refrigerator at 5°C. What effect, if any, would using the cold urea instead of urea at 25°C have on the experimentally obtained value of ΔH°_{soln}? Justify your answer.

ΔHsolution would be larger.

using cold urea would make the final temperature of urea/H_2O even lower, so the magnitude of ΔT would be larger (or "T would decrease more"), causing larger values for |q| and |ΔH|.

(#3) 7. Aluminum metal can be recycled from scrap metal by melting the metal to evaporate impurities. (2015 AP)

(a) Calculate the amount of heat needed to purify 1.00 mole of Al originally at 298 K by melting it. The melting point of Al is 933 K. The molar heat capacity of Al is 24 J/(mol·K), and the heat of fusion of Al is 10.7 kJ/mol.

① heat solid Al from 298 K to 933 K

q = mcΔT = (1.00 mole)(24 J/mol·K)(933 K − 298 K) = 15240 J or 15.24 KJ

② melt solid at 933 K

q = nΔHfusion = (1.00 mole)(10.7 KJ/mole) = 10.7 KJ

15.24 + 10.7 = 25.9 → **26 KJ**

(b) The equation for the overall process of extracting Al from Al_2O_3 is shown below. Which requires less energy, recycling existing Al or extracting Al from Al_2O_3? Justify your answer with a calculation.

$$Al_2O_3(s) \rightarrow 2\,Al(s) + \frac{3}{2}O_2(g) \qquad \Delta H^\circ = 1675\ \text{kJ/mol}_{rxn}$$

recycling requires less energy.

$\frac{1675\ KJ}{2\ mole\ Al}$ = 837.5 KJ / 1 mole Al

837.5 KJ > 26 KJ, so extracting Al from Al_2O_3 takes more energy, recycling requires less energy

#4

$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$ $\Delta H° = -114.1$ kJ, $\Delta S° = -146.5$ J K^{-1} (2001 AP)

~~2.~~ The reaction represented above is one that contributes significantly to the formation of photochemical smog.

(a) Calculate the quantity of heat released when 73.1 g of NO(g) is converted to $NO_2(g)$. *a positive amt of heat is released.*

$$(73.1\text{ g NO})\left(\frac{1\text{ mole}}{30.0061\text{ g}}\right)\left(\frac{114.1\text{ kJ}}{2\text{ mole NO}}\right) = 138.98 \rightarrow \boxed{139\text{ kJ released}}$$

(b) For the reaction at 25°C, the value of the standard free-energy change, $\Delta G°$, is −70.4 kJ.

(i) Calculate the value of the equilibrium constant, K_{eq}, for the reaction at 25°C.

(ii) Indicate whether the value of $\Delta G°$ would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer.

$$\Delta G° = -RT \ln K_{eq}$$

$$K_{eq} = e^{-\Delta G°/RT}$$

$$= e^{\frac{-(-70400\text{ J})}{(8.314\frac{J}{mol\cdot K})(298\text{ K})}}$$

$$= e^{28.415} = 2.1899 \times 10^{12}$$

$$K_{eq} = \boxed{2.2 \times 10^{12}}$$ 2 or 3 SF ok

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta S°$ is negative, so as T increases, "$-T\Delta S$" will become a larger positive number, so $\Delta G°$ will become less negative.

(c) Use the data in the table below to calculate the value of the standard molar entropy, $S°$, for $O_2(g)$ at 25°C.

	Standard Molar Entropy, $S°$ (J K^{-1} mol^{-1})
NO(g)	210.8
$NO_2(g)$	240.1

$$\Delta S°_{rxn} = 2\,S_f(NO_2) - 2\,S_f(NO) - 1\,S_f(O_2)$$

$$-146.5\tfrac{J}{K} = 2(240.1\tfrac{J}{K}) - 2(210.8\tfrac{J}{K}) - S_f(O_2)$$

$$S_f(O_2) = \boxed{205.1\text{ J/K}}$$

(d) Use the data in the table below to calculate the bond energy, in kJ mol^{-1}, of the nitrogen-oxygen bond in NO_2. Assume that the bonds in the NO_2 molecule are equivalent (i.e., they have the same energy).

	Bond Energy (kJ mol^{-1})
Nitrogen-oxygen bond in NO	607
Oxygen-oxygen bond in O_2	495
Nitrogen-oxygen bond in NO_2	?

$2(N{=}O) + 1(O{=}O) \rightarrow 2(O{\cdots}N{\cdots}O)$

$\Delta H°_{rxn} = \Sigma$ bonds broken $\Delta H - \Sigma$ bonds formed ΔH

Broken: $2(N{=}O) + 1(O{=}O)$

$= 2(607) + 1(495) = 1709$ kJ

Formed: $4(N{\cdots}O) = 4x$

4 SF ok too.

$-114.1\text{ kJ} = 1709\text{ kJ} - 4x$ $x = 455.8 \rightarrow \boxed{456\text{ kJ/mole}}$

#5 (AP 1998)

$$C_6H_5OH(s) + 7\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(\ell)$$

When a 2.000-gram sample of pure phenol, $C_6H_5OH(s)$, is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

Substance	Standard Heat of Formation, ΔH_f°, at 25°C (kJ/mol)	Absolute Entropy, S°, at 25°C (J/mol·K)
C(*graphite*)	0.00	5.69
$CO_2(g)$	–393.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(\ell)$	–285.85	69.91
$O_2(g)$	0.00	205.0
$C_6H_5OH(s)$	?	144.0

(a) Calculate the molar heat of combustion of phenol in kilojoules per mole at 25°C.

$$(2.000g\ C_6H_5OH)\left(\frac{1\text{mole}}{94.11289g}\right) = 0.021251 \text{ moles } C_6H_5OH$$

$$\frac{64.98 \text{ kJ released}}{.021251 \text{ moles}} = 3057.72 \rightarrow 3058 \text{ kJ released per mole of } C_6H_5OH.$$

$\Delta H_c = 3058$ kJ/mole ← some books report $\Delta H_{comb.}$ as a (+)

or $\Delta H_c = -3058$ kJ/mole

(b) Calculate the standard heat of formation, ΔH_f°, of phenol in kilojoules per mole at 25°C.

$$\Delta H_{rxn} = 6(\Delta H_f CO_2) + 3\Delta H_f(H_2O) - 1\Delta H_f(\text{phenol}) - 7(\Delta H_f O_2)$$

$$-3057.72 = 6(-393.5) + 3(-285.85) - X - 7(0)$$

$$X = -160.883 \rightarrow -160.8 \text{ kJ/mole}$$

1998 cont'd (#5 cont'd)

(c) Calculate the value of the standard free-energy change, $\Delta G°$, for the combustion of phenol at 25°C.

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta H° = -3057.(72)$ kJ/mole acc to part (a)

$\Delta S°_{rxn} = 6(213.6\ J/mol\cdot K) + 3(69.91) - 1(144.0) - 7(205.0) = -87.6(7)\ \frac{J}{mole\ K}$

$\Delta G° = \Delta H° - T\Delta S° = (-3057.(72)\ \frac{kJ}{mole}) - (298\ K)(-.0876(7)\ \frac{kJ}{mol\ K})$

$= -3031.594$

$\Delta G° = -3032$ kJ/mole

(d) If the volume of the combustion container is 10.0 liters, calculate the final pressure in the container when the temperature is changed to 110.°C. (Assume no oxygen remains unreacted and that all products are gaseous.)

$C_6H_5OH_{(l)} + 7O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(g)}$

$(2.000g\ C_6H_5OH)\left(\frac{1\ mole}{94.1128g}\right)\left(\frac{(6+3)\ moles\ gas}{1\ mole\ phenol}\right) = 0.1912599$ moles gas

$PV = nRT$

$P = \frac{nRT}{V} = \frac{(0.1912599\ mole)(.0821\ \frac{l\cdot atm}{mol\cdot K})(383\ K)}{10.0\ L}$

$= 0.60140$ atm

0.601 atm

Fun with Thermo, Continued!

6. $H_2O_{(l)}$ <-------> $H_2O_{(g)}$ $\Delta H°rxn = \pm 44.0 kJ$, $\Delta S°rxn = \pm 118.7$ J/mole-K

+44.0 kJ/mole   +118.7 J/mole·K

a. Determine the sign of ΔH°rxn and the sign of ΔS°rxn, based on what is happening in this process. Explain your choices.

This "rxn" shows the vaporization of H_2O.
vaporization is endothermic, so ΔH is positive.
moles of gas increase ($\Delta n_{gas} = +1$) so entropy increases; ΔS° is positive.

b. Calculate ΔG°rxn at 25°C.

$\Delta G° = \Delta H° - T\Delta S° = 44.0 \frac{kJ}{mole} - (298.15 K)(.1187 J/mole K) = 8.609$

8.6 kJ/mole

c. Calculate Kp for this reaction at 25°C.

$K_p = e^{\frac{-\Delta G°}{RT}} = e^{\frac{-8609.6 J/mole}{(8.314 \frac{kJ}{mol k})(298.15 K)}} = e^{-3.4733} = 0.03102$

$K_p = 0.031$

d. Write an expression for Kp for this reaction, in terms of the appropriate pressure(s) or concentration(s).

$K_p = P_{H_2O(g)}$ ← aka, the vapor pressure of water!

implied atmospheres for units since Kp

e. Based on the Kp value, what is the equilibrium vapor pressure of water at 25°C? Report your answer in atmospheres and in mmHg. (Note: the book value for the vapor pressure of water is 23.76 mmHg at this temperature.)

$K_p = .03102$ atm..

0.031 atm

$(.03102 atm)\left(\frac{760. mmHg}{1 atm}\right) = 23.57 \rightarrow$ 24 mmHg

f. Based on the values for ΔH and ΔS, calculate the temperature at which Kp = 1. Report in Celsius.

$\Delta G° = -RT \ln K_{eq} = -RT \ln(1) = 0$

$0 = \Delta G° = \Delta H° - T\Delta S° = 44.0 \frac{kJ}{mole} - T(.1187 \frac{kJ}{mol.K})$

$T = 370.6 K$ or $97.53°C$

98°C

g. The book value for (f) would be 100°C (aka the normal boiling point of water!) Why is your answer to (f) slightly different?

we used the ΔH° and ΔS° values for 25°C, and assumed that these values were independent of temperature. However, ΔH° and ΔS° are slightly dependent on temperature!

7. $2\ HI_{(g)}$ <-------> $H_{2\,(g)}$ + $I_{2\,(s)}$ $\Delta H^\circ rxn$ = - 51.88 kJ, ↙ or kJ/mole $\Delta S^\circ rxn = \pm$ 165.3 J/mole-K

a. Determine the sign of ΔS°rxn, based on what is happening in this process.
Justify your answer:

ΔS° must be negative. $\Delta n_{gas} = -1$. Since moles of gas decrease, entropy decreases.

b. Calculate ΔG°rxn at 25°C.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-51.88\ \tfrac{kJ}{mol}) - (298.15\ K)(-.1653\ \tfrac{kJ}{mol \cdot K})$$

$$= -2.5958\ kJ \rightarrow \boxed{-2.60\ kJ}$$

c. Calculate Kp for this reaction at 25°C.

$$K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{+2595.8\ J/mole}{8.314\ \frac{J}{mol\,K} \cdot 298.15\ K}} = e^{1.04719} = 2.8496$$

$\boxed{K_p = 2.8}$ or $\boxed{2.85}$

d. Calculate Kp for this reaction at 80°C.
Assume that ΔH and ΔS are not significantly temperature dependent for part (d) and (e).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -51.88\ kJ - (353.15\ K)(-.1653\ \tfrac{kJ}{K}) = 6.4957\ kJ$$

$$K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-6495.7\ J/mole}{(8.314\ \frac{J}{mol \cdot K})(353.15\ K)}} = e^{-2.212}$$

$K_p = .1094 \rightarrow \boxed{0.11}$ or $\boxed{0.109}$

sort of in between regular SF rules, and SF rules with log base 10.

e. Determine the temperature range for which this reaction is "thermodynamically favored."
Report answer in °C, and be sure to say whether it is spontaneous above or below the temperature you report.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$ ← solve for when $\Delta G^\circ = 0$ or $K_p = 1$

$$-51.88\ kJ - T(-.1653\ kJ/K) = 0$$

$T = 313.85\ K \rightarrow 40.7\ ^\circ C$

Rxn is spontaneous/favored $\boxed{\text{below } 40.7\ ^\circ C}$