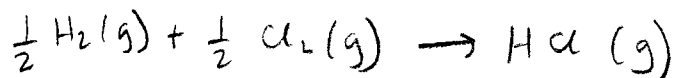1) Write equations for which the enthalpy change is the standard heat of formation per mole of the following compounds:

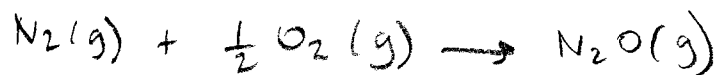(a) HCl(g)   (3 points)

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g)$$

Phase not included
(-1)
Equation not expressed
in terms of one mole 4
product -1
Not Balanced equation (-1)

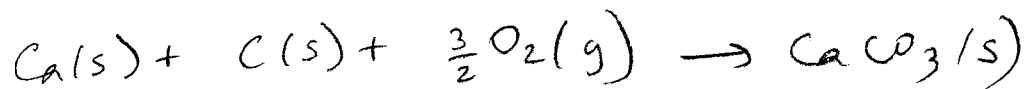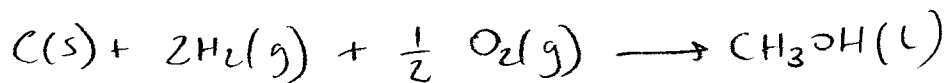(b) N₂O(g)   (3 points)

$$N_2(g) + \frac{1}{2} O_2(g) \longrightarrow N_2O(g)$$

(c) CaCO₃(s)   (3 points)

$$Ca(s) + C(s) + \frac{3}{2} O_2(g) \longrightarrow CaCO_3(s)$$

(d) CH₃OH(l)   (3 points)

$$C(s) + 2H_2(g) + \frac{1}{2} O_2(g) \longrightarrow CH_3OH(l)$$

2) Without performing calculations, state whether the entropy of the system increases or decreases during each of the each of the processes below. **For each explain your reasoning.**

a) oxidation of nitrogen: $N_2(g) + 2O_2(g) \rightarrow 2 NO_2(g)$ (4 points)

Decreases ②

#4 gas phase moles decrease from ② reactant to products.

b) sublimation of dry ice: $CO_2(s) \rightarrow CO_2(g)$ (4 points)

increases ②

Entropy of a gas typically greater than entropy of solid. Gas molecules are freer ② to move around than molecules in the solid phase

c) the evaporation of water from damp clothes (4 points)

increases. ②

Water molecules trapped in the clothes as a liquid have less entropy than ② water molecules in the vapor phase, free to move around

3) Although it is true that many spontaneous processes can be understood in terms of their moving in the direction that minimizes energy, not all spontaneous chemical reactions are exothermic. Explain how it is that an endothermic process can occur spontaneously. (9 points)

For a reaction to be spontaneous $\Delta G_r < 0$

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

Sign of ΔG_r depends on sign and relative magnitudes of ΔH_r & ΔS_r

For an endothermic reaction $\Delta H_r > 0$

if $\Delta S_r > 0$ and $T\Delta S_r > \Delta H_r$

then $\Delta G_r < 0 \implies$ spontaneous

4) Water expands when it freezes. How much work (**in kJ**) does 100g of water do when it freezes at $0^\circ C$ and bursts a water pipe with an opposing pressure of 1070 atm? The densities of $H_2O(l)$ and $H_2O(s)$ at $0^\circ C$ are 1.00 and 0.92 g/cm^3, respectively. (10 points)

$$\text{work} = -P_{ext} \, \Delta V \qquad ②$$

$$P_{ext} = 1070 \text{ atm} \qquad ①$$

$$\Delta V = V_{H_2O(s)} - V_{H_2O(l)} \qquad ①$$

$$V_{H_2O(s)} = \frac{100.g}{0.92 \, g/cm^3} = 109 \, cm^3 = 0.109 \, L \qquad ②$$

$$V_{H_2O(l)} = \frac{100.g}{1.00 \, g/cm^3} = 100 \, cm^3 = 0.100 \, L \qquad ②$$

$$\Delta V = 0.00900 \, L$$
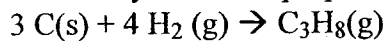
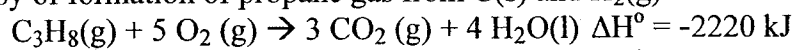$$\text{work} = -(1070 \text{ atm})(0.00900 \, L)$$
$$= -9.63 \, L\text{-atm}$$
$$= -976 \, J = -0.976 \, kJ \qquad ②$$

5) Consider the synthesis of propane, C_3H_8, a gas used as camping fuel:

$3 C(s) + 4 H_2 (g) \rightarrow C_3H_8(g)$

It is difficult to measure the enthalpy change of this reaction. However, standard enthalpies of combustion reactions are easy to measure. Given the following experimental data, determine the enthalpy of formation of propane gas from $C(s)$ and $H_2(g)$

$C_3H_8(g) + 5 O_2 (g) \rightarrow 3 CO_2 (g) + 4 H_2O(l)$ $\Delta H^\circ = -2220$ kJ

$C(s) + O_2 (g) \rightarrow CO_2 (g)$ $\Delta H^\circ = - 394$ kJ

$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)$ $\Delta H^\circ = - 286$ kJ

(12 points)

② $3 CO_2(g) + 4 H_2O(l) \longrightarrow C_3H_8(g) + 5O_2 (g)$ $\Delta H^\circ = +2220 kJ$

② $3 C(s) + 3 O_2(g) \longrightarrow 3 CO_2 (g)$ $\Delta H^\circ = 3(-394) kJ$

② $4 H_2(g) + 2 O_2 (g) \longrightarrow 4 H_2O(l)$ $\Delta H^\circ = 4 (-286) kJ$

③ $3 C(s) + 4 H_2(g) \longrightarrow C_3H_8(g)$
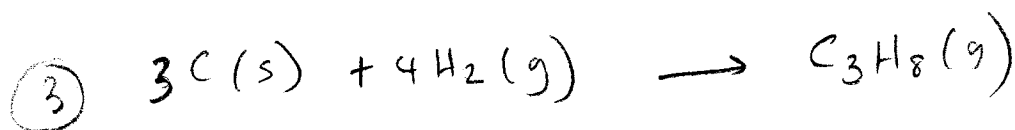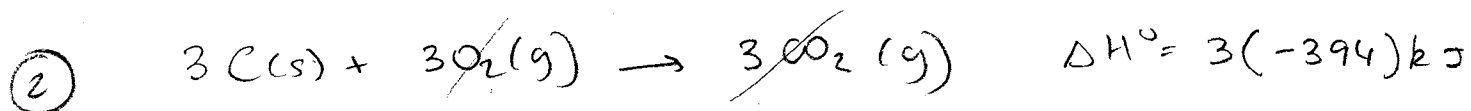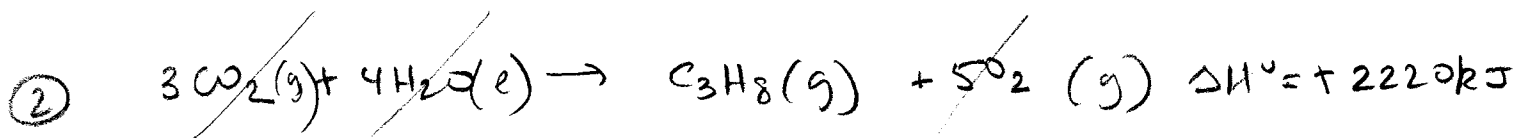
③ $\Delta H^\circ = +2220 kJ + 3(-394) kJ + 4(-286) kJ$

$= -106 kJ$

6) Amino acids are the building blocks of protein molecules. Amino acids undergo combustion in the body to urea, carbon dioxide gas, and liquid water. Consider the heat liberated per mole of the amino acid glycine, NH₂CH₂COOH(s), when it undergoes combustion to urea NH₂CONH₂(s), carbon dioxide gas and liquid water. Compare this value with the heat of combustion liberated per mole of glucose, C₆H₁₂O₆(s), to carbon dioxide gas and liquid water. **Which is a better fuel for the body, glucose or glycine? Explain your choice of answer.**
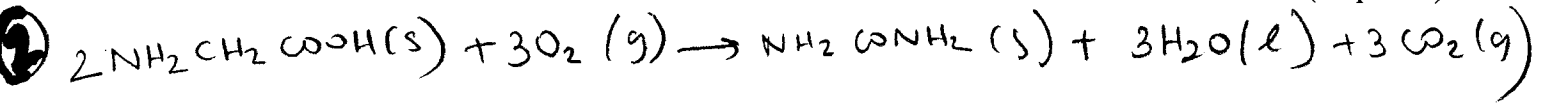
In addition to the thermodynamic data listed in the tables, use the information below as necessary.
ΔH_f° glycine (NH₂CH₂COOH(s)) = -532.9 kJ/mol
ΔH_f° urea (NH₂CONH₂(s)) = -333.51 kJ/mol
ΔH_f° glucose (C₆H₁₂O₆(s)) = -1268 kJ/mol

(12 points)

① $2\,NH_2CH_2COOH(s) + 3O_2(g) \longrightarrow NH_2CONH_2(s) + 3H_2O(\ell) + 3CO_2(g)$

②
$$\Delta H_v^\circ = \Delta H_f^\circ(NH_2CONH_2(s)) + 3\Delta H_f^\circ(H_2O(\ell)) + 3\Delta H_f^\circ(CO_2(g))$$
$$- 2\Delta H_f^\circ(NH_2CH_2COOH(s))$$
$$= -333.51\,kJ/mol + 3(-286\,kJ/mol) + 3(-393.50\,kJ/mol)$$
$$-2(-532.9\,kJ/mol)$$
$$= -1306.21\,kJ$$

Heat of combustion
$\Delta H_c^\circ / mole\ NH_2CH_2COOH(s) = -1306.21\,kJ / 2\,mol = -653.1\,kJ$ ①

② $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(\ell)$
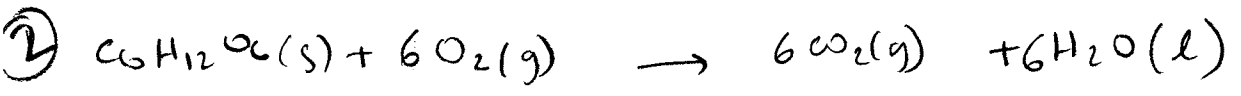
③
$$\Delta H_r^\circ = \Delta H_c^\circ = 6\Delta H_f^\circ(CO_2(g)) + 6\Delta H_f^\circ(H_2O(\ell)) - \Delta H_f^\circ(C_6H_{12}O_6(s))$$
$$= 6(-393.50\,kJ/mol) + 6(-286\,kJ/mol) - (-1268\,kJ/mol)$$
$$= -2809\,kJ$$

Heat of combustion /mole of glucose $\Delta H_c^\circ = -2809\,kJ$
On a molar basis glucose liberates more heat than glycine, hence glucose is a better fuel. ①

7) A typical bathtub can hold about 100 gallons of water. (1 gallon = 3.785 L). Estimate the mass (in grams) of natural gas that would be needed to be burned to heat the 100 gallons of water from 70°F (21°C) to 100°F (38°C). Assume that natural gas is pure methane, CH_4. Assume the density of water at 21°C = 1.00 g/cm³, and that the specific heat of water at 21°C is 4.184 J °C⁻¹ g⁻¹.   (12 points)

Amount of heat required to raise the temperature of 100 gallons of $H_2O(l)$ from 21°C to 38°C

$m_{H_2O} \; C_{H_2O} \; \Delta t$ ②

$m_{H_2O} = 100. \text{ gallons} \times \dfrac{3.785 \, L}{\text{gallon}} \times \dfrac{1000 \, cm^3}{L} \times 1.00 g/cm^3 = 3.78 \times 10^5 \, g$ ①

$C_{H_2O} = 4.184 \; J \; °C^{-1} \; g^{-1}$

$\Delta t = 17°C$ ②

$3.78 \times 10^5 \, g \times 4.184 \; J \; °C^{-1} \; g^{-1} \times 17°C = 2.69 \times 10^7 \, J$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{or} \; 2.69 \times 10^4 \, kJ$

Heat liberated per mole of CH_4 when heated is the heat of combustion of $CH_4(g)$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ ②
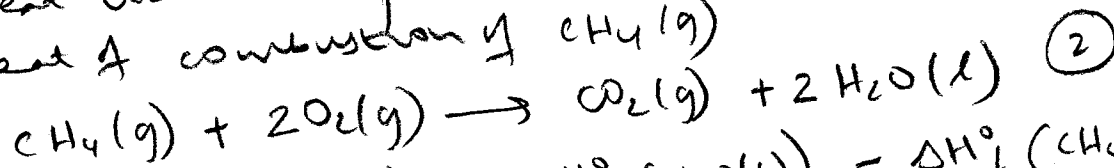
$\Delta H° = \Delta H°_f(CO_2(g)) + 2\Delta H°_f(H_2O(l)) - \Delta H°_f(CH_4(g))$

$\quad = (-393.505 \, kJ/mol) + 2(-286 \, kJ/mol) - (-74.9 \, kJ/mol)$ ②

$\quad = -890.6 \, kJ$

1 mole of CH_4 liberates $-890.6 \, kJ \Rightarrow$

To generate 2.69 × 10⁴ kJ of heat requires 30.2 mols CH_4

Amount of CH_4 (in grams) required = 484 g   ③

8) Consider the transformation of C(graphite) to C(diamond)

C(graphite) → C (diamond)

This reaction is significant, not only because diamond is a valued gemstone, but also because diamond is very hard and serves as a coating material to prolong the life of drilling tools and other objects used in demanding environments.

Based on thermodynamic data explain why for all temperatures the transformation of graphite to diamond can never occur spontaneously under standard conditions of 1 bar (1 atm).
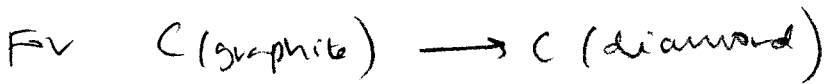
(11 points)

For a reaction to be spontaneous $\Delta G < 0$

$$\Delta G° = \Delta H° - T\Delta S°$$

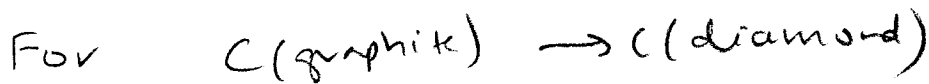if $\Delta H° > 0$ and $\Delta S° < 0$ then

$\Delta G° > 0$ for all T and hence never spontaneous

For $\quad$ C(graphite) $\longrightarrow$ C(diamond)

$\Delta H° = \Delta H°_f (C(diamond)) = +1.90 \, kJ/mol$ $\quad$ **2.5**

$\Delta S° = S°(C(diamond)) - S°(C(graphite))$

$\quad = 2.5 \, J/mol\text{-}k - 5.7 \, J/mol\text{-}k = -3.2 \, J/mol\text{-}k$ $\quad$ **2.5**

For $\quad$ C(graphite) $\longrightarrow$ C(diamond)

$\Delta H° > 0 \quad ; \quad \Delta S° < 0 \implies \Delta G° > 0$ for all T

Hence C(graphite) $\longrightarrow$ C(diamond) is not spontaneous for all Temperature.

9) a)From the plot of free energy versus temperature given below, explain why the liquid is never the stable phase, over the range of temperatures shown. (6 points)
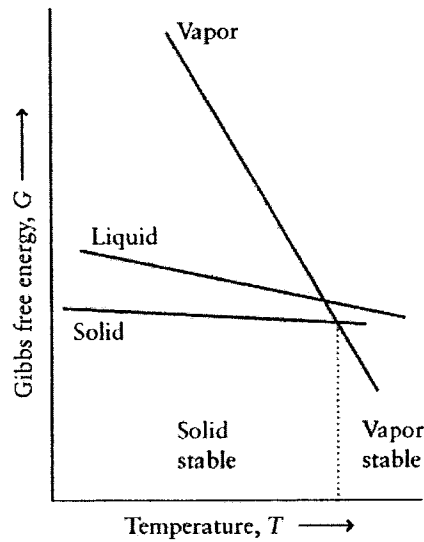
For a phase transition to be spontaneous, $\Delta G < T$

For a compound whose G of solid, liquid, gas phase varies with T as shown in the graph

for all T $G_{liquid} > G_{solid}$ & $G_{liq} > G_{gas}$

Hence a phase transition of liquid → solid has a $\Delta G > 0$.

and a phase transition of liquid → gas has a $\Delta G > 0$

Hence the liquid is never the stable phase over the range of T's shown

9 b) For a compound whose free energy varies with temperature as shown in the above plot, what phase transition does the solid undergo as heat is supplied at constant pressure? Explain your choice of answer. (4 points)

solid undergoes sublimation. The Temperature at which $G_{solid} = G_{gas}$ corresponds to $T_{sublimation}$. for $T > T_{sublimation}$ $G_{gas} < G_{solid}$ and solid sublimes to gas.