

Average 78.9

Examination I

Please answer each question in the space provided. All reasoning must be clearly indicated.

$$w = - \int_{V_1}^{V_2} p_{ext} dV$$

$$\Delta E = q + w$$

$$H = E + pV$$

$$R = .08206 \text{ (atm) / mol K}$$

$$\Delta H^0 = \Delta H_f^0 (\text{products}) - \Delta H_f^0 (\text{reactants})$$

I	20	20
II	30	30
III	30	30
IV	20	20
Σ	100	100

avg 18.2

Emma Fink

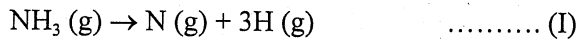
Name

Monday 2pm
Amogh - Bonnie
Discussion Section

1, 3, 5, 10
 2
 9.5
 2

19/7

- I. Consider the following reaction taking place at a constant pressure in the gas phase:



- a. Do you expect this reaction to be endothermic or exothermic? Why?

Energy is released

I expect this reaction to be endothermic.

3 mol of N-H bonds are broken in this reaction and no new bonds are formed. Since energy is required to break bonds and by the logic

$\Delta H = \sum \text{bonds broken} - \sum \text{bonds formed}$, I would expect ΔH to be positive and thus the reaction to be endothermic.

- b. The standard enthalpies of formation of $\text{NH}_3(\text{g})$, $\text{N}(\text{g})$, and $\text{H}(\text{g})$ are -46.1 kJ/mol , 472.7 kJ/mol , and 216.0 kJ/mol , respectively. Use this information to determine the standard enthalpy change (ΔH°) for the above reaction.

$$\Delta H^\circ = \Delta H_f^\circ \text{ products} - \Delta H_f^\circ \text{ reactants}$$

$$\Delta H^\circ = (1 \text{ mol})(472.7 \text{ kJ/mol}) + 3 \text{ mol}(216.0 \text{ kJ/mol}) - (1 \text{ mol})(-46.1 \text{ kJ/mol})$$

$$\Delta H^\circ = 1166.8 \text{ kJ} \quad (\text{For 1 mol } \text{NH}_3 \text{ reacting})$$

$$\Delta H^\circ \approx 1170 \text{ kJ}$$

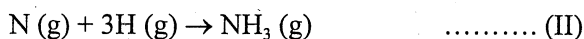
c. Estimate (in kJ/mol) the strength of the N-H covalent bond in ammonia (NH₃).

Since three moles of N-H covalent bonds were broken in the reaction $\text{NH}_3(\text{g}) \rightarrow \text{N}(\text{g}) + 3\text{H}(\text{g})$ and no new bonds were formed,

(5) the strength of the N-H covalent bond in NH₃ is an average of $\frac{1166.8 \text{ kJ}}{3 \text{ mol bonds}} = 388.933333 \text{ kJ/mol} \approx 389 \text{ kJ/mol}$

Bond energies are always recorded positive

d. Consider now reaction (II), which is the reverse of reaction (I) above:



Is this atm pressure?
yes

How much heat is released (or absorbed) by reaction (II) at constant pressure when 35.0 g of N (g) (AW = 14.01) reacts with excess H (g)? (Please note that this question does not depend on part c.)

For 1 mol NH₃ (g) reacting to form 1 mol N(g) and 3 mol H(g)

the ΔH was 1166.8 kJ. Since this is the reverse reaction, ΔH is negated; thus ΔH for 1 mol N(g) + 3 mol H(g) is -1166.8 kJ.

But we only have 35 g N(g) $\left(\frac{1 \text{ mol N(g)}}{14.01 \text{ g}} \right) = 2.49821556 \text{ mol} \approx 2.5 \text{ mol}$ reacting.

So $(-1166.8 \text{ kJ})(2.49821556) = -2914.917916 \text{ kJ}$

$-2914.917916 \text{ kJ} \approx -2915 \text{ kJ} \approx 2910 \text{ kJ}$

Constant atmospheric pressure
ΔH = q

Thus 2915 kJ is released.

II. The following experiment was conducted in a double coffee cup calorimeter, just like the one used in the laboratory last week:

100.0 g of solid sodium thiosulfate decahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, density 1.050 g ml^{-1}) is mixed with 100 g of water (H_2O , density 1.000 g ml^{-1}) in a double coffee cup calorimeter, at a constant atmospheric pressure of 1.00 atm. The initial temperatures of the water and the sodium thiosulfate are 25°C , but after the salt has dissolved, the temperature of the solution inside the double coffee cup calorimeter is 20.0°C . The resulting salt solution has a density of 1.100 g ml^{-1} and specific heat $4.69 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$. Assuming that the densities and specific heat values quoted are independent of temperature, and that the heat capacity of the double coffee cup calorimeter is zero.

a) Find, for the process exactly as described (i) q (ii) w (iii) ΔE (iv) ΔH

1/2 i) Since the process is performed in a calorimeter, it is adiabatic (assuming a perfect calorimeter). Thus $q=0$ since there is no heat flow.

ii) $w = -P\Delta V$

Volume before

$$100.0 \text{ g } \text{Na}_2\text{S}_2\text{O}_3 \cdot 10\text{H}_2\text{O} \left(\frac{1 \text{ ml}}{1.050 \text{ g}} \right) = 95.23809524 \text{ ml} \approx 95.2 \text{ ml}$$

$$100 \text{ g } \text{H}_2\text{O} \left(\frac{1 \text{ ml}}{1.000 \text{ g}} \right) = 100 \text{ ml}$$

total before = $95.23809524 \text{ ml} \approx 195 \text{ ml}$

After

$$200 \text{ g salt solution} \left(\frac{1 \text{ ml}}{1.100 \text{ g}} \right) = 181.8181818 \text{ ml} \approx 182 \text{ ml}$$

$$\Delta V = 181.8181818 - 195.23809524 \text{ ml} = -13.41991342 \text{ ml} \approx -13.4 \text{ ml}$$

to back

(over)

$$w_{\text{work}} = -P\Delta V$$

$$w = -(1 \text{ atm})(-13.41991342 \text{ ml})$$

$$w = 13.41991342 \text{ ml atm}$$

$$\frac{5}{5} \quad w = 13.41991342 \text{ ml atm} \left(\frac{1 \text{ L}}{1000 \text{ ml}} \right) = 0.0134199134 \text{ L atm}$$

$$0.0134199134 \text{ L atm} \left(\frac{101.3 \text{ J}}{\text{L atm}} \right) = 1.35943723 \text{ J}$$
$$w \approx 1.36 \text{ J}$$

$$\text{III) } \Delta E = q + w$$

$$\frac{2}{2} \quad q = 0 \quad w = 1.35943723 \text{ J}$$

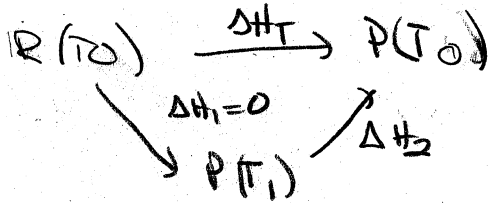
$$\Delta E = 1.35943723 \text{ J} \approx 1.36 \text{ J}$$

IV) Since this is being performed at constant atmospheric pressure $\Delta H = q$.

$$q = 0 \text{ so } \Delta H = 0$$

$\frac{2}{2}$

b) Explain how thermodynamics allows one to determine from this experiment the ΔH for the process where 100.0 g of sodium thiosulfate is dissolved in 100.0 g of water isothermally at 25 °C and 1.00 atm.



$$\Delta H_T = \Delta H_2 + \Delta H_1$$

$$\Delta H_T = \Delta H_2$$

Since $\Delta H_1 = 0$

Since enthalpy is a state function, we can perform the reaction in multiple steps as long as the final and initial states of the system are the same in the target reaction and our steps overall. Performing the reaction in a calorimeter allows determination of T_f adiabatically, so no heat is transferred to the surroundings and ΔT can be measured accurately.

Excellent

Since we know that the products will eventually return to T_0 with the same ΔT that was observed in the calorimeter, we can solve for ΔH_2 and thus ΔH of the reaction.

c) Calculate ΔH for the isothermal dissolution of 100.0 g of this salt in 100.0 g of water, where both salt and water start and end at 25 °C and 1.00 atm.

Assuming mixing is ideal

Since constant atmospheric pressure $\Delta H = q$

$$q = (200g) / (4.184 J/gC) / (5^{\circ}C)$$

$$q = 4690 J$$

$$\Delta H = 4690 J \quad \text{Heat flows into the system, } \Delta H \text{ is } +$$

5/5

Since the step in the calorimeter is adiabatic $\Delta H_1 = 0$ and $\Delta H_{\text{overall}} = \Delta H_2$, the ΔH_2 value can be determined because at constant atmospheric pressure $\Delta H = q$ and we can determine q , and thus $\Delta H_2 = \Delta H_T$ from $\Delta T = T_f - T_0$ and the heat capacity

d) How does ΔE differ from ΔH for the process described in (c)?

$$\Delta H = \Delta E + \Delta(pV)$$

$$\Delta E = q + w$$

Since the reaction is being performed at constant atmospheric pressure, $\Delta H = q$ in this case. However,

$\Delta E = q + w$ or $\Delta E = \Delta H + w$. Thus ΔE differs from

ΔH because it has the additional component of pV work, which in this scenario is $1.359437235 \approx 1.36 \text{ J}$.

$$\Delta E = 1.359437235 + 4690 \text{ J}$$

$$\Delta H = 4690 \text{ J}$$

e) If the same experiment as in (a) were done in a double coffee cup calorimeter with heat capacity $C_{\text{cal}} = 20.9 \text{ J } ^\circ\text{C}^{-1}$. Would the final temperature still be $20.0 \text{ }^\circ\text{C}$? If not, will it be higher or lower? Justify your answer.

No, the final temperature will not be $20.0 \text{ }^\circ\text{C}$

The temperature will be higher.

$$q = -4690 \text{ J} \quad q = C\Delta T$$

$$4690 \text{ J} = (200 \text{ g} / (4.18 \text{ J/g}^\circ\text{C}) + 20.9 \text{ J/}^\circ\text{C}) \Delta T$$

$$4690 \text{ J} = (938 \text{ J/}^\circ\text{C} + 20.9 \text{ J/}^\circ\text{C}) \Delta T$$

$$4690 \text{ J} = 958.9 \text{ J/}^\circ\text{C} (\Delta T)$$

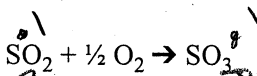
$$4.891020962 \text{ }^\circ\text{C} = \Delta T$$

Since this $\Delta T < 5^\circ$ when q was negative ΔT , the temperature will be higher, i.e. it

will decrease by less than 5°

III. Calorimetry measurements conducted on combustion reactions, especially in which gases are involved, are often performed in a special kind of calorimeter called a bomb calorimeter. Bomb calorimeters contain rigid, explosion-proof walls, and maintain constant volume inside.

Consider the gas phase reaction



conducted entirely in the gas phase, and in a bomb calorimeter. The standard enthalpies of formation of sulfur dioxide and sulfur trioxide are -297 kJ/mol and -396 kJ/mol respectively. 0.100 mole of SO_2 is mixed with 0.0500 mol of O_2 at an initial temperature of 298 K and an initial pressure of 1.00 atm. The heat capacity of the calorimeter and its contents is 1.00 J/K

(a) Determine the final temperature inside the calorimeter just after the chemical reaction.

$$\Delta H^\circ = \Delta H_f^\circ \text{ products} - \Delta H_f^\circ \text{ reactants}$$

$$\Delta H^\circ = (-396 \text{ kJ/mol})(1 \text{ mol}) - (-297 \text{ kJ/mol})(1 \text{ mol})$$

$$\Delta H^\circ = -99 \text{ kJ} \text{ For 1 mol SO}_2 \text{ reacting in excess O}_2$$

For 0.1 mol SO_2 and 0.05 mol O_2

$$\Delta H^\circ = (-99 \text{ kJ})(0.1) = -9.9 \text{ kJ}$$

Since these ΔH° values are at constant atmosphere pressure where $\Delta H = q$ (NOT in bomb calorimeter), these are the q values we would expect had the reaction not been in a bomb calorimeter.

$$9900 \text{ J} \leq 1 \text{ J/K}(\Delta T)$$

$$9900 \text{ k} = \Delta T$$

initial temp = 298 K

$$\text{Final temperature} = 10198 \text{ K}$$

$PV = nRT$

- b) Determine q for this process exactly as described (with the final temperature at the value you calculated in part a)). *perfect calorimeter - yes*

Since the reaction occurs in a calorimeter (and we are assuming it is adiabatic. Thus $q=0$ a perfect calorimeter.

- c) Calculate w for the process.

Since the volume is constant, no pv work is performed. Thus $w=0$.

- d) Calculate ΔE .

$$\Delta E = q + w$$

Since $w=0$

$$\Delta E = q$$

Since $q=0$, $\Delta E=0$

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Can we assume ideal gases here too?

Yes

- e) Find the pressure inside just after the reaction.

$$PV = nRT$$

initial $PV = nRT$

$$(1 \text{ atm})V = (.15 \text{ mol}) \left(.08206 \frac{\text{L atm}}{\text{K mol}} \right) (298 \text{ K})$$

$$V = 3.668082 \text{ L} \approx 3.67 \text{ L}$$

after $PV = nRT$

Volume is constant

$$P(3.668082 \text{ L}) = (.1 \text{ mol}) \left(.08206 \frac{\text{L atm}}{\text{K mol}} \right) (10198 \text{ K})$$

$$P = 22.81431767 \text{ atm}$$

$$P \approx 22.8 \text{ atm} \quad P_{\text{just after rxn}}$$

- f) Calculate ΔH . (Remember that $H = E + pV$. You may assume that the gaseous reactants before the combustion, and the gaseous combustion product, behave like ideal gases.)

$$\Delta H = \Delta E + \Delta(pV)$$

$\Delta n \Delta T R$

since $\Delta E = 0$

$$\Delta H = \Delta(pV)$$

$$\Delta H = V \Delta P$$

$$\Delta H = 3.668082 \text{ L} (22.8 \text{ atm} - 1 \text{ atm})$$

$$\Delta H = 79.9641876 \text{ L atm}$$

IV. A sample of a non-ideal gas expands adiabatically into a vacuum. Its temperature is observed to have fallen after the expansion. Determine whether each of the following is positive, negative, or zero:

a) $q = 0$

Since it's adiabatic, $q = 0$

b) $w = 0$

Since it is expanding into a vacuum, $p_{\text{ext}} = 0$ and

$$w = 0, \quad -P_{\text{ext}} \Delta V = 0$$

c) $\Delta E = 0$

$\Delta E = q + w$. q and w are both 0 so ΔE is 0.

d) Provide a physical explanation for the observation that the temperature falls.

In non-ideal gases, intermolecular forces play a role.

20 Since we are expanding the gas, these intermolecular forces must be disrupted, which requires energy. The temperature fell because the increased chemical energy caused a decrease in thermal energy when $\Delta E = 0$, meaning that no ^{net} energy was interchanged with the surroundings.