Chemistry 240 Semester 01-2009
Homework for Submission #4 - Key

1) Calculate the work done on the system and on the surroundings when

   a) 1 mol of $KClO_3$ decomposes at 1 atm and a constant temperature of 300K.

Solution

The equation for the decomposition is

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g) \text{ or for one mole of } KCl_3(s)$$

$$KClO_3(s) \rightarrow KCl(s) + \tfrac{3}{2}O_2(g)$$

For an expansion at constant pressure, work done on system, $w = -P\Delta V$. Since the volumes of solids are negligible compared to those of gases under these conditions, we can apply $PV = nRT$. Since the temperature is constant this gives $P\Delta V = RT\Delta n$. Hence $w = -RT\Delta n = -8.31 \times 300 \times (\tfrac{3}{2} - 0) = -3.740 \times 10^3$ J = -3.7 kJ to 2 sig. figs.

The work done on the surroundings is the negative of this, +3.7 kJ

   b) 1 kg of ice melts at 0°C and 5 atm pressure. The densities of ice and water at these temperatures is $0{\cdot}915$ gcm^{-3} and $1{\cdot}000$ gcm^{-3}.

Solution

Since the process occurs at constant pressure, $w = -P\Delta V = -P(V_2 - V_1)$.

But V_2 = mass/density = 1 kg / 1.000 g cm^{-3} = 1000 cm^3 = 1×10^{-3} m^3

and V_1 = 1.000 kg / 0.915 g cm^{-3} = 1093 cm^3 = 1.093×10^{-3} m^3

But P = 5 atm = 5 × 101000 Pa = 505000 Pa

$\therefore w_{sys} = -505000 \times (1.000 - 1.093) \times 10^{-3} = 46.91$ J or 47 J to 2 sig. figs.

And w_{surr} = -47 J

2) Look up and tabulate the standard enthalpies of combustion of ethanol, hexane and octane. Compare them as possible fuels by

Solution

From an internet search we have the following values. Note that they must be negative. (Your values may differ slightly.)

Fuel	Ethanol	Hexane	Octane
Standard Enthalpy of Combustion	-1366.7 kJ mol^{-1}	–4194.7 kJ/mol	-5471 kJ·mol^{-1}

   a) Calculating the heat produced per kilogram for each of these substances under standard conditions.

Solution

The above figures are for the combustion of 1 mol. Molar masses are:

Fuel	Ethanol (CH_3CH_2OH)	Hexane (C_6H_{14})	Octane (C_8H_{18})
Molar mass	46.1 g mol^{-1}	86.2 g mol^{-1}	114.2 g mol^{-1}
Enthalpy of combustion per g	-1366.7 kJ mol^{-1} / 46.1 g mol^{-1} = -29.65 kJ g-^{1}	–4194.7 kJ/mol / 86.2 g mol^{-1} = -48.66 kJ g^{-1}	-5471 kJ·mol^{-1} / 114.2 g mol^{-1} = -47.91 kJ g^{-1}
Enthalpy of combustion per kg	-29650 kJ kg-^{1}	-48660 kJ kg^{-1}	-47910 kJ kg^{-1}

b) Use your result from (a) to determine the heat produced per litre of each substance under standard conditions.

Solution

Fuel	Ethanol (CH_3CH_2OH)	Hexane (C_6H_{14})	Octane (C_8H_{18})
Enthalpy of combustion per kg	-29650 kJ kg-^{1}	-48660 kJ kg^{-1}	-47910 kJ kg^{-1}
Density @ 25°C	0.789 g cm^{-3} = 0.789 kg L^{-1}	0.659 g cm^{-3} = 0.659 kg L^{-1}	0.703 g cm^{-3} = 0.703 kg L^{-1}
Enthalpy of combustion per L	-29650 kJ kg-^{1} × 0.789 kg L^{-1} = -20910 kJ L^{-1}	-48660 kJ kg^{-1} × 0.659 kg L^{-1} = -32070 kJ L^{-1}	-47910 kJ kg^{-1} × 0.703 kg L^{-1} = -33680 kJ L^{-1}

c) Find the lowest prices you can for each of the above substances using the internet or a chemical catalogue (the lowest quality grade is acceptable) and by determining the heat produced per dollar's worth, rank the fuels in order of economy.

Solution

d)

Fuel	Ethanol (CH_3CH_2OH)	Hexane (C_6H_{14})	Octane (C_8H_{18})
Enthalpy of combustion per L	-20910 kJ L^{-1}	-32070 kJ L^{-1}	-33680 kJ L^{-1}
Price	\$0.31 L^{-1}	\$229 per 4 × 4 L	\$68.25 per 100 ml
Price per litre	\$0.31 L^{-1}	\$14.31 L^{-1}	\$682.5 L^{-1}
kJ \$$^{-1}$	-20910 kJ L^{-1} / \$0.31 L^{-1} = -67450 kJ \$$^{=1}$	-32070 kJ L^{-1} / \$14.31 L^{-1} = -22410 kJ \$$^{-1}$	-33680 kJ L^{-1} / \$682.5 L^{-1} = -49.35 kJ \$$^{-1}$

Ranking in terms of economy, least economical (most expensive) first:

Octane < Hexane < Ethanol

Notes: Negative signs are not necessary once it is accepted that these values are for heat released.

The prices of hexane and octane are artificially high, since they are for *fine* chemicals. Fuels do not have to be pure, just free of involatile compounds. (Gasoline is a crude form of octane.) Your prices may differ substantially from the values I found on the internet, depending on source and quality.

3) Look up and tabulate the standard enthalpies of combustion of carbon and hydrogen, and use them together with the standard enthalpy of combustion of ethanol to determine the standard enthalpy of formation of ethanol.

Solution

The book does not seem to give standard enthalpies of combustion for these compounds in the appendices, but they are the same as the standard enthalpies of formation for carbon dioxide and water, as can be seen from the defining equations.

Substance	Carbon	Hydrogen	Ethanol
Standard enthalpy of combustion	-393.51 kJ mol^{-1}	-285.83 kJ mol^{-1}	-1366.7 kJ mol^{-1}

Hence

$C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H_r^{\ominus}$ = -393.51 kJ (1)

$H_2(g) + ½O_2(g) \rightarrow ½H_2O(l)$, $\Delta H_r^{\ominus}$ = -285.83 kJ (2)

The equation for the combustion of ethanol is

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$, $\Delta H_r^\ominus = -1366.7$ kJ (3)

The equation for the formation of ethanol is

$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$, $\Delta H_r^\ominus = \Delta H_f^\ominus$ (4)

But $2 \times (1) + 3 \times (2) - (3) = (4)$

$\therefore \Delta H_r^\ominus(4) = 2 \times \Delta H_r^\ominus(1) + 3 \times \Delta H_r^\ominus(2) - \Delta H_r^\ominus(4) = (2 \times -393.51 \text{ kJ}) + (3 \times -285.83 \text{ kJ}) - (-1366.7 \text{ kJ}) = -277.8 \text{ kJ mol}^{-1}$

(The first three figures agree with the value given in the textbook.)

4) Calculate the molar values of H, C_p, and C_v for a an ideal gas at 300 K.

Solution

For an ideal gas, the only form of energy the molecules can have is kinetic energy. Hence $U = \frac{3}{2}nRT$.

But $H = U + PV$ and for an ideal gas, $PV = nRT$

$\therefore H = \frac{3}{2}nRT + nRT = 2\frac{1}{2}nRT = 2\frac{1}{2} \times 1 \times 8.31 \times 300 =$ 6.233 kJ mol^{-1}

But $C_p = \Delta H/\Delta T = \Delta(2\frac{1}{2}nRT)/\Delta T = (2\frac{1}{2}nR\Delta T)/\Delta T = 2.5 \times 1 \times 8.31 =$ 20.78 J mol-1 K-1

and $C_v = \Delta U/\Delta T = \Delta(\frac{3}{2}nRT)/\Delta T = (\frac{3}{2}nR\Delta T)/\Delta T = \frac{3}{2} \times 1 \times 8.31 =$ 12.47 J mol-1 K-1

5) a) Explain the meaning of term ***entropy***. Illustrate your answer by referring to, and explaining, the relative amounts of entropy in water and steam at 100°C, both at 1 atmosphere pressure. Which of the three states of matter has the lowest entropy at a given temperature? Why?

Answer

Entropy is a measure of the disorder in a system. Thus steam has more entropy than water, because in steam the molecules are completely disordered whereas in water there is a degree of short-range order caused by the intermolecular forces of attraction. In general the solid state has the lowest entropy because the molecules are arranged in a regular lattice and their (mean) positions are fixed.

b) Look up and tabulate the boiling point and standard enthalpy of vaporisation for ethanol, and then calculate the entropy change of the system when 1.00 mol of ethanol is vaporized at its boiling point and 1 atm pressure

Solution

Substance	Ethanol
Boiling point	351.47 K
Standard enthalpy of vaporisation[1]	42.59 kJ mol^{-1}

(Note: the standard enthalpy of vaporisation can be found from the standard enthalpies of formation of gaseous ethanol and liquid ethanol, which are given in appendix 2.)

But $\Delta S = q_{rev} / T$. This will be a *standard* value if the pressure is 1 atm and T is the boiling point of the liquid, and so

$\Delta S_{vap}^\ominus = 42.59 \times 10^3 / 351.47 =$ 121.2 J mol^{-1} K^{-1}

c) One criterion for the feasibility of a change is that the total entropy of the system and its surroundings increases if the change is feasible.

i) Show that for the vaporization of water at 100°C and 1 atmosphere pressure, when the surroundings are at a higher temperature than the system, the total entropy of system and surroundings increases. (Assume the process is carried out reversibly.)

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[1] This actually give the standard enthalpy of vaporisation at 25°C because the standard enthalpies of formation are given at 25°C. As a result the value is slightly different from the "official" figure which is quoted at the boiling point of ethanol. My value is in fact rather higher than the value at 351.47 K. This can be attributed to more extensive hydrogen bonding in the liquid at the lower temperature.

Solution

$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$ where

$\Delta S_{sys} = q_{rev} / T_{sys}$ and $\Delta S_{surr} = -q_{rev} / T_{surr}$ since the heat liberated by the system must be absorbed by the surroundings.

$\therefore \Delta S_{tot} = q_{rev} / T_{sys} - q_{rev} / T_{surr}$

But if $T_{surr} > T_{sys}$, $q_{rev} / T_{surr} < q_{rev} / T_{sys}$

Hence $\Delta S_{tot} > 0$

ii) Not all feasible reactions will actually occur even when the correct reactants are mixed. Give a chemical example to illustrate this and explain why it is so.

Answer

Some reactions are very slow and so cannot be observed even though $\Delta S_{tot} > 0$. An example is the reaction of hydrogen and oxygen, which can be mixed without reaction at room temperature, though once the reaction is initiated, violent combination occurs to form water.