***PART II: Intro to thermodynamics, work and heat***

5. We measure heat in Joules because it is a form of energy; but another unit for energy is the calorie. The calorie is defined as the amount of energy necessary to increase the temperature of 1 gram of liquid water by 1 °C. Knowing that the molar heat capacity for water is 75.24 J/K mol and using dimensional analysis, calculate the conversion factor between calorie and joule.

$$75.24 \frac{J}{K \cdot mol} \cdot \frac{1\ K}{1\ °C} \cdot \frac{1\ mol}{18\ g} = 4.18 \frac{J}{g \cdot °C}$$

$$C_s \text{ in } J = C_s \text{ in } Cal \Rightarrow 4.18 \frac{J}{g \cdot °C} = 1 \frac{cal}{g \cdot °C}$$

$$\Rightarrow \boxed{1\ cal = 4.18\ J}$$

6. When a ball of mass 5.6Kg is dropped through an height, its potential energy changes. Suppose that, when the ball hits the ground, all its energy is converted into heat, increasing the temperature of the ball. If the specific heat capacity of the material of the ball is 0.850 J $K^{-1}$ $g^{-1}$, from what height do we need to drop the ball to increase its temperature by 1.00°C?

All the energy (heat) of the ball comes from its initial potential gravitational energy.

$$V_g = q \Rightarrow mgh = mC_s \Delta T \Rightarrow h = \frac{C_s \Delta T}{g}$$

$$= 0.850 \frac{J}{K \cdot g} \cdot \frac{1\ K}{9.8\ m/s^2} = 0.087 \frac{J s^2}{m\ g} = 0.087 \times 10^3 \frac{J s^2}{m\ Kg} = \boxed{87\ m}$$

7. During the process to prepare ammonia ($NH_3$), nitrogen ($N_2$), is heated slowly, maintaining the external pressure close to the internal one of 50.0 atm, until its volume has increased from 542 L to 974 L. Calculate the work done on the nitrogen as it is heated.

Since the expansion is the result of a change in T, the expansion will happen in an irreversible manner.

Thus: $W = -P_{ex} \Delta V = -50.0\ atm\,(974 - 542\ L)$

$$= -21600\ L \cdot atm = \boxed{-2.19 \times 10^6\ J}$$

8. A cylinder confines 2.00 L of gas under a pressure of 1.00 atm. The external pressure is also 1.00 atm. The gas is heated slowly, with the piston sliding freely to maintain the pressure of the gas close to 1.00 atm. The heating continues until the volume is 3.50 L. Calculate the work done on the gas.

For the same reason in problem 7:

$$w = -P_{ex}\Delta V = -1.00\ atm\,(3.50L - 2.00L) = -1.50\ atm \cdot L$$

$$= \boxed{-152\ J}$$

9. In the "Memoir on heat", published in 1783, Lavoisier and Laplace reported, "The heat necessary to melt ice is equal to three quarters of the heat that can raise the temperature of the same amount from its melting to its boiling point.". Knowing that the heat capacity of liquid water is 4.18 J/°Cg, use this observation to calculate how much heat is needed to melt 1.00 g of ice.

the heat needed to go from 0°C to 100°C is:

$$q = 1g \cdot \frac{4.18\ J}{°C\ g} \cdot (100 - 0)°C = 418\ J$$

the heat of melting is:

$$\Delta H_{fus} = \frac{3}{4} q = \frac{3}{4} \cdot 418 = \boxed{314\ J}$$

2. Heat:

a. In the “Memoir on heat”, published in 1783, Lavoisier and Laplace reported, “The heat necessary to melt ice is equal to three quarters of the heat that can raise the temperature of the same amount from its melting to its boiling point.”. Knowing that the heat capacity of liquid water is 4.18 J/°Cg, use this observation to calculate how much heat is needed to melt 1.00 g of ice.

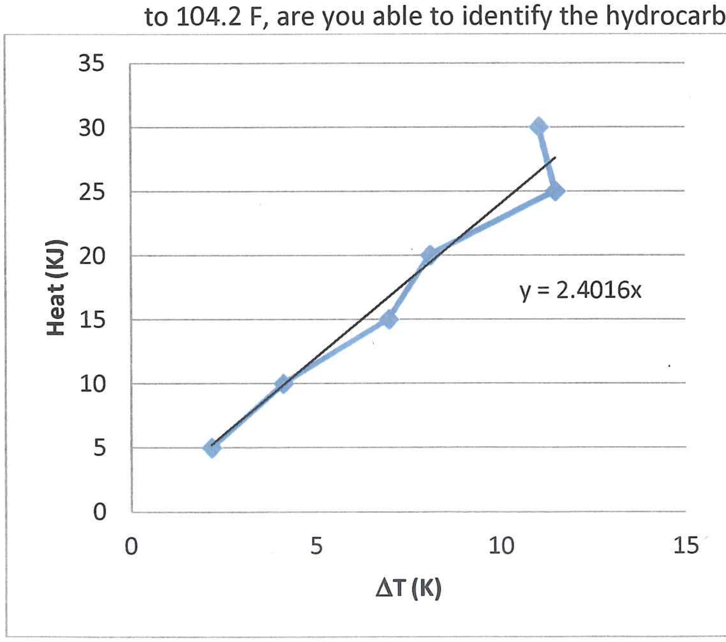
If $4.18 \frac{J}{°C \cdot g}$ is how much energy is needed to increase by 1°C the temperature of 1 g of water; to go from mp (0°C) to bp (100°C), we'll need 4.18x 100 = 418 J. The heat need to melt ice is 3/4 this latter value.

Hence $\Delta H_{melting} = \frac{3}{4} \cdot 418 = 314 J$

b. A calorimeter is calibrated using the following experimental data:

| Heat (KJ) | Delta T (°C) | Heat (KJ) | Delta T (°C) |
|---|---|---|---|
| 5.00 | 2.17 | 20.0 | 8.10 |
| 10.0 | 4.12 | 25.0 | 11.50 |
| 15.0 | 6.98 | 30.0 | 11.06 |

After calibration, that same calorimeter was used to calculate the heat released by the combustion of an unknown hydrocarbon. Referring to the table on page A17 of the book (Appendix 2A/Organic Compounds/Hydrocarbons), and knowing that the combustion of 10.00 mol of this unknown gas cause the temperature in the calorimeter to raise from 7.00 F to 104.2 F, are you able to identify the hydrocarbon?




From the calibration of the Calorimeter we can calculate the $C_{CAL}$ as the slope of q vs ΔT.

$C_{CAL} = 2.40 \frac{KJ}{°C \cdot mol}$

$\Delta H_C = -n \cdot C_{CAL} \cdot \Delta T =$

$= -10.00 \text{ mol} \cdot 2.40 \frac{KJ}{°C \cdot mol} \cdot \left( \frac{104.2 - 7.00}{1.8} \right)$

$= -10.00 \cdot 2.40 \cdot 54 = -1296$

From the table in the book, we can find which hydrocarbon has such Enthalpy of Combustion: Acetylene $-1300 \frac{KJ}{mol}$

3. Enthalpy of physical changes:
   a. Steam (water vapor) at 167 C is bubbled in liquid water at 25 C to quickly heat it up. Calculate how much steam is needed to bring to ebullition 1.24 Kg of water.

Ebullition of water happens at 100 °C. Both phases, liquid and gas, are present.

Heat needed to warm up $H_2O_{(l)} = 1240\,g \cdot 4.184\,\frac{J}{g \cdot °C} \cdot 75\,°C$

$= 389.1\ kJ$

Heat released by steam $= x\,g \cdot 2.01\,\frac{J}{g \cdot °C} \cdot 67\,°C = 398.1\ kJ$

$$x = \frac{398.1}{2.01 \cdot 67} = 2.96\ Kg$$

   b. Calculate how much steam would be needed if instead of liquid water, you were to use 1.24Kg of solid ice at -18 C.

Now the needed heat is $= 1.24\left[\left(C_{ICE} \cdot \underset{-18 \to 0\,°C}{\Delta T}\right) + \frac{\Delta H_{FUS}}{MM} + \left(C_{WATER} \cdot \underset{0 \to 100\,°C}{\Delta T}\right)\right]$

$$= 1.24 \cdot \left[\left(2.03 \cdot 18\right) + \frac{6010}{18} + \left(4.18 \cdot 100\right)\right] = 173.1 \times 10^6\ J$$

$$x = \frac{173.1 \times 10^6}{2.01 \cdot 67} = 1285.4\ Kg$$

   c. Once the water from question 3b is boiling, how much more ice at -18 C would be needed to freeze the overall amount of water?

So, now we have $1285.4 + 1.2 = 1286.6\ Kg$

Heat needed $= 1286.6\left(4.18 \cdot 100 + \frac{6010}{18}\right) = 967.4$ tonn

Kind of an industrial amount ☺

4. Enthalpy of chemical changes:

a. For each of the following reaction, the ΔH is the enthalpy change when the number of moles indicated by the stoichiometric coefficients react. Calculate the ΔH when 1.00 g of the bold substance is consumed or produced:

$4Na\ (s) + O_2\ (g) \rightarrow \underline{2Na_2O\ (s)}$ ΔH = -828 KJ

1 g $Na_2O$ = 0.0161 mol

$-828 : 2 = x : 0.0161$ $x = -6.67$ KJ

$CaMg(CO_3)_2\ (s) \rightarrow CaO\ (s) + \underline{MgO\ (s)} + 2CO_2\ (g)$ ΔH = +302 KJ

1 g MgO = 0.0248 mol

$302 : 1 = x : 0.0248$ $x = +7.48$ KJ

$H_2\ (g) + \underline{2CO\ (g)} \rightarrow H_2O_2\ (l) + 2C\ (s)$ ΔH = +33.3 KJ

1g CO = 0.0357 mol

$33.3 : 2 = x : 0.0357$ $x = +0.594$ KJ

b. Calculate the enthalpy change for the formation of 1.00 mol of strontium carbonate (the material used to obtain red colored fireworks) from its elements. Note: all reactions need to be balanced.

$Sr\ (s) + C\ (graphite, s) + \frac{3}{2}O_2\ (g) \rightarrow SrCO_3\ (s)$

Available information is:

| | | | |
|---|---|---|---|
| 1 × | $Sr\ (s) + \frac{1}{2}O_2\ (g) \rightarrow SrO\ (s)$ | ΔH = -592 KJ | × 1 |
| 1 × | $SrO\ (s) + CO_2\ (g) \rightarrow Sr(CO_3)\ (s)$ | ΔH = -234 KJ | × 1 |
| 1 × | $C\ (graphite, s) + O_2\ (g) \rightarrow CO_2\ (g)$ | ΔH = -394 KJ | × 1 |

$Sr + \frac{1}{2}O_2 + C + O_2 \rightarrow Sr(CO_3)$

⇓

$Sr_{(s)} + \frac{3}{2}O_{2(g)} + C_{(s)} \rightarrow SrCO_{3\ (s)}$

ΔH = ~~-1454~~ KJ
-1220 KJ

c. The molar enthalpy of formation for $FeBr_2$ is -249.8 KJ/mol and that for $FeBr_3$ is -268.2 KJ/mol. What is the $\Delta$H of the following reaction?

$$2FeBr_2\,(s) + Br_2\,(l) \rightarrow 2\,FeBr_3\,(s)$$

$\Delta H_{FeBr_3} - \Delta H_{FeBr_2} = -18.4\ \mathrm{kJ/mol}$

$\Delta H$ of the rxn $= 2 \cdot \left(-18.4\ \frac{kJ}{mol}\right) = -36.8\ kJ$

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Summary problem: **Methanol as a gasoline substitute.**

Methanol ($CH_3OH$) is used as a substitute for gasoline in certain high-performance vehicles. To design engines that will run on it, its thermochemistry must be understood.

a. The methanol in an automobile engine must be in the gas phase before it can react. Calculate the heat (in KJ) that must be added to 1.00 Kg of liquid methanol to raise its temperature from 25°C to its normal boiling point, 65°C, knowing that the molar heat capacity of liquid methanol is 81.6 J/°Cmol.

b. Once the methanol has reached its boiling point, it must be vaporized. The molar enthalpy of vaporization for methanol is 38 KJ/mol. How much heat must be added to vaporize 1.00 Kg of methanol?

c. Once it is in the vapor phase, the methanol can react with oxygen in the air according to

$$CH_3OH\,(g) + 3/2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$$

Use average bond enthalpies to estimate the enthalpy change in this reaction, for one mole of methanol reacting.

d. Use data from Appendix 2A of your textbook to calculate the actual enthalpy change in this reaction, assuming it to be the same at 65°C as at 25°C.

e. Calculate the heat released when 1.00 Kg of gaseous methanol is burned in air at constant pressure. Use result of part d.

f. Calculate the difference between the change in enthalpy and the change in internal energy when 1.00 Kg of gaseous methanol is oxidized to gaseous $CO_2$ and $H_2O$ at 65°C.

g. Suppose now that the methanol is burned inside the cylinder of an automobile. Taking the radius of the cylinder to be 4.0 cm and the distance moved by the piston during one stronk to be 12.0 cm, calculate the work done on the gas per stroke as it expands against an external pressure of 1.00 atm. Express your answer in both, L atm and J.

See next page →

a.

$$q = m \cdot C_s \cdot \Delta T = 1000\,g \cdot 2.545 \frac{J}{g \cdot {}^\circ C} \cdot 40\,{}^\circ C =$$

$$= 101.8\ kJ \simeq 102\ kJ$$

b.

$$q = \Delta H_{VAP} \cdot n = 38 \frac{kJ}{mol} \cdot 1000\,g \cdot \frac{1}{32 \frac{g}{mol}} = 1.2 \times 10^3\ kJ$$

c.

Breaking:

$\sigma_{C-O}$

$3/2 \times (\sigma_{O-O} + \pi_{O-O})$

$3 \times (\sigma_{C-H})$

$\sigma_{O-H}$

Making:

$2 \times (\sigma_{C-O} + \pi_{C-O})$

$4 \times (\sigma_{O-H})$

$$\Delta H = +351 + \frac{3}{2} \times 498 + 3 \times 413 + 463$$

$$- 2 \times 728 - 4 \times 463 =$$

$$= -508\ kJ$$

1.

Enthalpies of formation of products
- Enthalpies of formation of reagents

$$\Delta H = (-393.51) + (2 \times (-241.82)) - (-200.66) =$$

$$= 676.49 \text{ KJ}$$

e. $1.00 \text{ Kg}_{CH_3OH} = 31.3 \text{ mol}$

$$676.49 : 1 = x : 31.3$$

$$x = 2.11 \times 10^4 \text{ KJ}$$

f. $\Delta H = \Delta U + P\Delta V$ by definition.

So $\Delta H - \Delta U = P\Delta V$

For the Gas law $P\Delta V = \Delta(nRT)$

P & T are constant, so the only variation is the number of moles of gas ($\Delta n_g$)

$$P\Delta V = \Delta n_g RT$$

There are: 31.3 mol of $CH_3OH$ ] Reagents

$3/2 \times 31.3$ mol of $O_2$ ]

31.3 mol of $CO_2$ ] Products

$2 \times 31.3$ mol of $H_2O$ ]

So, $\Delta n_g = \left|\left(1 + \frac{3}{2} - 1 - 2\right) \times 31.3\right| = |-15.65|$

$P\Delta V = |-15.65| \cdot R \cdot T$

$= 15.65 \cdot 8.314 \cdot 338 = 43{,}979\ J$

$\Delta H - \Delta U = 44.00\ kJ$

g.

$w = -P_{ex}\Delta V = -1\ atm \cdot (\pi \cdot 16 \cdot 12)\ cm^3 =$

$= -6.0 \times 10^2\ cm^3 \cdot atm = -0.60\ L \cdot atm$

$= -61\ J$