

THERMODYNAMICS EXTRA PROBLEMS.

Note: silly error in #5 fixed (MM value was used in place of moles; previous method correct, but wrong # written down)

#1.

in cylinder
 When gas was compressed INTO cylinder
 $V_i = 6320 \text{ L}$
 $T_i = 0^\circ\text{C}$
 $P_i = 1 \text{ atm}$

vs. rapid release from cylinder
 $V_f = ?$ same volume as ~~was~~ before gas was compressed INTO cylinder...
 $T_f = 0^\circ\text{C}$
 $P_f = 1 \text{ atm}$

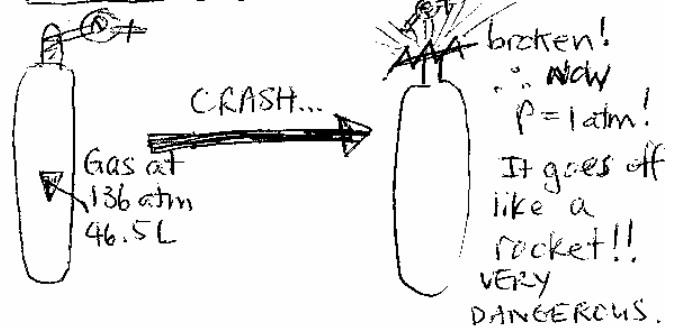
Use $PV = nRT$
 $\therefore n = 282.1 \text{ mol} =$ moles inside cylinder

$n = 282.1 \text{ mol}$
 $\therefore V_f = \frac{nRT}{P} = 6320 \text{ L}$

Now: Pressurized in cylinder

$P = 136 \text{ atm}$
 $n = 282.1 \text{ mol}$
 $\therefore V_i = \frac{nRT}{P} = 46.5 \text{ L}$

PICTURE WHAT IS GOING ON:



WORK: when gas expands from cylinder all at once
 we have $\Delta V = \cancel{46.5} V_f - V_i$
 $= 6320 \text{ L} - 46.5 \text{ L}$
 $= 6273.5 \text{ L}$

We assume a simple expansion against $P_{ext} = 1 \text{ atm}$

$\therefore \text{work} = -P\Delta V$
 $= -(1.0 \text{ atm})(6273.5 \text{ L})$
 $= -6273.5 \text{ L} \cdot \text{atm}$

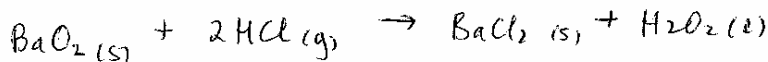
Convert to Joules:

$= -635606.6 \text{ J}$
 $= -635.6 \text{ kJ}$

$R = 0.08206 \frac{\text{Latm}}{\text{molK}} = 8.314 \frac{\text{J}}{\text{molK}}$
 $\Rightarrow 1 \text{ atm} = 101.3 \text{ J}$

$w = -636 \text{ kJ}$ ← That is a lot of energy. Gets converted into pushing the tank through walls, & the like, because system doing work.

#2 Barium peroxide rocket fuel



$$\begin{aligned} \text{(a)} \quad \Delta H^\circ_{\text{rxn}} &= \sum n \Delta H_f^\circ \text{ products} - \sum n \Delta H_f^\circ \text{ reactants} \\ &= [-859.2 + (-187.3)] - [-601.1 + (2)(-92.4)] \\ &= -1046.5 - (-805.9) \\ &= -240.6 \text{ kJ} \quad (\text{per 1 mole BaO}_2(\text{s})) \end{aligned}$$

(b) To produce 500 kcal of heat:

$$Q = (500 \text{ kcal}) \left(\frac{4.184 \text{ kJ}}{\text{kcal}} \right) = -2092 \text{ kJ}$$

$$\# \text{ moles BaO}_2 = \frac{-2092 \text{ kJ}}{-240.6 \text{ kJ} \cdot \text{mol}^{-1}} = 8.695 \text{ mol BaO}_2$$

$$\begin{aligned} \# \text{ g BaO}_2 &= \# n \cdot \text{MM} = (8.695 \text{ mol})(170.332 \text{ g/mol}) \\ &= 1480.95 \text{ g} \end{aligned}$$

mass required \approx 1500 g

#3 Drinking diet soda: 350 mL, 5°C.

$$\begin{aligned} \text{(a)} \quad \text{Raise temp. to body temp.} \quad & \left. \begin{array}{l} T_f = 37^\circ\text{C} \\ T_i = 5^\circ\text{C} \end{array} \right\} \Delta T = 32^\circ\text{C} \end{aligned}$$

$$Q = c \cdot m \cdot \Delta T$$

$$= \left(\frac{4.184 \text{ J}}{\text{g}^\circ\text{C}} \right) (350 \text{ g}) (32^\circ\text{C})$$

$$= 46860.8 \text{ J}$$

$$\approx 47 \text{ kJ}$$

note 350 mL = 350 g
if assume same dens.
as water.

energy spent by body. = -ve
opposite in sign to heat absorbed by liquid

$$\begin{aligned} \text{(b)} \quad \text{Caloric value: } 1 \text{ Calorie} &= 1 \text{ kcal} = 1000 \times 4.184 \text{ J} \\ &= 4.184 \text{ kJ} \end{aligned}$$

$$\text{Net change in energy: } -47 + 4.184 \text{ kJ}$$

$$= -42.8 \text{ kJ}$$

$$= -43 \text{ kJ}$$

The body actually burns 43 kJ when you drink this stuff!

#4 Burning peanuts as fuel to heat water to 100°C.

- To heat water: e.g. from RT. to 100°C
(250 mL) $\Delta T = 100 - 25 = 75^\circ\text{C}$.

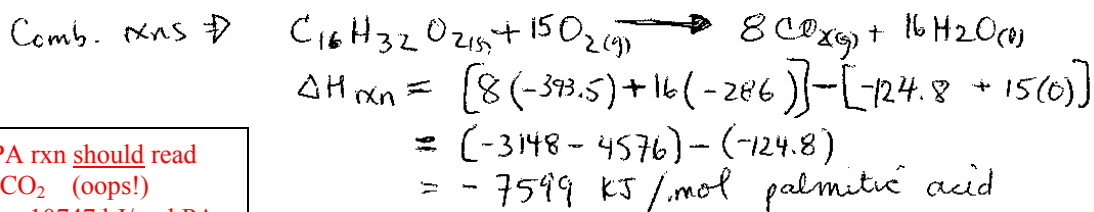
$$Q = C \times m \times \Delta T = \left(\frac{4.184 \text{ J}}{\text{g}^\circ\text{C}} \right) (250 \text{ g}) (75^\circ\text{C})$$

$$= 78450 \text{ J}$$

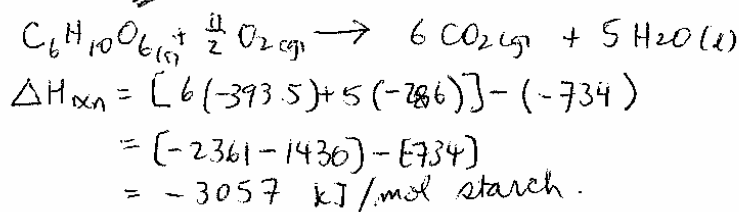
$$\approx 78 \text{ kJ}$$

- 1 peanut \Rightarrow 0.73 g containing palmitic acid $\text{C}_{16}\text{H}_{32}\text{O}_2$ + starch $\text{C}_6\text{H}_{10}\text{O}_6$
fuel per peanut = $(0.73 \text{ g} \times 0.49 \text{ peanut oil}) + (0.73 \text{ g} \times 0.29 \text{ starch}) + \text{rest}$
 $= 0.358 \text{ g peanut oil} + 0.212 \text{ g starch}$
 $= \frac{0.358 \text{ g palmitic acid}}{256.44 \text{ g} \cdot \text{mol}^{-1}} + \frac{0.212 \text{ g starch}}{178.15 \text{ g} \cdot \text{mol}^{-1}}$
 $= 1.396 \times 10^{-3} \text{ mol P.A.} + 1.19 \times 10^{-3} \text{ mol starch}$

$$\text{energy } \Delta H_{\text{comb}}^\circ = \Delta H_f^\circ \text{ products} - \Delta H_f^\circ \text{ reactants}$$



Balanced PA rxn should read
 31O_2 & 16CO_2 (oops!)
 So: $\Delta H_{\text{rxn}} = -10747 \text{ kJ/mol PA}$



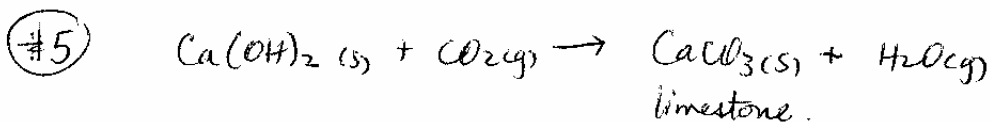
So: in 1 peanut: enthalpy of combustion ...

$$(1.396 \times 10^{-3} \text{ mol})(-7599) = -10.6 \text{ kJ from palmitic acid}$$

$$(1.19 \times 10^{-3} \text{ mol})(-3057) = -3.6 \text{ kJ from starch}$$

REQUIRED: $\frac{78 \text{ kJ}}{14.2 \text{ kJ}} = 5.5 \text{ peanuts!}$ $\frac{-14.2 \text{ kJ}}{-10.6 \text{ kJ} - 3.6 \text{ kJ}} = 1.1 \text{ peanuts!}$

Using correct ΔH_{rxn} : 1 peanut yields -15.00 kJ from PA + -2.6 kJ from starch = total -18.6 kJ
 THUS need $78 \text{ kJ} / 18.6 \text{ kJ/peanut} = 4.2 \text{ peanuts}$



(a) $\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ \text{ products} - \sum n \Delta H_f^\circ \text{ reactants}$
 $= [-1207 + (-242)] - [-987 - (-393.5)]$
 $= -1447 + 1380.5$
 $= -66.5 \text{ kJ/mol}$

Note: data taken from a textbook whose thermodynamic data had fewer decimal places. THUS: rounding error in my answers here relative to if data taken from Kotz

(b) If 1.00 kg Ca(OH)_2 reacts \bar{c} stoich. CO_2 :

$Q = \left(1.00 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{\text{mol Ca(OH)}_2}{74} \right) \times -66.5 \frac{\text{kJ}}{\text{mol}}$
 $= (13.495 \text{ mol})(-66.5 \text{ kJ})$
 $= -897.42 \text{ kJ}$
 $= -897 \text{ kJ per mol Ca(OH)}_2$ heat RELEASED

(c) Logic: no change in # moles gas OR # molecules
 \therefore expect ΔS to be small; can't guess sign.

Calculation:

$\Delta S_{\text{rxn}}^\circ = (93 + 189) - (83 + 214)$
 $\Delta S_{\text{rxn}}^\circ = -15 \frac{\text{J}}{\text{mol}\cdot\text{K}}$ \leftarrow matches logic.

(d) $\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$
 $= -897 \frac{\text{kJ}}{\text{mol}} - (35 + 273 \text{ K})(-0.015 \frac{\text{kJ}}{\text{mol}\cdot\text{K}})$

$\Rightarrow \Delta G_{\text{rxn}} = -893 \text{ kJ/mol}$ clearly spontaneous, since $\Delta G < 0$.

\rightarrow enthalpically favoured ($\Delta H < 0$)

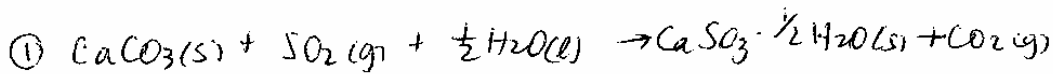
\rightarrow entropically disfavoured \rightarrow at 298 K ($\Delta S_{\text{rxn}}^\circ = -15 \text{ J/mol}\cdot\text{K}$)

\downarrow ~~at 308 K~~
 $T \Delta S$ term at 308 K $\Rightarrow +4620 \frac{\text{J}}{\text{mol}} = +4.6 \text{ kJ/mol}$

Rxn driven by enthalpy.

#6

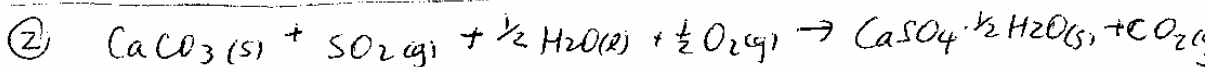
which is more "product favoured" means: which has the larger driving force for rxn... ie: ΔG !!



$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [-1311.7 + (-393.5)] - [-1207 + (-297) + (0.5)(-286)] \\ &= -1705.2 - (-1647) \\ &= -58.2 \text{ kJ/mol of product} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [131.3 + 214] - [93 + 248 + 0.5(70)] \\ &= 335.3 - 376 \\ &= -40.7 \text{ J/mol K} \end{aligned}$$

$$\Rightarrow \Delta G^\circ_{\text{rxn}} = -58.2 - (298\text{K})(-0.0407) = -70.3 \text{ kJ/mol at } 298\text{K}$$



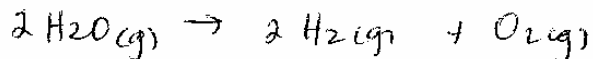
$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [-1574.65 + (-393.5)] - [-1207 + (-297) + 0.5(-286)] \\ &= -1968.15 - (-1647) \\ &= -321.15 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [134.8 + 214] - [93 + 248 + 0.5(70) + 0] \\ &= 348.8 - 376 \\ &= -27.2 \text{ J/mol K} \end{aligned}$$

$$\Rightarrow \Delta G^\circ_{\text{rxn}} = -321.15 - (298\text{K})(-0.0272) = -313 \text{ kJ/mol at } 298\text{K}$$

The rxn involving formation of hydrated calcium sulfate ~~is not~~ has a higher gibbs' free energy \therefore is more product-favoured.

#7 When would this be spontaneous?



$$\Delta H^\circ_{\text{rxn}} = [2(0) + 0] - [2(-242)]$$

(disfavourable) $= +484 \text{ kJ} = +242 \text{ kJ/mol H}_2\text{O decomposed}$

$$\Delta S^\circ_{\text{rxn}} = [2(131) + 205] - [2(189)]$$

(favourable) $= +89 \text{ J/K} = 44.5 \text{ J/mol}\cdot\text{K}$

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T \Delta S$$
$$= +484 - T(0.089)$$

Let $0 = 484 - 0.089T$

$$T = \frac{-484}{-0.089} = 5438 \text{ K} !!$$

note:

per 1 mole

$$0 = 242 - T(0.0445)$$

$$T = 5438.$$

Same thing...

This reaction would only be spontaneous at temperatures above $5438 \text{ K} = 5165^\circ\text{C} !$



(a) $\Delta H_{rxn}^{\circ} = \Delta H_f^{\circ} \text{ diamond} - \Delta H_f^{\circ} \text{ graphite}$
 $= 2 - 0$
 $= 2 \text{ kJ/mol.}$ endothermic.

$\Delta S_{rxn}^{\circ} = S_{diamond}^{\circ} - S_{graphite}^{\circ}$
 $= 2 - 6$
 $= -4 \text{ J/mol}\cdot\text{K}$ disfavoured...

$$\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ}$$

$$= 2 - (298)(-0.004)$$

$$= +3.192 \text{ kJ/mol}$$

oh! means reverse process is spontaneous (diamonds should convert to pencil lead)

$$\Delta S_{univ}^{\circ} = \left(\frac{-\Delta H^{\circ}}{T} \right) + (\Delta S_{rxn}^{\circ})$$

$$= \left(\frac{-2 \text{ kJ}}{298 \text{ K}} \right) + \left(-0.004 \frac{\text{kJ}}{\text{K}} \right)$$

$$= -0.0067 - 0.004$$

$$\Delta S_{univ}^{\circ} = -0.0071 \frac{\text{kJ}}{\text{K}}$$

) The contradiction: at high T, P, this rxn does occur.

⊗ Is it due to the temperature? NO.

$$\Delta G = \underbrace{\Delta H}_{+} - \underbrace{T\Delta S}_{-}$$

no matter how large T is, $(-T\Delta S)$ in this case will always be +
 $\therefore \Delta G$ always + too...

⊙ It is the high pressure!