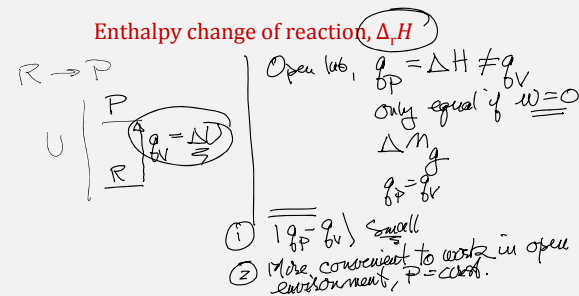


Lecture 10 CH131 Summer 1

Thursday, June 6, 2019

- Enthalpy change of reaction, $\Delta_r H$
- Hess's law
- Standard enthalpy of formation of X, $\Delta_f H^\circ(X)$
- Example thermochemistry problems.

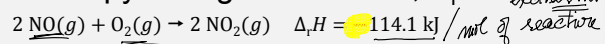
Next lecture: Continue Ch13: Spontaneous Processes ✓



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Enthalpy change of reaction, $\Delta_r H$ *exothermic*

"114.1 kJ of heat are released for each 2 mol of $\text{NO}_2(g)$ formed."

"114.1 kJ of heat are released for each 2 mol of $\text{NO}(g)$ consumed."

"114.1 kJ of heat are released for each 1 mol of O_2 consumed."

"114.1 kJ of heat are released for each reaction unit."

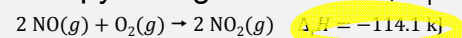
"114.1 kJ of heat are released for each mol of reaction."



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Enthalpy change of reaction, $\Delta_r H$ 

If 2.90 mol $\text{NO}(g)$ react completely with excess oxygen, what is q_p ?

$$q_p = 2.90 \text{ mol NO} \times -114.1 \text{ kJ}/(2 \text{ mol NO})$$

$$= -165 \text{ kJ}$$

If 11.5 g $\text{NO}(g)$ react completely with excess oxygen, what is q_p ?

$$q_p = 11.5 \text{ g} \times \text{mol NO} / (30.0 \text{ g}) \times -114.1 \text{ kJ}/(2 \text{ mol NO})$$

$$= -21.8 \text{ kJ}$$



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[Quiz] The enthalpy change of reaction for
 $2A + 3B \rightarrow 4C + D$
 is $\Delta_r H^\circ = -45 \text{ kJ}$. If 1 mol of A reacts with 1 mol of B with 100% yield, then q_p for the process is ...

0% 1. -90 kJ
 0% 2. -45 kJ
 0% 3. -30 kJ
 100% 4. -15 kJ
 0% 5. Further information required

Handwritten notes:
 $1 \text{ mol B} \text{ forms } \frac{1}{3} \text{ mol D} \text{ } \times \text{ limiting reagent}$
 $1 \text{ mol A} \text{ forms } \frac{1}{2} \text{ mol D}$
 $1 \text{ mol B} + \frac{1 \text{ mol A}}{3 \text{ mol B}} \times \frac{-45 \text{ kJ}}{1 \text{ mol A}} = -15 \text{ kJ}$

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$\Delta_r H^\circ$ via Hess's law

Consider

$A \rightarrow B \quad \Delta_r H^\circ_1$
 $C \rightarrow B \quad \Delta_r H^\circ_2$
 $A \rightarrow C \quad \Delta_r H^\circ_3 = ?$

Handwritten diagram:
 $A \rightarrow B \quad \Delta H_1$
 $B \rightarrow C \quad -\Delta H_2$
 $A \rightarrow C \quad \Delta H_1 - \Delta H_2$

Handwritten diagram:
 H
 $R \rightarrow P \quad \Delta H$
 $P \rightarrow R \quad -\Delta H$

Since energy is conserved ...

$\Delta_r H^\circ_3 = \Delta_r H^\circ_1 - \Delta_r H^\circ_2$

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$\Delta_r H^\circ$ via Hess's law

Consider

$A \rightarrow B \quad \Delta_r H^\circ_1 = +85 \text{ kJ}$
 $C \rightarrow B \quad \Delta_r H^\circ_2 = -52 \text{ kJ}$
 $A \rightarrow C \quad \Delta_r H^\circ_3 = ?$

Since energy is conserved ...

$\Delta_r H^\circ_3 = \Delta_r H^\circ_1 - \Delta_r H^\circ_2 = +85 \text{ kJ} - (-52 \text{ kJ}) = +137 \text{ kJ}$

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$\Delta_r H^\circ$ via Hess's law

Consider

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H^\circ_1$
 $S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta_r H^\circ_2$
 $CS_2(l) + 3 O_2(g) \rightarrow CO_2(g) + 2 SO_2(g) \quad \Delta_r H^\circ_3$
 $C(s) + 2 S(s) \rightarrow CS_2(l) \quad \Delta_r H^\circ_4 = ?$

Since energy is conserved ...

$\Delta_r H^\circ_4 = \Delta_r H^\circ_1 + 2 \Delta_r H^\circ_2 - \Delta_r H^\circ_3$

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$\Delta_r H^\circ$ via Hess's law

Consider

$$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta_r H^\circ_1 = -393.5 \text{ kJ}$$

$$\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g) \quad \Delta_r H^\circ_2 = -296.8 \text{ kJ}$$

$$\text{CS}_2(l) + 3 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{SO}_2(g) \quad \Delta_r H^\circ_3 = -1103.9 \text{ kJ}$$

$$\text{C}(s) + 2 \text{S}(s) \rightarrow \text{CS}_2(l) \quad \Delta_r H^\circ_4 = ?$$

Since energy is conserved ...

$$\Delta_r H^\circ_4 = \Delta_r H^\circ_1 + 2 \Delta_r H^\circ_2 - \Delta_r H^\circ_3 = +116.8 \text{ kJ}$$

$$-393.5 + 2(-296.8) - (-1103.9)$$

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Calculation of q_V and q_P

$$2 \text{Al}(s) + 6 \text{HCl}(aq) \rightarrow 2 \text{AlCl}_3(aq) + 3 \text{H}_2(g) \quad \Delta_r H^\circ_1 = -1049 \text{ kJ}$$

$$\text{HCl}(g) \rightarrow \text{HCl}(aq) \quad \Delta_r H^\circ_2 = -79 \text{ kJ}$$

$$\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2 \text{HCl}(g) \quad \Delta_r H^\circ_3 = -185 \text{ kJ}$$

$$\text{AlCl}_3(s) \rightarrow \text{AlCl}_3(aq) \quad \Delta_r H^\circ_4 = -323 \text{ kJ}$$

(a) Calculate $\Delta_r H^\circ$ for the reaction

$$2 \text{Al}(s) + 3 \text{Cl}_2(g) \rightarrow 2 \text{AlCl}_3(s)$$

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Calculation of q_V and q_P

$$2 \text{Al}(s) + 6 \text{HCl}(aq) \rightarrow 2 \text{AlCl}_3(aq) + 3 \text{H}_2(g) \quad \Delta_r H^\circ_1 = -1049 \text{ kJ}$$

$$\text{HCl}(g) \rightarrow \text{HCl}(aq) \quad \Delta_r H^\circ_2 = -79 \text{ kJ}$$

$$\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2 \text{HCl}(g) \quad \Delta_r H^\circ_3 = -185 \text{ kJ}$$

$$\text{AlCl}_3(s) \rightarrow \text{AlCl}_3(aq) \quad \Delta_r H^\circ_4 = -323 \text{ kJ}$$

(a) Calculate $\Delta_r H^\circ$ for the reaction

$$2 \text{Al}(s) + 3 \text{Cl}_2(g) \rightarrow 2 \text{AlCl}_3(s)$$

$$\Delta_r H^\circ = \Delta_1 H^\circ + 6 \Delta_2 H^\circ + 3 \Delta_3 H^\circ - 2 \Delta_4 H^\circ = -1432 \text{ kJ}$$

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Calculation of q_V and q_P

$$2 \text{Al}(s) + 3 \text{Cl}_2(g) \rightarrow 2 \text{AlCl}_3(s) \quad \Delta_r H^\circ = -1432 \text{ kJ}$$

(b) When 1.35 g of Al(s) reacts with 0.71 g of Cl₂(g), 25 J of work is involved. Calculate q_V for the reaction, to confirm that q_P differs only a little from q_V .

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Calculation of q_V and q_P



(b) When 1.35 g of $\text{Al}(s)$ reacts with 0.71 g of $\text{Cl}_2(g)$, 25 J of work is involved. Calculate q_V for the reaction, to confirm that q_P differs only a little from q_V .

$$q_P = -4.77 \text{ kJ}$$

$$w = +0.25 \text{ kJ}$$

$$q_V = \Delta U = q_P + w = -4.74 \text{ kJ}$$



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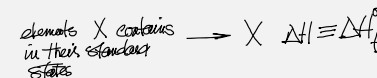
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Standard enthalpy of formation, $\Delta_f H^\circ$, of X

Form **one mole** of X ...

... from the **elements** it contains, ...

... each in their **standard state**.



Recall, the **standard state** of an **element** is its **most stable** form.



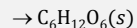
14

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$\Delta_f H^\circ$ of sugar, $\text{C}_6\text{H}_{12}\text{O}_6(s)$

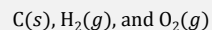
Form **one mole** of sugar ...



... from the **elements** it contains, ...

C, H, and O

... each in their **standard state**,



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$\Delta_f H^\circ$ of sugar, $\text{C}_6\text{H}_{12}\text{O}_6(s)$

The **standard** enthalpy of formation of sugar is defined as the enthalpy change when **one mole** of sugar is formed from its elements, each in their **standard states**.



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 $\Delta_f H^\circ$ of sugar, $C_6H_{12}O_6(s)$

Task: Write down the balanced chemical equation whose **enthalpy change** is the **standard enthalpy of formation** of sugar, $C_6H_{12}O_6(s)$

The enthalpy change of the chemical reaction
 $6 C(s) + 6 H_2(g) + 3 O_2(g) \rightarrow C_6H_{12}O_6(s)$
 is the standard enthalpy of formation of sugar.

$$\Delta H_r \equiv \Delta H_f^\circ$$



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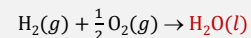
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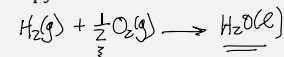
 $\Delta_f H^\circ$ of water, $H_2O(l)$

Task: Write down the balanced chemical equation whose **enthalpy change** is the **standard enthalpy of formation** of water, $H_2O(l)$

The enthalpy change of the chemical reaction



is the standard enthalpy of formation of **water**.



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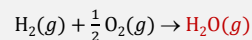
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 $\Delta_f H^\circ$ of steam, $H_2O(g)$

Task: Write down the balanced chemical equation whose **enthalpy change** is the **standard enthalpy of formation** of steam, $H_2O(g)$.

The enthalpy change of the chemical reaction



is the standard enthalpy of formation of **steam**.



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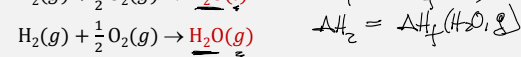
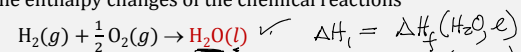
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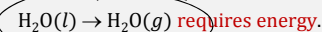
 $\Delta_f H^\circ$ of water and steam

Is the standard enthalpy of formation of **water** *the same* as that of **steam**?

The enthalpy changes of the chemical reactions



are **different**, since



$$\Delta H_2 - \Delta H_1 \neq 0$$



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Enthalpy change terms of ΔH_f

gr

$$\boxed{\text{CH}_4(g)} + \boxed{2\text{O}_2(g)} \rightarrow \boxed{\text{CO}_2(g)} + \boxed{2\text{H}_2\text{O}(l)} \quad \checkmark$$

$$\begin{array}{l} \text{CH}_4(g) \rightarrow \text{C}(s) + 2\text{H}_2(g) \\ 2\text{O}_2(g) \rightarrow 2\text{O}(g) \\ \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \\ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) \end{array} \quad \left\{ \begin{array}{l} -\Delta H_f(\text{CH}_4, g) \\ -\Delta H_f(\text{O}_2, g) = 0 \\ +\Delta H_f(\text{CO}_2, g) \\ +2\Delta H_f(\text{H}_2\text{O}, l) \end{array} \right.$$

$$\Delta H_{rxn} = \Delta H_f(\text{CO}_2, g) + 2\Delta H_f(\text{H}_2\text{O}, l) - \Delta H_f(\text{CH}_4, g) - \Delta H_f(\text{O}_2, g)$$

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Example thermochemistry problems

$$\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2 \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) =$$

1 mol of sugar $\xrightarrow{?}$ $\frac{1}{12}$ $\frac{1}{16}$

$$\Delta H_{rxn} = 6 \Delta H_f(\text{CO}_2, g) + 6 \Delta H_f(\text{H}_2\text{O}, l) - \Delta H_f(\text{C}_6\text{H}_{12}\text{O}_6, s)$$

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Problem 7e & 8e: 12.39

39. Calculate the standard enthalpy change ΔH° at 25°C for the reaction

$$\text{N}_2\text{H}_4(l) + 3\text{O}_2(g) \rightarrow 2\text{NO}_2(g) + 2\text{H}_2\text{O}(l)$$

using the standard enthalpies of formation (ΔH_f°) of reactants and products at 25°C from Appendix D.

$$\Delta H_{rxn} = 2\Delta H_f(\text{NO}_2, g) + 2\Delta H_f(\text{H}_2\text{O}, l) - \Delta H_f(\text{N}_2\text{H}_4, l)$$

$$= -555.93 \text{ kJ}$$

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