

Lecture 11 Energy changes in reactions.

- Gibbs free energy
 - Enthalpy
- } examples

- Calorimetry
- } measuring heat released/
absorbed in reactions
& other processes

[ie measuring energy released
by burning things

↳ 'enthalpy of
combustion']

Example Questions

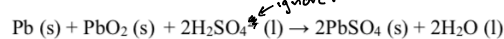
- calculate free energy/enthalpy (from table etc)
- state: spontaneous? Exothermic? Exergonic?

2018
(Summer school)

29) Given the table of standard Gibbs free energies of formation below:

Substance	Phase	Chemical Formula	ΔG_f° (kJ.mol ⁻¹)
Water	liquid	H ₂ O	-237.14
Water	gas	H ₂ O	-228.61
Oxygen	gas	O ₂	0
Hydrogen	gas	H ₂	0
Carbon dioxide	gas	CO ₂	-394.39
Lead	solid	Pb	0
Lead sulfate	solid	PbSO ₄	-813.2
Lead oxide	solid	PbO ₂	-215.48
Sulfuric acid	liquid	H ₂ SO ₄	-744.63

- a. Determine the overall change in Gibbs free energy for the following lead acid battery reaction under standard conditions. Show your working



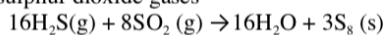
(3 marks)

- b. Does this reaction take place spontaneously under standard conditions? Justify your answer. (1 mark)

Answer: _____

2017

34) Solid sulphur is commonly formed at the vents of volcanoes in a reaction between hydrogen sulphide and sulphur dioxide gases



The enthalpy change $\Delta H = -1876$ kJ / mol

The entropy change $\Delta S = -3.424$ kJ / mol °K

- a. Is this reaction exothermic or endothermic? (1 mark)

$$\Delta H < 0$$

Answer: _____

- b. Why is the entropy change for this reaction negative? (1 mark)

Answer:

- c. Is this reaction exergonic or endergonic at temperature $T = 298\text{K}$? Justify your answer. (2 marks)

Answer:

$$\Delta G ? \quad G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \quad \text{for fixed T}$$

$$\Delta G < 0$$

- d. Does this reaction take place spontaneously at 298K? Justify your answer. (1 mark)

Answer:

yes ($\Delta G < 0$)

$\Delta G < 0$
exergonic

$\Delta H > 0$
endergonic

Example questions : Calorimetry

2018
SS.

31) A secret substance, called 'substance X', is being investigated for its potential as a new type of fuel. A 1.0 g sample of substance X is burned in a bomb calorimeter containing 1000 grams of water at an initial temperature of 23°C. After the reaction, the final temperature of the water is 30.1°C. The heat capacity of the calorimeter (also known as the "calorimeter constant") is 850 J/°C. The specific heat of water is 4.184 J/g °C and the molar mass of the substance is 110 g/mol.

a. Calculate the heat absorbed by the water.

(1 mark)

Heat absorbed by water: _____

b. Calculate the heat absorbed by the calorimeter

(1 mark)

Heat absorbed by calorimeter: _____

c. What is the total amount of heat released by the reaction?

(1 mark)

Total heat released: _____

d. Calculate the heat of combustion of substance X in kJ/mol.

(1 mark)

Heat of combustion of substance X (kJ/mol): _____

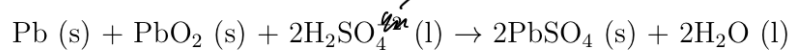
Example cont'd

Example Problems 9: Gibbs free energy

1. Calculate the energy released if you oxidised the entire glucose content of a 65g chocolate bar. Assume the glucose content of the bar is 70g per 100g. Gibbs free energy of glucose is -2870 kJ/mol. The molecular weight of glucose is 180.16 g/mol.

cont'd

2. A typical lead acid battery undergoes the following chemical reaction to produce energy:



Given the values for Gibbs free energy of formation in the table above, determine the electrochemical work produced at 298 K.

ie overall ΔG .

$$2. \Delta G = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$

$$= [2 \times (-813.2) + 2 \times (-237.14)] - [0 + (-215.44) + 2 \times (-744.63)]$$

$$\approx -396 \text{ kJ} \quad (\Delta G < 0 \Rightarrow \text{spontaneous})$$

$$(\quad = n \cdot \Delta N \quad \text{'chemical work'})$$

\hookrightarrow changes N

'chemical pressure' n .

(chemical potential)

Example Problems 10: Enthalpy

- 1) Calculate the heat of reaction (enthalpy of reaction) ΔH_f for the chemical reaction of the lead acid battery in the problem above.
- 2) Describe whether this reaction is endothermic or exothermic.
- ~~3. Compare the Gibbs free energy value with the heat of reaction. What does this mean in terms of heat to/from the environment?~~
- 4) Calculate ΔH if a piece of metal with a specific heat of $0.98 \text{ kJ}/(\text{kg}\cdot\text{K})$ and a mass of 2 kg is heated from 22°C to 28°C .

what is the relation bet.
 ΔG , ΔH &
 ΔS ?

Answers

$$\begin{aligned}
 1. \quad \Delta H &= \Delta H^{\text{product}} - \Delta H^{\text{reactant}} \\
 &= [2 \times (-285.83) + 2 \times (-919.24)] \\
 &\quad - [0 + (-274.47) + 2 \times (-909.27)] \\
 &\approx \underline{\underline{-319 \text{ kJ}}}
 \end{aligned}$$

2. $\Delta H < 0 \Rightarrow$ exothermic ($\Delta H = Q^m$ for constant P
 \rightarrow Heat expelled, $Q^m < 0$)

3. $\Delta G = \Delta H - T \Delta S$
 for 'standard' constant T, P conditions.

4. Assume here:

$$\begin{aligned}\Delta H &= Q = c_p m \Delta T \\ &= \frac{0.98 \text{ kJ}}{\text{kg} \cdot \text{K}} \times 2 \text{ kg} \times 6 \text{ K} \\ &\approx 11.8 \text{ kJ}\end{aligned}$$

Note:
 $T(\text{K}) = T(^{\circ}\text{C}) + 273.15$
 $\Delta T(\text{K}) = \Delta T(^{\circ}\text{C})$
 $\rightarrow 273$ cancels
 (just a ref).

2.8 Calorimetry and the enthalpy of combustion

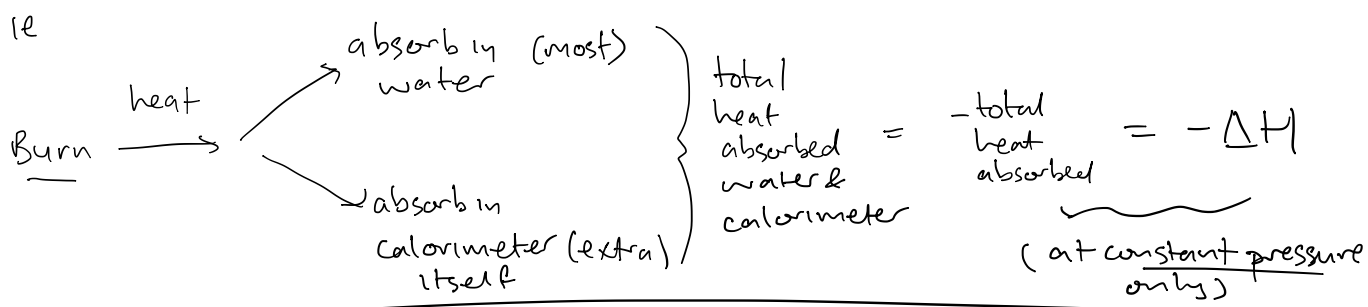
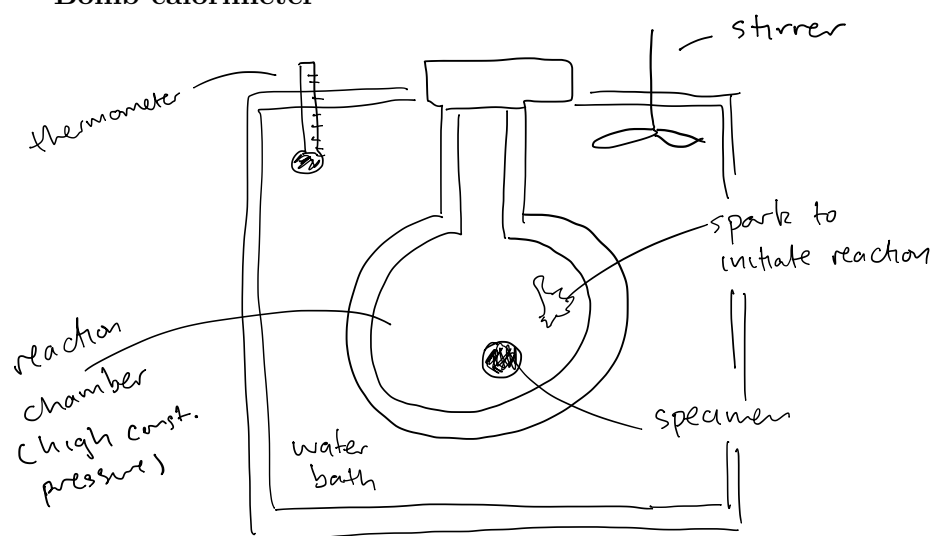
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Calorimetry is the science of measuring heat transfer during physical or chemical processes such as chemical reactions. As briefly mentioned previously, it can also be used to measure heat capacities.

It is often used to measure the enthalpy of combustion, also called the heat of combustion. This is the heat energy available by 'burning' or 'exploding' a substance - i.e. when it reacts rapidly and completely with oxygen in a high-temperature/ exothermic redox reaction. This clearly involves the conversion of chemical energy to heat (which, typically in engineering applications, is then used to produce work). A related term is energy density, which is the enthalpy of combustion per unit mass.

Calorimetry could hence be used to determine the energy available from a new potential fuel source. The basic example for doing this is a so-called bomb calorimeter. We discuss how this is used below.

— Bomb calorimeter —

**Example Problems 11: Calorimetry**

1. A 1 g sample of octane is burned in a bomb calorimeter containing 1200 g of water an initial temperature of 25 °C. After the reaction the final temperature of the water is 33°C. The heat capacity of the calorimeter (the calorimeter constant) is 837 J/°C. The specific heat of water is 4.184 J/(g.°C). Calculate the heat of combustion of octane in kJ/mol.

use: /
molar mass of
octane = 114 g/mol.

—Answers—

steps : $\left. \begin{array}{l} Q_{\text{water}} \\ Q_{\text{calorimeter}} \end{array} \right\}$ add then get signs & units right

1. Heat absorbed by water $\Delta T = (33 - 25)^{\circ}\text{C} = 8^{\circ}\text{C}$.

$$Q_w = c_w \times m \times \Delta T = 4.184 \frac{\text{J}}{\text{g}^{\circ}\text{C}} \times 1200 \text{g} \times 8^{\circ}\text{C} \approx \boxed{40.2 \text{ kJ}}$$

2. Heat absorbed by calorimeter (extra, not absorbed by water)

$$Q_c = C_c \times \Delta T = 837 \frac{\text{J}}{^{\circ}\text{C}} \times 8 \approx \boxed{6.70 \text{ kJ}}$$

3. Total absorbed = $Q_w + Q_c \approx \boxed{46.9 \text{ kJ}}$

4. Heat released $\boxed{Q = -46.9 \text{ kJ}}$ (exothermic)

5. $\Delta H = Q$ (assume constant pressure)

Per mol: $\Delta H = \frac{-46.9 \text{ kJ}}{1 \text{ g burned}} \times \frac{114 \text{ g}}{\text{mol}} \approx -5350 \text{ kJ/mol} = \boxed{-5.35 \text{ MJ/mol}}$

[cf $\sim -5.5 \text{ MJ/mol}$ in table
—close!
—conditions might be diff.]

Table 4 gives some typical **standard enthalpies of combustion**, ΔH_c^0 , which is defined as the enthalpy change when **1 mole of a compound is completely burnt in oxygen gas at 298 K and 1 atm.**

Substance	Phase	Chemical Formula	ΔH_c° (kJ.mol ⁻¹)
Octane	liquid	C ₈ H ₁₈	-5471
Benzene	liquid	C ₆ H ₆	-3268
Glucose	liquid	C ₆ H ₁₂ O ₆	-2808
Propane	gas	C ₃ H ₈	-2220
Ethanol	liquid	C ₂ H ₅ OH	-1368
Acetylene	gas	C ₂ H ₂	-1300
Methane	gas	CH ₄	-890
Carbon	solid	C	-394
Hydrogen	gas	H ₂	-286

Table 4: Examples of standard enthalpy of combustion values at 298 K and 1 atm. (From notes by Thor Besier.)

Example Problems 12: Enthalpy of combustion

- How much heat is released when 4.5 g of methane gas is burned at constant pressure? Molar mass of methane is 16.04 g/mol.
- For fuels used in transportation the enthalpy/weight ratio is important

const. pressure

$$1. \quad Q = \Delta H = -890 \frac{\text{kJ}}{\text{mol}} \times \frac{\text{mol}}{16.04 \text{ g}} \times 4.5 \text{ g}$$

$$\approx \underline{-250 \text{ kJ}} \quad (\text{exothermic, heat released})$$

because the car/plane has to carry the fuel. Compare the energy densities in MJ/kg of the following fuels to petrol (approx. 46 MJ/kg):

- (a) Methane: molar mass 16 g/mol
- (b) Ethanol: molar mass 46 g/mol
- (c) Propane: 44 g/mol

— Answers —

$$\begin{aligned}
 2. a) \quad & -890 \frac{\text{kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{16 \text{ g}} = -55 \frac{\text{kJ}}{\text{g}} \times \left(\frac{\text{MJ}}{10^3 \text{ kJ}} \right) \times \left(\frac{10^3 \text{ g}}{\text{kg}} \right) \\
 & = \underline{-55 \text{ MJ/kg}} \quad (\text{Higher energy density than petrol})
 \end{aligned}$$

$$\begin{aligned}
 b) \quad & -1365 \frac{\text{kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{46 \text{ g}} = -30 \frac{\text{kJ}}{\text{g}} \\
 & = \underline{-30 \text{ MJ/kg}} \quad (\text{Lower energy density than petrol})
 \end{aligned}$$

$$\begin{aligned}
 c) \quad & -2220 \frac{\text{kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{44 \text{ g}} = -50 \frac{\text{kJ}}{\text{g}} \\
 & = \underline{-50 \text{ MJ/kg}} \quad (\text{Higher energy density than petrol})
 \end{aligned}$$