

Thermodynamic contexts: answers

Education in Chemistry

May 2021

<https://rsc.li/3epLoHH>

Teacher notes

The following problems allow learners to apply their skills at processing thermodynamic data in new contexts. These contexts are taken from the infographic 'Tremendous Thermodynamics' and supporting information can be found in the downloadable factsheet on that page.

Part 1 involves a Hess' Law calculation, followed by use of atomic mass and density to convert to energy per unit volume and unit mass.

Part 2 tests understanding of intermolecular forces, their relative strength compared to covalent bonds and also reinforces the idea that making bonds is exothermic.

Parts 1 and 2 should be accessible to learners who are working through the first year of a 16–18 chemistry course.

Part 3 involves calculation of entropy change from absolute entropies and use of the expression $\Delta G = \Delta H - T\Delta S$ to calculate the free energy change and the temperature at which the reaction is no longer favourable in the forward direction.

Part 3 is accessible to learners who are in the second year of a 16–18 chemistry course.

Note. In Part 3, teachers may get asked why the entropy of the aqueous hydrogen ions has a value of zero, which might suggest that there is no disorder at all. This is because [entropies of aqueous ions](#) are by convention quoted as a difference from that of the aqueous hydrogen ion (in a similar way to the use of the standard hydrogen electrode as a reference for cell potentials).

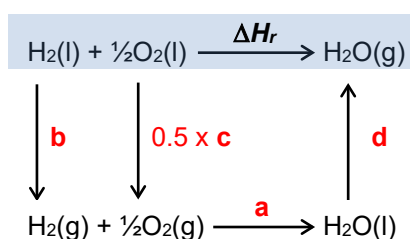
Thermodynamic contexts

These questions are based on the information about the NASA SLS rocket, heat pumps and raising agents given on the fact sheet and will allow you to further explore the thermodynamics behind these applications.

Part 1: Energy needed to get us back to the Moon

The concept of energy was originally developed during the Industrial Revolution. It allowed engineers to quantify processes taking place in machines such as steam engines. Questions could now be answered such as 'How much fuel do you need to burn to move an object over a distance with a certain force?'. You can do the same type of calculation for the NASA SLS rocket.

1. The energy cycle below shows how the enthalpy change of the reaction of liquid hydrogen and oxygen in the core stage rocket (ΔH_r) can be estimated using Hess' Law by combining several other known enthalpy changes.



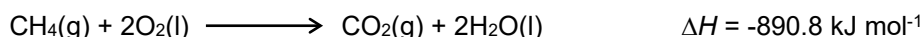
Identify which steps in the energy cycle corresponds to each of enthalpy changes given below and then show by calculation that the enthalpy change for the core stage fuel reaction is -241 kJ mol^{-1} .

Standard enthalpy change of combustion of hydrogen	$-285.8 \text{ kJ mol}^{-1}$	a
Enthalpy change of vaporisation of hydrogen	$+0.9 \text{ kJ mol}^{-1}$	b
Enthalpy change of vaporisation of oxygen	$+6.8 \text{ kJ mol}^{-1}$	c
Enthalpy change of vaporisation of water	$+40.7 \text{ kJ mol}^{-1}$	d

$$\Delta H_r = \mathbf{b} + (0.5 \times \mathbf{c}) + \mathbf{a} + \mathbf{d} = 0.9 + 3.4 + (-285.8) + 40.7 = -240.8 = -241 \text{ kJ mol}^{-1}$$

2. The enthalpy change calculated above is for the combustion of 1 mole of liquid hydrogen with 0.5 moles of liquid oxygen. You can now go on and calculate how much energy the total amount of hydrogen/oxygen mixture in the rocket would produce, as follows.
 - a. If the density of liquid hydrogen is 0.0709 g cm^{-3} , calculate the volume of 1 mole of liquid hydrogen (atomic mass of hydrogen = 1.01).
 $1 \text{ mole H}_2 = 2.02 \text{ g}$ $\text{volume} = \text{mass} \div \text{density} = 2.02 \div 0.0709 = \mathbf{28.5 \text{ cm}^3}$
 - b. If the density of liquid oxygen is 1.14 g cm^{-3} , calculate the volume of 0.5 moles of liquid oxygen (atomic mass of oxygen = 16.00).
 $0.5 \text{ mole O}_2 = 16.00 \text{ g}$ $\text{volume} = \text{mass} \div \text{density} = 16.00 \div 1.14 = \mathbf{14.0 \text{ cm}^3}$
 - c. Use the total volume of liquid hydrogen and oxygen needed for the combustion of 1 mole of hydrogen to calculate the amount of energy produced by 2500 m^3 of the mixture that is used in the core stage rocket (assuming they are mixed in the same 2:1 mole ratio).
 $\text{Total volume to produce } -240.8 \text{ kJ} = 28.5 + 14.0 = \mathbf{42.5 \text{ cm}^3}$ $2500 \text{ m}^3 = 2.5 \times 10^9 \text{ cm}^3$
 $\text{Total energy produced from } 2500 \text{ m}^3 = 240.8 \times 2.5 \times 10^9 \div 42.5 = \mathbf{1.42 \times 10^{10} \text{ kJ}}$

3. It has been suggested that methane might be a better rocket fuel than hydrogen because it has a higher standard enthalpy change of combustion than hydrogen.



- a. Calculate the total mass of methane and oxygen used when 1 mole of methane is completely oxidised (atomic mass of carbon = 12.01).
- b. Use this mass to calculate the energy in MJ produced by 1 kg of the methane/oxygen mixture. Compare your answer with value for hydrogen of 13.4 MJ kg⁻¹ (13,400 kJ kg⁻¹) and comment on why hydrogen is still the preferred fuel for the rocket.

$$1 \text{ mole CH}_4 = 16.05 \text{ g} \quad 2 \text{ moles O}_2 = 64.00 \text{ g} \quad \text{total mass} = 80.05 \text{ g}$$

$$\text{Total energy produced from 1 kg} = 890.8 \times 1000 \div 80.05 = 11128 \text{ kJ} = 11.1 \text{ MJ kg}^{-1}$$

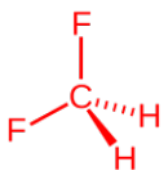
The energy per kg is less for methane than for hydrogen, so hydrogen is still preferred. Also, methane produces carbon dioxide, which is a greenhouse gas, whereas hydrogen does not.

Part 2: Intermolecular forces in refrigerants

The heat pump relies on the change in boiling point of the refrigerant that results from the change in the surrounding pressure as it is pumped between the inside and the outside of the house. The gas liquefies when the intermolecular forces are able to overcome the kinetic energy of the molecules. These forces become stronger when the molecules are pushed closer together by higher pressures.

Difluoromethane, CH₂F₂, is one of the refrigerants used in heat pumps.

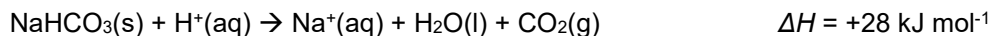
4. Draw a 3-D displayed formula to show the structure and shape of the difluoromethane molecule.



5. State the types of intermolecular forces that exist between difluoromethane molecules and explain how these forces arise.
- Dipole-dipole forces – attraction between permanent dipoles on the molecules that arise due to the bond dipoles on the C-F bonds, which do not cancel out, as the molecule is not symmetrical.
- London dispersion forces – attraction between temporary dipoles, due to random electron movement, which induce dipoles on the nearby molecules.
6. Compare the value of the enthalpy of vaporisation of difluoromethane with the average bond enthalpies of the C-H and C-F bonds within the molecule, which are 413 kJ mol⁻¹ and 485 kJ mol⁻¹, respectively. Comment on the relative strengths of the intermolecular forces compared to the covalent bonds within the molecule.
- The enthalpy of vaporisation (+20 kJ mol⁻¹) is much smaller than the covalent bond enthalpies. This is because the intermolecular forces are much weaker than covalent bonds.
7. Condensation of the refrigerant inside the house is an exothermic process, which is how it warms the surroundings. Explain why condensation is an exothermic process.
- Condensation is exothermic because energy is transferred as heat to the surroundings when the intermolecular forces are able to attract the molecules – ie bonds are being made. The attractions create movement that results in an increase in thermal motion of the molecules, increasing their average kinetic energy and that of the surrounding molecules as well.

Part 3: The effect of temperature on the direction of the raising agent reaction

The sodium hydrogen carbonate in the raising agent reacts with acids because the increase in entropy is sufficient to outweigh the positive enthalpy change that would otherwise favour the reverse reaction.



8. Use the standard entropies given below to show by calculation that the overall entropy change for this reaction is $+241 \text{ J K}^{-1} \text{ mol}^{-1}$

Substance	$S^\ominus \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$
Solid sodium hydrogen carbonate	102.1
Aqueous hydrogen ions	0.0
Aqueous sodium ions	59.0
Water	69.9
Carbon dioxide gas	213.7

$$\text{Entropy change} = \sum (\text{product entropies}) - \sum (\text{reactant entropies}) = (59.0 + 69.9 + 213.7) - (102.1 + 0.0) = 240.5 = 241 \text{ J K}^{-1} \text{ mol}^{-1}$$

9. With an enthalpy change of $+28 \text{ kJ mol}^{-1}$, the expression $\Delta G = \Delta H - T\Delta S$ gives an overall free energy change at 298 K of -44 kJ mol^{-1} (as shown on the factsheet).
- Calculate the overall free energy change at a typical cake baking temperature of 180°C
 $180^\circ\text{C} = 453 \text{ K} \quad \Delta G = +28 - (453 \times 0.241) = -81.2 \text{ kJ mol}^{-1}$ (or $80.9 \text{ J K}^{-1} \text{ mol}^{-1}$ if the unrounded ΔS of $240.5 \text{ J K}^{-1} \text{ mol}^{-1}$ is used)
 - If the temperature is low enough, the free energy change will become positive and the reaction will no longer be favourable. Calculate the temperature in $^\circ\text{C}$ at which the overall free energy change goes from negative to positive, by letting $\Delta G = 0$ and rearranging the free energy equation to give a value for T .
 $0 = \Delta H - T\Delta S \quad T = \Delta H \div \Delta S = +28 \div 0.241 = 116 \text{ K} = -157^\circ\text{C}$