## Thermodynamic contexts

## 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 '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 factsheet 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. This allowed them to answer questions such as 'How much fuel do you need to burn to move an object over a certain 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 $\left(\Delta H_{r}\right)$ can be estimated using Hess' Law by combining several other known enthalpy changes.


Identify which step 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 $-241 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

| Standard enthalpy change of combustion of hydrogen | $-285.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| :--- | ---: |
| Enthalpy change of vaporisation of hydrogen | $+0.9 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| Enthalpy change of vaporisation of oxygen | $+6.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| Enthalpy change of vaporisation of water | $+40.7 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |

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 $0.0709 \mathrm{~g} \mathrm{~cm}^{-3}$, calculate the volume of 1 mole of liquid hydrogen (atomic mass of hydrogen $=1.01$ ).
b. If the density of liquid oxygen is $1.14 \mathrm{~g} \mathrm{~cm}^{-3}$, calculate the volume of 0.5 moles of liquid oxygen (atomic mass of oxygen $=16.00$ ).
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 $2500 \mathrm{~m}^{3}$ of the mixture that is used in the core stage rocket (assuming they are mixed in the same $2: 1$ mole ratio).
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.

$$
\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{l}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \Delta H=-890.8 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

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 $M J$ produced by 1 kg of the methane/oxygen mixture. Compare your answer with value for hydrogen of $13.4 \mathrm{MJ} \mathrm{kg}^{-1}\left(13,400 \mathrm{~kJ} \mathrm{~kg}^{-1}\right)$ and comment on why hydrogen is still the preferred fuel for the rocket.

## 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, $\mathrm{CH}_{2} \mathrm{~F}_{2}$, is used a refrigerant 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.
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 $413 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $485 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively. Comment on the relative strengths of the intermolecular forces compared to the covalent bonds within the molecule.
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.

## 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.

$$
\mathrm{NaHCO}_{3}(\mathrm{~s})+\mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta H=+28 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

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

| Substance | $\left.\boldsymbol{S}^{\circ} \mathbf{( J ~ K}^{-1} \mathbf{~ m o l}^{-1}\right)$ |
| :--- | :---: |
| Solid sodium hydrogen carbonate | 102.1 |
| Aqueous hydrogen ions | 0.0 |
| Aqueous sodium ions | 59.0 |
| Water | 69.9 |
| Carbon dioxide gas | 213.7 |

9. With an enthalpy change of $+28 \mathrm{~kJ} \mathrm{~mol}^{-1}$, the expression $\Delta \boldsymbol{G}=\Delta \boldsymbol{H}-\boldsymbol{T} \Delta \boldsymbol{S}$ gives an overall free energy change at $298 \mathrm{~K}^{\circ}$ of $-44 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (as shown on the factsheet).
a. Calculate the overall free energy change at a typical cake baking temperature of $180^{\circ} \mathrm{C}$.
b. 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 ${ }^{\circ} \mathrm{C}$ 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 $T$.
