



Introduction to NMR Spectroscopy



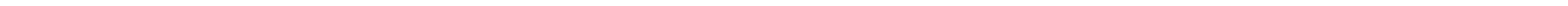
NMR (nuclear magnetic resonance) spectroscopy is a very powerful spectroscopic technique that helps with the characterisation of substances and structure determination. In this question, we will focus in on carbon NMR specifically.

Part A Spin-active nuclei

NMR can only be used on nuclei that have a non-zero value of a property called *spin*. In particular, atoms containing even numbers of both protons and neutrons have a spin of zero, and so are not spin-active and will not be visible to our NMR instrument. All other nuclei have a non-zero spin, though not all are equally suitable for NMR spectroscopy.

The most common isotope of carbon is with protons and neutrons in its nucleus. It is therefore . A less common isotope of carbon, with about 1% abundance, is , which has protons and neutrons in its nucleus and is therefore . It is only the isotope that we will see in NMR spectroscopy.

Items:



When placed in a magnetic field, nuclei with non-zero spin can take on different energy levels, and transitions between these energy levels can occur. It is the transition between these energy levels that NMR spectroscopy relies on. The differences in energy depend on the magnetic field: the stronger the field, the larger the energy differences and vice versa. To a large part, the magnetic field experienced by the nucleus is determined by the external magnetic field it is placed in. However, the field is modified somewhat by the electrons around the nucleus in question, giving rise to different nuclei within an atom potentially experiencing a slightly different magnetic field. Frozen in time, the electron distribution around any given nucleus would be different, but what matters is the average environment experienced by a given nucleus on the NMR timescale.

Rotations around single bonds and bond vibrations take place fast enough on the NMR time scale for the two carbons in an ethane molecule to be equivalent, so ethane only has carbon environment(s). In propane, the two carbons are equivalent, as we can draw a plane of symmetry through the molecule, and the carbon is different, so propane has carbon environment(s). Straight-chain butane has carbon environments while straight-chain pentane has carbon environments.

Items:

Part C Shifts

Carbons in different environments will give rise to signals at different *chemical shift* values in the NMR spectrum. A higher shift corresponds to more *deshielded* nuclei that experience a higher magnetic field, as they are surrounded by less electron density.

Saturated carbons have the lowest shifts, falling into the region. When saturated carbons are attached to electronegative atoms, the electron density around their nuclei is meaning they have slightly higher shifts, falling into the region. At the higher end of this is also where we usually find triple-bonded carbons. Double-bonded (and aromatic) carbons actually appear at a slightly higher shift, in the region. The highest shift region of is where we find carbons that are double-bonded and have bonds to particularly electronegative atoms, most notably the carbonyls.

Items:

increased

reduced

0–50 ppm

50–100 ppm

100–150 ppm

150–200 ppm



Physics. *You work it out.*

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Counting Environments



For each of the molecules below, specify how many signals you expect to see in the ^{13}C and ^1H NMR spectra.

Part A Ethanol

Specify the number of ^{13}C NMR environments in ethanol.

Specify the number of ^1H NMR environments in ethanol.

Part B Benzene

Specify the number of ^{13}C NMR environments in benzene.

Specify the number of ^1H NMR environments in benzene.

Part C **1,4-dichlorobenzene**

Specify the number of ^{13}C NMR environments in 1,4-dichlorobenzene.

Specify the number of ^1H NMR environments in 1,4-dichlorobenzene.

Part D **4-nitrophenol**

Specify the number of ^{13}C NMR environments in 4-nitrophenol.

Specify the number of ^1H NMR environments in 4-nitrophenol.

Part E **2-methylbut-2-ene**

Specify the number of ^{13}C NMR environments in 2-methylbut-2-ene.

Specify the number of ^1H NMR environments in 2-methylbut-2-ene.

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Gameboard:

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Propanal Spectrum



Fill in the gaps in the table with details of the signals you expect to see in the ^1H NMR spectrum of propanal. Order the signals based on the expected chemical shift, starting with the *highest expected shift at the top*.

Expected shift	Relative integral	Splitting pattern
<input type="text"/>	1	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>

Items:

0 to 2 ppm

2 to 4 ppm

4 to 6 ppm

6 to 8 ppm

8 to 10 ppm

1

2

3

singlet

1 : 1 doublet

1 : 2 : 1 triplet

1 : 3 : 3 : 1 quartet

1 : 4 : 6 : 4 : 1 quintet

other

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Competing Reactions

A compound X can produce two possible products, Y and Z, under the same reaction conditions. An energy profile for this reaction can be represented as shown below.

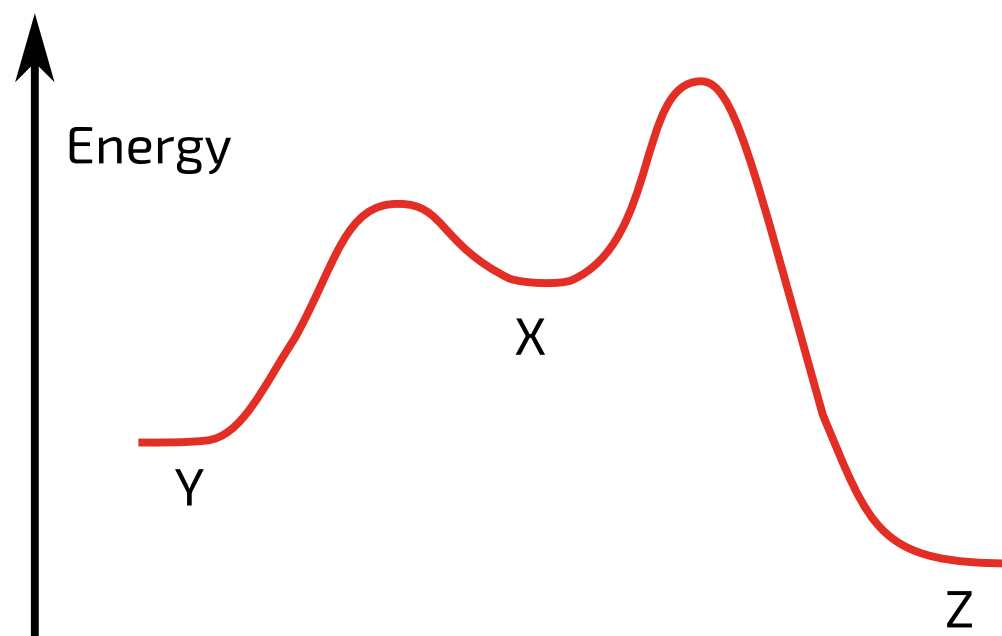


Figure 1: A reaction profile for the reaction described.

Part A Activation energy

The *activation energy* is the energy required for a reaction to take place. It is given by the difference in energy between the and the . In the set-up above, the reaction producing product Y has a activation energy than the process producing product Z due to the state being in energy for the former.

Items:

minimum

maximum

optimal

starting materials

products

transition

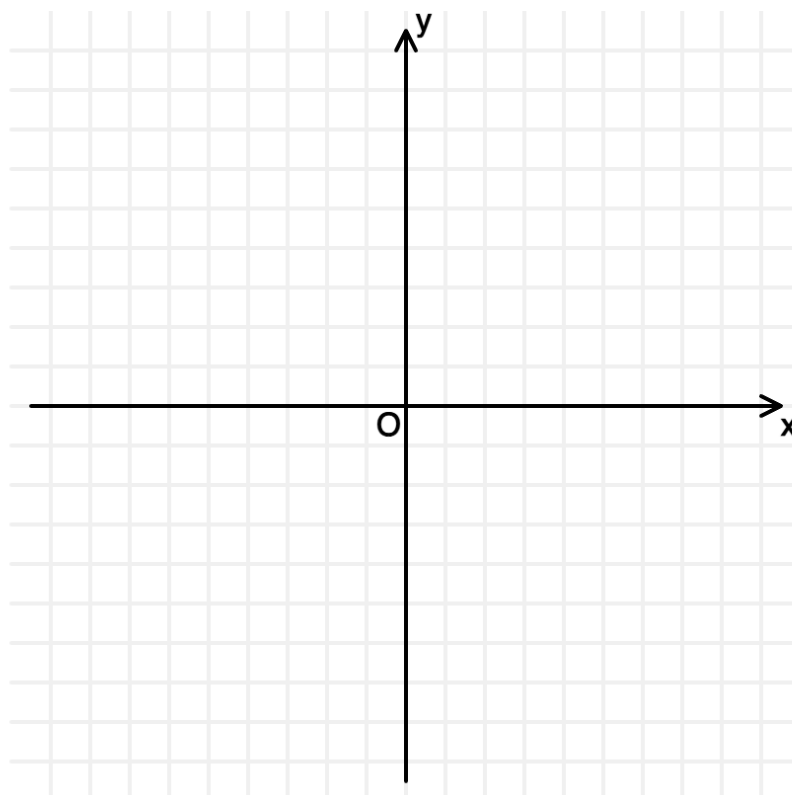
higher

lower

Part B Molecular speed distribution

What do we call the distribution of molecular speeds?

What does this distribution look like (assume particle speed is on the x-axis, and number of particles on the y-axis)?



Part C Temperature dependence

Which product (Y or Z) will be favoured at lower temperatures and which will be favoured at higher temperatures? Explain your reasoning.

At lower temperatures, the reaction is under control, and so the reaction with the lower is favoured. This means product is favoured at low temperatures. At higher temperatures, the reaction is under control, and so the reaction with the lower is favoured. This means product is favoured at high temperatures.

Items:

kinetic

thermodynamic

energy of products

energy of reactants

activation energy

Y

Z

Part D Gold catalyst

The addition of a gold catalyst to the above reaction results in the formation only of Z, regardless of the temperature at which the reaction is carried out. Which of the following statements help(s) to explain this observation?

- ☐ Gold increases the activation energy for the formation of Y
 - ☐ Gold decreases the activation energy for the formation of Y
 - ☐ Gold increases the activation energy for the formation of Z
 - ☐ Gold decreases the activation energy for the formation of Z
 - ☐ Gold lowers the energy of X
 - ☐ Gold lowers the energy of Y
 - ☐ Gold lowers the energy of Z
-

Adapted with permission from OCSEB, STEP Chemistry, Jun 1996, Question 1

Gameboard:

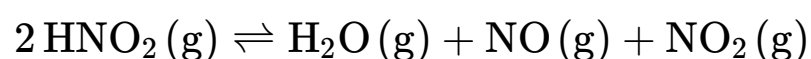
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Gaseous Gases

For the reaction



$$\Delta_r H^\ominus = 40.6 \text{ kJ mol}^{-1}, \quad \Delta_r S^\ominus = 131.4 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Part A Gibbs free energy change

Calculate $\Delta_r G^\ominus$ at 298 K.

Part B Logarithm of equilibrium constant

Calculate $\ln(K)$ at 548 K, where K is the equilibrium constant.

Part C Temperature of reaction

2.00 mol of $\text{HNO}_2 (\text{g})$ is put in a reaction container. The reaction is heated slowly until there are 0.500 mol of $\text{NO} (\text{g})$. The total pressure is 101 kPa. What temperature is the reaction at?
