CH10137 Thermodynamics

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Welcome

The notes have been prepared in a package called BookDown for RStudio so that the equations are accessible to screen readers. However, by providing the notes as a .html webpage I can also embed short videos to further describe some of the topics. If you want videos on any topic please ask and I will do my best to produce the most requested ones.

Further you can download the notes in a format that suits you (either pdf or epub) to view offline, or change the way this document appears for ease of reading.

This document is written in markdown, and particularly in equations typos can creep in. If you spot any typos or think there are any errors please let me know and I will do my best to fix them.

Notes and Workshops for CH10137

This 'book' will be updated weekly with content and embedded 'micro lecture' video content.

Questions and answers will be provided and some answers will include 'process' as well as answer. Please contact me if you need help. Questions on later topics will rely on earlier knowledge.

I am using this format as it is an accessible format. However I have moved over to this format this year and so I would appreciate you pointing out any areas of confusion or where error may have crept in.

Recommended text

There is no single recommended text for this section of the course because multiple books can offer valuable extra insight. It may be useful for you to refer to any of the following:

The Elements of Physical Chemistry

Atkins' Physical Chemistry

Chemistry^3

Version history

The initial commit of this book is dated 16nd October 2020.

Chapter 1

Week 1 - Part 1: Preliminaries

1.1 Why thermodynamics matters

The laws of thermodynamics are some of the most fundamental laws of nature, and in this course I hope you will learn to understand these laws and be able to apply them to explain the world around you.

Thermodynamics is fundamental to the way we live, to our dream of living a better, less impactful life and to how we as 'life' work.

1.2 State functions - (products - reactants)

Many properties in thermodynamics are *state functions*, that is properties that only depend upon the current state of the system. State functions are completely independent of the path by which that final state was reached.

Enthalpy (H) is a state function, as are entropy (S), internal energy (U), Gibbs' free energy (G), Helmholtz free energy (F), temperature (T), pressure (p), and chemical composition.

Path functions are unlike state functions in that they depend on the path taken to determine their value. Heat (q) and work (w) are both examples of path functions.

- Internal energy, U The internal energy is the sum of all of the kinetic and potential energy contributions of the molecules in the system.

- Enthalpy, H The enthalpy is related to the internal energy, but also takes into account any expansion work done by the system, formally ΔH = ΔU + Δ(pV).
- Entropy, S The entropy is a measure of the number of possible arrangements of a system (multiplicity, Ω), formally S = k_B ln Ω
- Gibbs' free energy, G The Gibbs' free energy is a measure of the energy available to 'do work' in a reaction system. It accounts for both the enalpic and entropic contributions of the reaction. ΔG = ΔH − TΔS

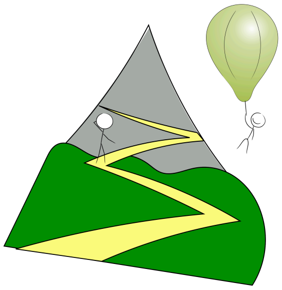

Figure 1.1: State functions - no matter how you got here, here you are... ...altitude is a good analogy for a state function, whether climbing the mountain or flying on the balloon if your altitude is 1000 m it is 1000 m!.

1.2.1 Useful equations - State functions

Hess' Law (Equation (1.1)) is something most will be familiar with already. You should try to think about it in terms of an equation however, not the cylces of which you may already be familiar.

$$\Delta_r H^{\ominus} = \sum_{products} v\Delta H^{\ominus}_{\mathrm{X}} - \sum_{reactants} v\Delta H^{\ominus}_{\mathrm{X}} \tag{1.1}$$

Similar equations can be used for heat capacity (Equation (1.2)), this equation for heat capacity will then be used later in the course when we look at the effect of temperature on the enthalpy and entropy of reaction.

$$\Delta_r C^{\ominus}_p = \sum_{products} vC^{\ominus}_{p,n} - \sum_{reactants} vC^{\ominus}_{p,n} \tag{1.2}$$

Entropy, just like enthalpy is a state function.

$$\Delta_r S^{\ominus} = \sum_{products} vS^{\ominus} - \sum_{reactants} vS^{\ominus} \tag{1.3}$$

As is Gibbs' free energy.

$$\Delta_r G^\ominus = \sum_{prod} vG_n^\ominus - \sum_{react} vG_n^\ominus \tag{1.4}$$

The value of each of these variables is independent of the path used to form them. Hence, the same *'products − reactants'* approach always works!

1.3 Types of thermodynamic system

When we consider anything in thermodynamics we have to consider both the system and its surroundings. The relationship between the system and the surroundings defines the different types of thermodynamic system.

1.4 Extensive and intensive properties

The difference between extensive and intensive properties is whether the property depends upon the amount of 'stuff' you have.

1.4.1 Intensive properties

Properties which are *independent* of the amount of stuff are called 'intensive properties'.

Temperature is an example of an intensive property as are all of 'molar' properties (the quantity of something 'per mole'): molar heat capacity, molar enthalpy, molar entropy, molar Gibbs' energy, *etc*... in physics the term 'specific' is often used such as specific heat capacity and specific enthalpy, these are also intensive properties based on the fixed amount of a 'gram' (g).

1.4.2 Extensive properties

Conversely, properties which are *dependent* on the amount of stuff you have are called extensive properties.

Many intensive properties have extensive equivalents, so whilst we have 'molar heat capacity' we also have 'heat capacity'; one looks at the amount of energy it takes to raise one mole of a thing by one kelvin, whereas the other looks at how much energy it takes to raise the temperature how ever much of a thing we have by on kelvin.

Consequently extensive properties have different units to their ‘equivalent’ intensive property.

Other examples of extensive properties are unsurprisingly: volume, mass, amount (as in moles), and length.

Whilst knowing the terms extensive and intensive isn’t vital it is hugely important to recognise that sometimes terms will appear with different units to suit the particular situation.

1.5 Classical vs. Statistical thermodynamics

Thermodynamics is quite an old subject, much of our understanding of why chemical reactions happen is based in 19th century science. This understanding was based on emperical observation of things like steam engines and battery piles. It scientists trying to understand how things work in order to make them better, make them more efficient, and make them safer.

This 19th century (and earlier) view of the world didn’t even consider things we take for granted now, nowhere in thermodynamics do we ever really think about atoms. We talk about ideal systems (those that follow the rules nicely), but never really care about the reaction taking place, it is all just the bulk average behaviour of the system.

Then in the late 19th century Ludwig Boltzmann proposed a different way of thinking about thermodynamics. He started to think about the ‘average’ behaviour of individual atoms. This version of statistical mechanics gave an explanation of what concepts like entropy were and it helped explain macroscopic phenomena (such as pressure and temperature) on an atomic and molecular level.

Statistical thermodynamics started to be able to explain the values of what had until then been emperical constants.

Consequently in this course we will look at thermodynamics from both a classical and statistical point of view.

1.6 Example calculations

1.6.1 Example calculation - Hess’s Law

How much energy is released when 4.60 g of sodium reacts with excess water to give NaOH (aq) & H_2 (g)?

- ΔH_f NaOH $= -425.61$ kJ mol^{-1}
- ΔH_f $H_2O = -285.83$ kJ mol^{-1}

The enthalpy of formation of elements in their standard state (*e.g.* Na (s) & H_2 (g)) is zero.

Therefore using equation (1.1):

$$\Delta H^{\ominus}_{rxn} = \Delta H^{\ominus}_{f}(\mathrm{NaOH}) - \Delta H^{\ominus}_{f}(\mathrm{H_2O}) = -425.61 \text{ kJ mol}^{-1} - -285.83 \text{ kJ mol}^{-1} = -139.78 \text{ kJ mol}^{-1}$$

R_M Na = 22.989769 g mol^{-1} Therefore:

$$n(\mathrm{Na}) = \frac{m}{R_M} = \frac{4.60 \text{ g}}{22.989769 \text{ g mol}^{-1}} = 0.200 \text{ mol}$$

note sf!

Therefore if 4.60g reacts:

$$\Delta H_{rxn}(\mathrm{kJ}) = \Delta H_{rxn}(\mathrm{kJ\ mol}^{-1}) \times \mathrm{mol} = -139.78 \mathrm{kJ\ mol}^{-1} \times 0.200 \mathrm{mol} = -28.0 \text{ kJ}$$

The '$-$' sign indicates that heat is released (evolved) and the temperature of the surroundings increases.

1.6.2 Example Calculation - Kirchoff's law

Kirchoff's laws may be used to adjust calculated values of enthalpy and entropy of reaction to different temperatures, they use the difference in heat capacity of products and reactants to do this. Determine $\Delta C_{p,m}$ for the following reaction:

CH_3CH_2OH (aq) + CH_3COOH (aq) $CH_3COOCH_2CH_3$ (aq) + H_2O (l)

	$\Delta C_{p,m}$ / J K^{-1} mol^{-1}
CH_3CH_2OH (aq)	111.46
CH_3COOH (aq)	124.3
$CH_3COOCH_2CH_3$ (aq)	170.1
H_2O (l)	33.58

$$\Delta C_{p,m\ \mathrm{rxn}} = (C_{p,m}\mathrm{CH_3COOCH_2CH_3\ (aq)} + C_{p,m}\mathrm{H_2O\ (l)}) - (C_{p,m}\mathrm{CH_3CH_2OH\ (aq)} + C_{p,m}\mathrm{CH_3COOH\ (aq)})$$

$$\Delta C_{\mathrm{p,m\ rxn}} = (170.1+33.58) - (111.46+124.3) \text{ J K}^{-1} \text{ mol}^{-1}) = -32.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

1.7 Questions

Later in this course you will learn about the origin of these equations, for now it is enough to be able to balance chemical equations and use the fact that each of the variables in teh following equations are state functions.

1. What is the standard Gibbs' free energy of the oxidation of ammonia (NH_3) to nitric acid (NO)?

Hint: This is a redox reaction.

$\Delta G_{f,\mathrm{NH_3}} = -16.45$ kJ mol^{-1}

$\Delta G_{f,\mathrm{NO}} = +86.55$ kJ mol^{-1}

$\Delta G_{f,\mathrm{H_2O}} = -228.57$ kJ mol^{-1}

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2. Methanol fuel cells have been proposed as replacements for internal combustion engines. Methanol (density, $\ = 792$ kg m^{-3}) is reacted in a fuel cell to be completely oxidised.

Given the enthalpies of formation required are listed below determine the amount of energy released per mL of methanol.

$\Delta H_{f,\mathrm{CH_3OH}} = -425.61$ kJ mol^{-1}

$\Delta H_{f,\mathrm{H_2O}} = -241.82$ kJ mol^{-1}

$\Delta H_{f,\mathrm{CO_2}} = -393.51$ kJ mol^{-1}

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3. Ammonium dichromate decomposes upon heating in a spectacular 'volcano' reaction:

$(NH_4)Cr_2O_7$ (s) N_2 (g) + 4 H_2O (g) + Cr_2O_3 (s)

Determine the enthalpy of reaction for this process given the following data.

$\Delta H_{f,\mathrm{(NH_4)Cr_2O_7\ (s)}} = -1810$ kJ mol^{-1}

$\Delta H_{f,\mathrm{H_2O\ (g)}} = -240$ kJ mol^{-1}

$\Delta H_{f,\mathrm{Cr_2O_3\ (g)}} = -1140$ kJ mol^{-1}

How would the enthalpy of reaction differ if liquid water was formed? Justify your answer.

1.8 Answers

1. $\Delta G_{rxn} = -239.86$ kJ ${\mathrm{mol}^{-1}}_{NH_3}$ (per mole of NH_3)
2. ΔH_{rxn} = -11.2 kJ cm^{-3}
3. ΔH_{rxn} = -290 kJ mol^{-1}, become more negative as heat is released upon condensing (we will cover this later in the course if you don't understant this last part, please don't stress).