


Slide 4



Joe's Rule of the Possible


If it can happen, it will happen.

But, that doesn't tell you how much,
how fast, how often, how easily...

...Thermodynamics picks up where
Joe's Rule leaves off.

4

Slide 5




Thermodynamics

Thermodynamics deals with energy,
as the name implies, but not just
energy. It includes the study of all
the different possible states of a
system and how the system moves
between different states.

5

Slide 6



States

I mix 1 molecule of O_2 and 1 molecule
of H_2 in an evacuated 1 L flask.
How many different states of this
system are there?

A nearly infinite number of them!

6

Slide 7

“States” of a system

7

Slide 8

“States” of a system

8

Slide 9

What the &^%* can we do?

Thermodynamics deals with statistical analysis of ensembles of states.

In our case, we are usually looking at a single representative state of the system that is the “most probable” state.

9

Slide 10

Clicker Question

Consider the following reaction:
 $2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{H}_2\text{O} (\text{g})$

If $\Delta H_{\text{rxn}} < 0$, it means:

- A) The products have less energy than the reactants – you could make a hot pack.
- B) The reactants have less energy than the products – you could make a cold pack.
- C) The products have less energy than the reactants – you could make a cold pack.
- D) The reactants have less energy than the products – you could make a hot pack.

10

Slide 11

Putting the "thermo" in thermodynamics

As the name implies, "thermodynamics" is about energy (thermo=heat).

What does this mean for a reaction?

11

Slide 12

Reaction Energies

The energy change associated with a chemical reaction is called the **enthalpy of reaction** and abbreviated ΔH .

$\Delta H = H_{\text{final}} - H_{\text{initial}}$

12

Slide 13

Enthalpy of Reactions

There are actually a number of different types of enthalpies because enthalpy depends on conditions. THEY ARE ALL JUST SPECIFIC TYPES OF A GENERAL CONCEPT CALLED "ENTHALPY".

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

13

Slide 14

General Reaction Scheme – "hot pack"

14

Slide 15

Endothermic Reaction – "cold pack"

15

Slide 16

Where does the Energy go?

In the case of a chemical reaction, you need to keep the different types of energy separate in your mind:

- Bond energy – energy INSIDE the molecules
- Thermal energy (heat) – kinetic energy of the molecules
- Energy of the “bath” – kinetic energy of solvent or other molecules in the system

16

Slide 17

CONSERVATION OF ENERGY

The BIG rule: No energy is created or destroyed.

We have different types of energy: bond energy, thermal energy, energy of the bath (“surroundings”).

But all we ever do is move the joules around.

17

Slide 18

Where'd the ΔH energy come from?

18

Slide 19

Energy changes

ΔH represents the change in INTERNAL MOLECULAR ENERGY.

$\Delta H = H_{\text{final}} - H_{\text{initial}}$

19

Slide 20

Exothermic Reaction – “hot pack”

20

Slide 21

Exothermic energy changes

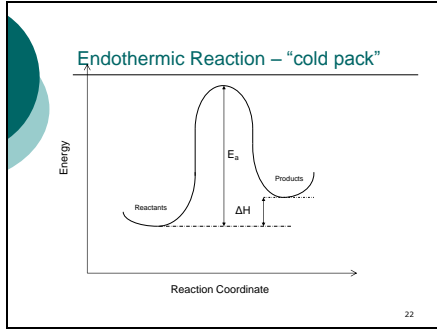
$\Delta H = H_{\text{final}} - H_{\text{initial}} < 0$

$H_{\text{initial}} > H_{\text{final}}$

This energy is internal to the molecule. The excess gets absorbed by the rest of the system as heat causing the molecules to move faster (more kinetic energy) and the temperature to increase.

21

Slide 22



Slide 23

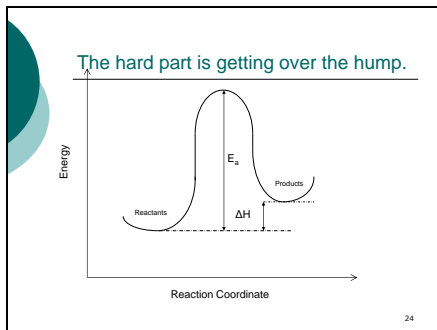
Endothermic energy changes

$$\Delta H = H_{\text{final}} - H_{\text{initial}} > 0$$
$$H_{\text{initial}} < H_{\text{final}}$$

This energy is internal to the molecule and must come from somewhere.
The additional energy required by the system gets absorbed from the rest of the system as heat causing the molecules to move slower (less kinetic energy) and the temperature to decrease.

23

Slide 24



Slide 25

E_a = Activation Energy

The tale of a reaction is not limited strictly to the identity and energetics of the products and reactants, there is a path (reaction coordinate) that must get followed.

The "hump" represents a hurdle that must be overcome to go from reactants to products.

25

Slide 26

How do you get over the hump?

If you are at the top, it is easy to fall down into the valley (on either side), but how do you get to the top?

Energy

Reaction Coordinate

Reactants

Products

E_a

ΔH

26

Slide 27

How do you get over the hump?

The molecules acquire or lose energy the same way: by colliding with each other!

The energy comes from the "bath", the rest of the system.

Energy

Reaction Coordinate

Reactants

Products

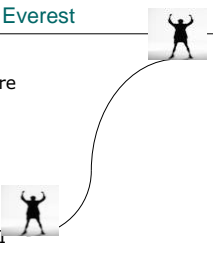
E_a

ΔH

27

Slide 31

Climbing Mt. Everest



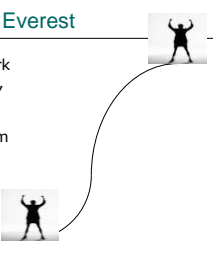
Back at base camp, I figure out my altitude change. What is it?

ZERO - I'm back where I started

31

Slide 32

Climbing Mt. Everest



I did a lot of work along the way, but all that matters is I'm back where I'm started. The net change in altitude is NADA, ZERO, ZILCH!

32

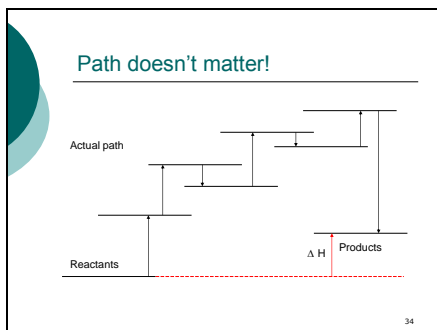
Slide 33

Enthalpy as a State Function

Enthalpy is like that. It doesn't care how you got where you are going, it simply looks at the difference from where you started.

33

Slide 34



Slide 35

Formation Enthalpies

The advantage here is that I can pick a path whose enthalpy change is known.

$$\text{H}_2\text{O} (\text{g}) + \text{N}_2\text{O}_3 (\text{g}) \leftrightarrow 2 \text{HNO}_2 (\text{g})$$

Maybe I don't know ΔH_{rxn} but I DO HAVE APPENDIX B.

35

Slide 36

Formation Enthalpies

One way to do the reaction is to "start" with pure elements in their natural state at STP.

$$\text{H}_2\text{O} (\text{g}) + \text{N}_2\text{O}_3 (\text{g}) \leftrightarrow 2 \text{HNO}_2 (\text{g})$$

Doing the reaction would be the same as making the products from elements, making the reactants from elements, and looking at the difference!

36

Slide 37

Path doesn't matter!

Good old Appendix II
 "f" for FORMATION!

Sea of elements at STP
 $H_2(g)$ $O_2(g)$ $Na(s)$ $Hg(l)$

37

Slide 38

Energy Considerations

Energy is an important consideration
 in any physical or chemical process.

You need to "climb the hill"!

We've seen that the "hill" (E_A) relates
 to the rate (k) and the equilibrium
 position (K).

38

Slide 39

If energy were the whole story...

Why would water evaporate?

It is an endothermic process with an
 activation barrier, so it requires
 energy to be put into the system.
 Yet, water spontaneously
 evaporates even at near freezing
 temperatures. (And actually
 sublimates when frozen!)

39

Slide 40

For a chemical reaction...

...the ENERGY is all about ΔH
What is the enthalpy change for creating steam from hydrogen and oxygen at 298K?

$$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{H}_2\text{O}(\text{g})$$

40

Slide 41

The process we care about is...

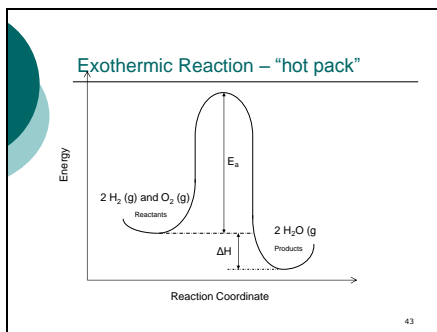
41

Slide 42

Maybe this...

42

Slide 43



Slide 44

But I can't get there directly...

I don't know H(H₂O) or H(O₂) or H(H₂)

44

Slide 45

$$\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$$

2 H₂ (g) + O₂ (g)

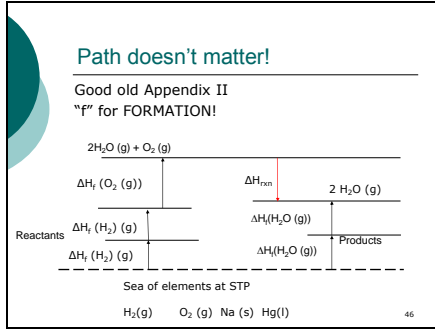
ΔH_{rxn}

2 H₂O (g)

If only I knew the H's... Then again, H is a state function so I just need to find a path using H's that I do know!

45

Slide 46



Slide 47

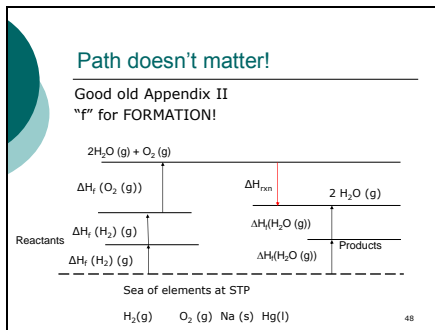
So...

All I have to do is make the products out of elements, make the reactants out of elements, see what the difference in energy is.


In both cases, I'm starting from a sea of "free" elements. "H" is a state function, so path doesn't matter!

47

Slide 48




Slide 52



**BUT...
ENERGY CHANGES
AREN'T THE
WHOLE STORY!**

52

Slide 53




The rest of the story...

The energy of the molecules and their motions are one part of the story – the “thermo part”.

There is also the distribution of atoms within the allowed states. It not only matters what the average energy of the system is, but which molecules have what energies and what positions!

53

Slide 54



What has more energy

- A. H₂O (g) AT 298 k
- B. H₂O (l) at 298 K
- C. They are the same, it's 298 K
- D. I need more information
- E. The people near me are talking and distracting me, please hit them hard in the head.

54

Slide 58

Some examples

What has more entropy: 1 mole of water or 1 mole of steam? Why?

1 mole of steam – the molecules in steam are not associated with each other and are, therefore, free to explore more positions and energy states!

58

Slide 59

Some examples

What has more entropy: 1 mole of water or ½ mole of water mixed with ½ mole of methanol? Why?

The mixture – there are the same number of molecules in both systems, but the mixture allows for more possible distributions of the molecules!

59

Slide 60

The Laws of Thermodynamics

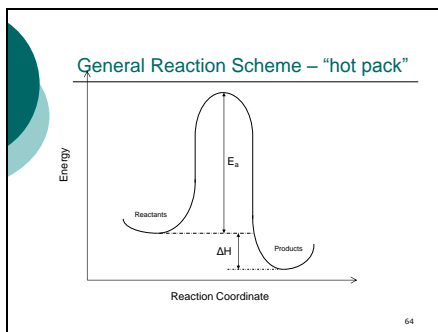
1st Law – Conservation of Energy

2nd Law – The Entropy of the universe is always increasing for spontaneous changes.

3rd Law – A perfect crystal at 0 K has no entropy.

60

Slide 64



Slide 65

Just like the rock needing a shove to get rolling, a reaction needs to get “over the hump” (overcome E_a). But an exothermic reaction is always better than an endothermic reaction because the final state (products) are lower in energy.

65

Slide 66

What about entropy and the Universe?

Turns out the Universe likes MORE entropy. (The little trickster likes “disorder”!)

Increasing entropy means ΔS would be: greater than 0, less than 0?

Greater than 0 (products – reactants)

66

Slide 67

Increasing entropy means delta S
nis

- A. Positive
- B. Negative
- C. Zero
- D. Shut up I'm watching youtube videos

67

Slide 68

If the Universe gets to choose:

It prefers an exothermic reaction ($\Delta H < 0$) that increases entropy ($\Delta S > 0$).

Such a reaction is called "spontaneous" – it happens without you needing to force it.

68

Slide 69

Spontaneous change

A spontaneous change is one that happens "naturally", without being forced by an outside agent.

Spontaneous change:
Water evaporating at room temperature.
A rock rolling down hill.

Non-spontaneous change:
Freezing water at room temperature.
Rolling a rock uphill.

69

Slide 70

Spontaneous change

A spontaneous change is thermodynamically favorable.

70

Slide 71

Spontaneous change

Thermodynamics is all about balancing enthalpy and entropy.

Some processes are enthalpically and entropically favorable. ($\Delta H < 0$ and $\Delta S > 0$). They happen.

Some process are enthalpically and entropically unfavorable. ($\Delta H > 0$ and $\Delta S < 0$). They DON'T happen.

What about when one property is favorable and the other is unfavorable?

71

Slide 72

The Universe has a choice:

There are two other cases:

$\Delta H < 0$ and $\Delta S < 0$. Enthalpy good, entropy bad!

$\Delta H > 0$ and $\Delta S > 0$. Enthalpy bad, entropy good!

What's a poor old Universe supposed to do?
Find a balance!

72

Slide 73

Balancing entropy and enthalpy

Gibb's Free Energy:

$$\Delta G = \Delta H - T \Delta S$$

If $\Delta G > 0$ then reaction is NOT spontaneous.
If $\Delta G < 0$ then reaction IS spontaneous
If $\Delta G = 0$ then...the reaction is at equilibrium!

73

Slide 74

2 ways to calculate ΔG

1. Good old appendix! The 3rd column of data are ΔG_f° which you can use just like ΔH_f° !
2. Use ΔH and ΔS to get ΔG :
$$\Delta G = \Delta H - T \Delta S$$

Especially helpful when T is not 298 K

74

Slide 75

Clicker question

What is the Gibbs Free Energy for the following reaction at 298 K:

$$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$$

75
