

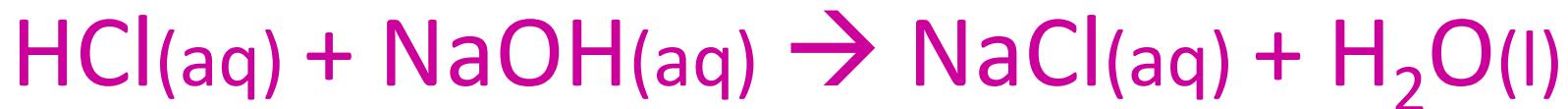
Chapter 8: Chemical Thermodynamics

Dr Chris Fellows

Room 2.18 Riggs Building cfellows@une.edu.au
[@cfellows65536](https://twitter.com/cfellows65536)

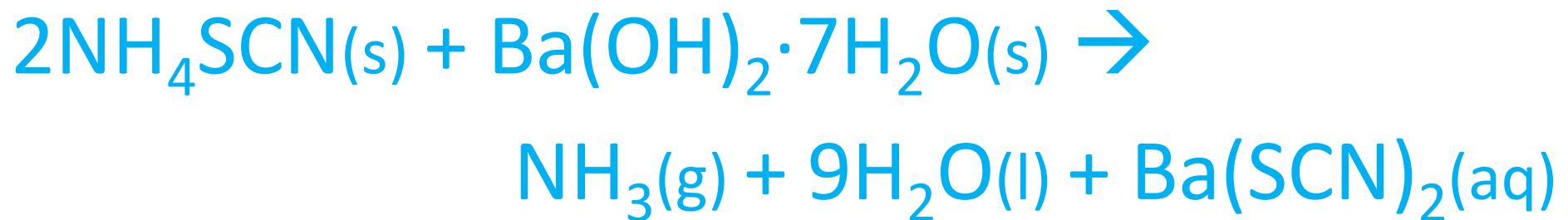
Exothermic Reactions

- Hydrochloric acid + sodium hydroxide



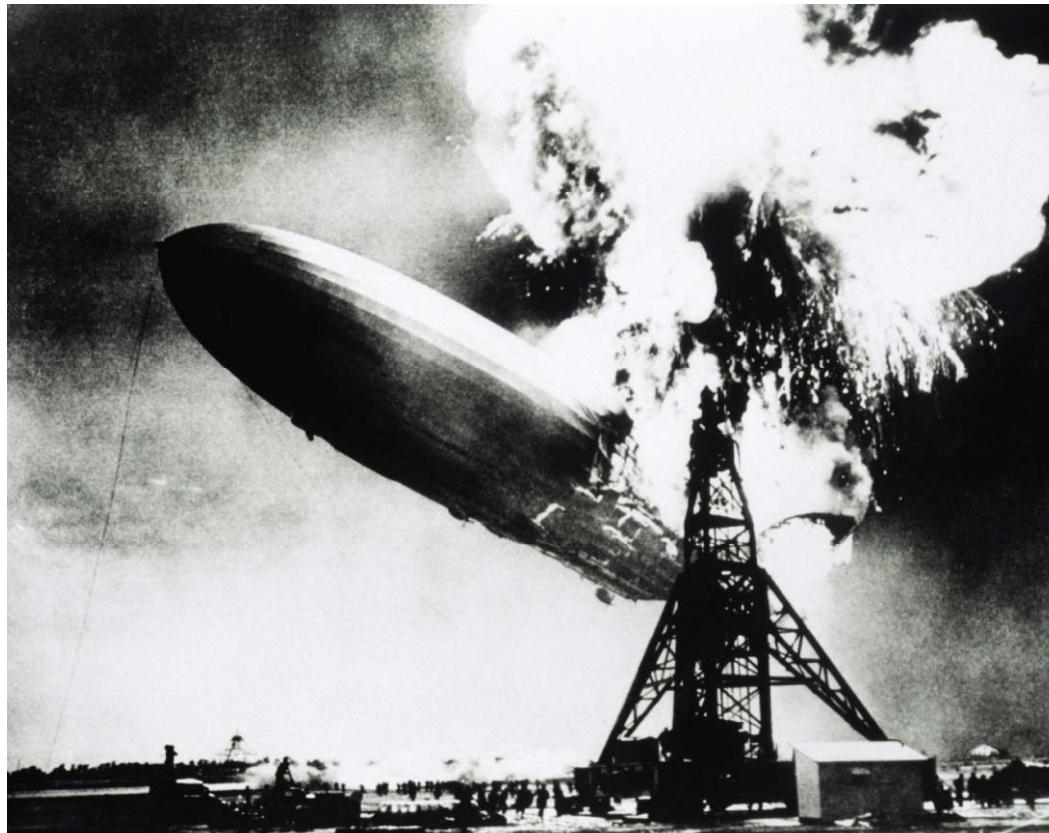
Endothermic Reactions

- Ammonium thiocyanate + barium hydroxide heptahydrate



Spontaneous and Non-Spontaneous

- $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ non-spontaneous
- $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ spontaneous



Key Questions

- Why are some reactions spontaneous and some non-spontaneous?
- Why do some reactions spontaneous under some conditions but not under others?
- How can we predict if a reaction is spontaneous or not?
- Why are some reactions endothermic and others exothermic?
- How can we measure and quantify all this stuff?

Heat and Temperature

- If two substances are at the same temperature, no heat will flow between them when they are in contact
- Temperature is a measure of kinetic energy on the molecular scale: 0 kinetic energy = 0 Kelvin
- $273.15\text{ K} = 0\text{ }^{\circ}\text{C}$
- Heat is kind of like current, temperature is kind of like voltage
- If that High School science analogy does not help, ignore it

Heat Capacity

- Telling you heat and temperature are different without giving you this equation would be mean

$$q = C \times \Delta T$$

q = heat (J)

C = heat capacity (JK^{-1})

ΔT = change in temperature (K)

$$q = c \times m \times \Delta T$$

c = specific heat capacity ($\text{Jg}^{-1}\text{K}^{-1}$)

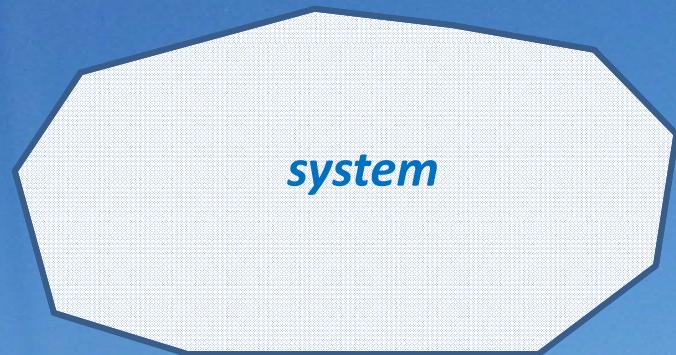
m = mass (g)

Joule

- $J = \text{Joule} = \text{unit for energy}$
 $J = \text{kg}\text{m}^2\text{s}^{-2}$
- Kinetic energy = $\frac{1}{2} mv^2$
 $\text{kg.(ms}^{-1})^2$
- In chemical reactions, we usually operate in the range of kilojoules, kJ
- Energy needed to heat 1 g of water 1 °C is a calorie
1 calorie = 4.18 J

System, surroundings, and the universe

The bit of the universe we are interested in



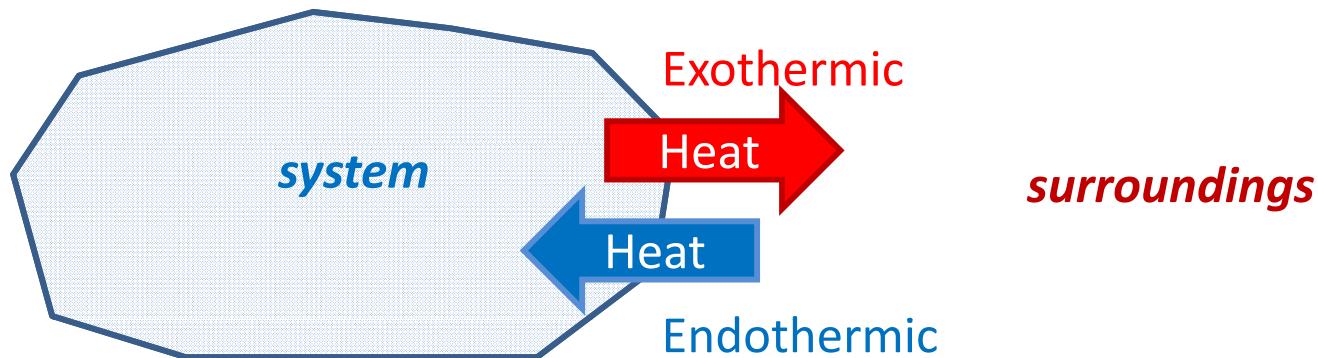
system

The rest of the universe

surroundings

- A beaker
- A 100 tonne reactor
- A human body

System, surroundings, and the universe



- **Exothermic** = heat goes out of system
- **Endothermic** = heat goes into system
- **Open System** = can exchange **heat** and **mass** with surroundings
- **Closed System** = can exchange **heat** only with surroundings
- **Isolated System** = cannot exchange anything with surroundings

Thermodynamic Functions

- U = Total Internal Energy (J)

All the energy of a system

We will explain all these later

- H = Enthalpy (J)

Heat content at constant pressure

- S = Entropy (JK^{-1})

Measure of how dispersed energy is in the system

- G = Gibbs Energy (J)

$$G = H - TS$$

We will almost always talk about changes in these functions, rather than the functions themselves

Change in X = ΔX

You will meet lots of ' Δ '
quantities:
 ΔT , Δq , Δm , etc.

By convention,

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

So if the value of X has
gone down, ΔX will be
negative.



Change in X = ΔX

- ΔU = Change in Total Internal Energy (J)

Change in energy in some process

- ΔH = Change in Enthalpy (J)

Change in heat at constant pressure

- ΔS = Entropy (JK^{-1})

Change in how dispersed energy is in the system

- ΔG = Gibbs Energy (J)

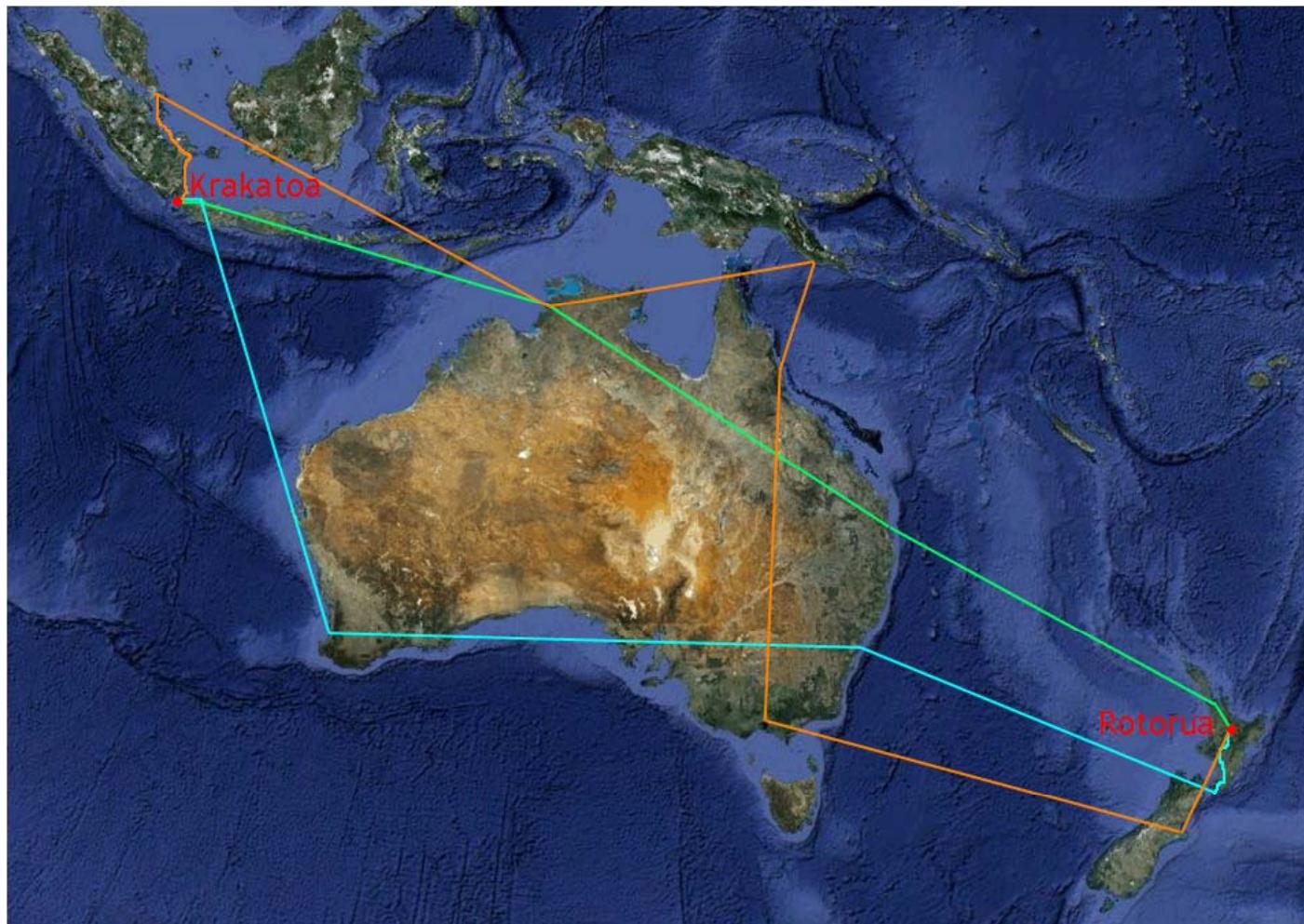
$$\Delta G = \Delta H - T\Delta S$$

For Chemistry, this is The One



State Functions

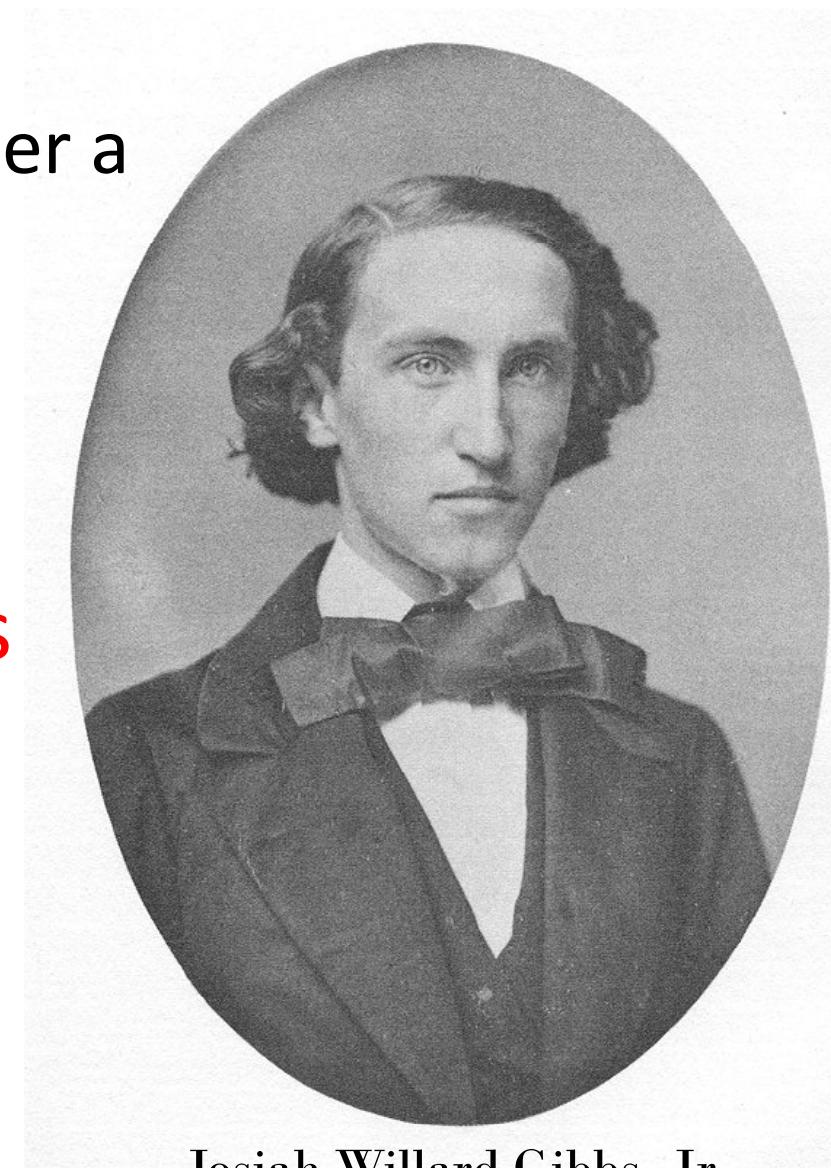
- These all depend only on the starting state and final state of the system, not on how we got from one to the other



ΔG and Spontaneity

- ΔG is our touchstone for whether a reaction is spontaneous or not
- $\Delta G < 0 \rightarrow$ spontaneous
- $\Delta G > 0 \rightarrow$ non-spontaneous
- Important: Negative ΔG is a spontaneous reaction

We will get back to ΔG later...



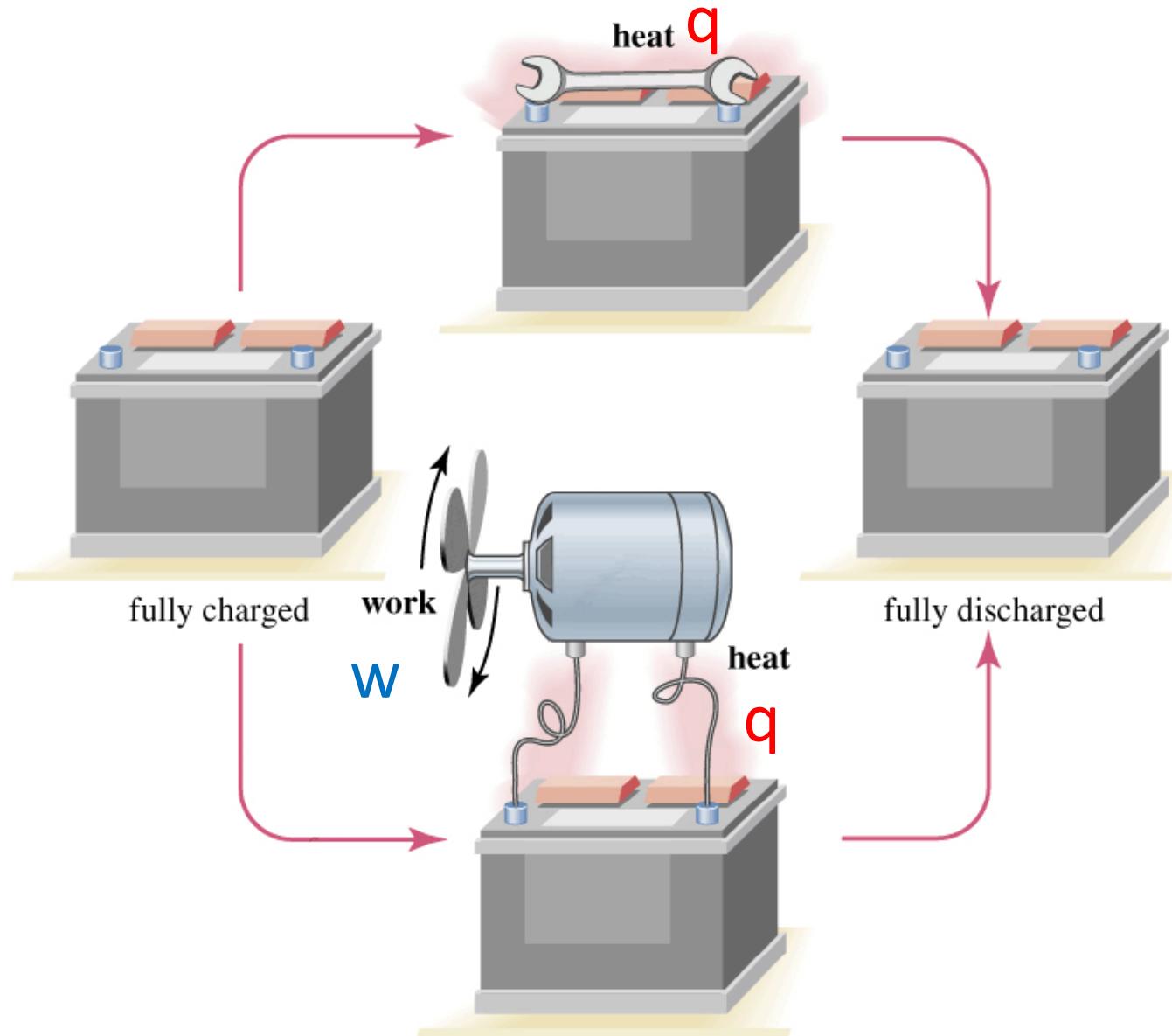
Josiah Willard Gibbs, Jr.

The First Law

- Energy cannot be created or destroyed
- For a closed chemical system, this means that all energy involved in a change must be heat (**q**) or work (**w**)

$$\Delta U = q + w$$

The First Law



Work?

- You do work on an object when you apply a force to it and move it a distance (units = N.m)
- Since pressure is a force divided by an area (N.m^{-2})...
- Pressure (p) \times volume (V) is the same as force times distance ($\text{N.m}^{-2} \cdot \text{m}^3 = \text{N.m}$)
- Work done when the volume of the system increases in a chemical reaction:

$$w = -p \Delta V$$

- Negative because energy is going **out** of the system to make the volume expand...

The First Law

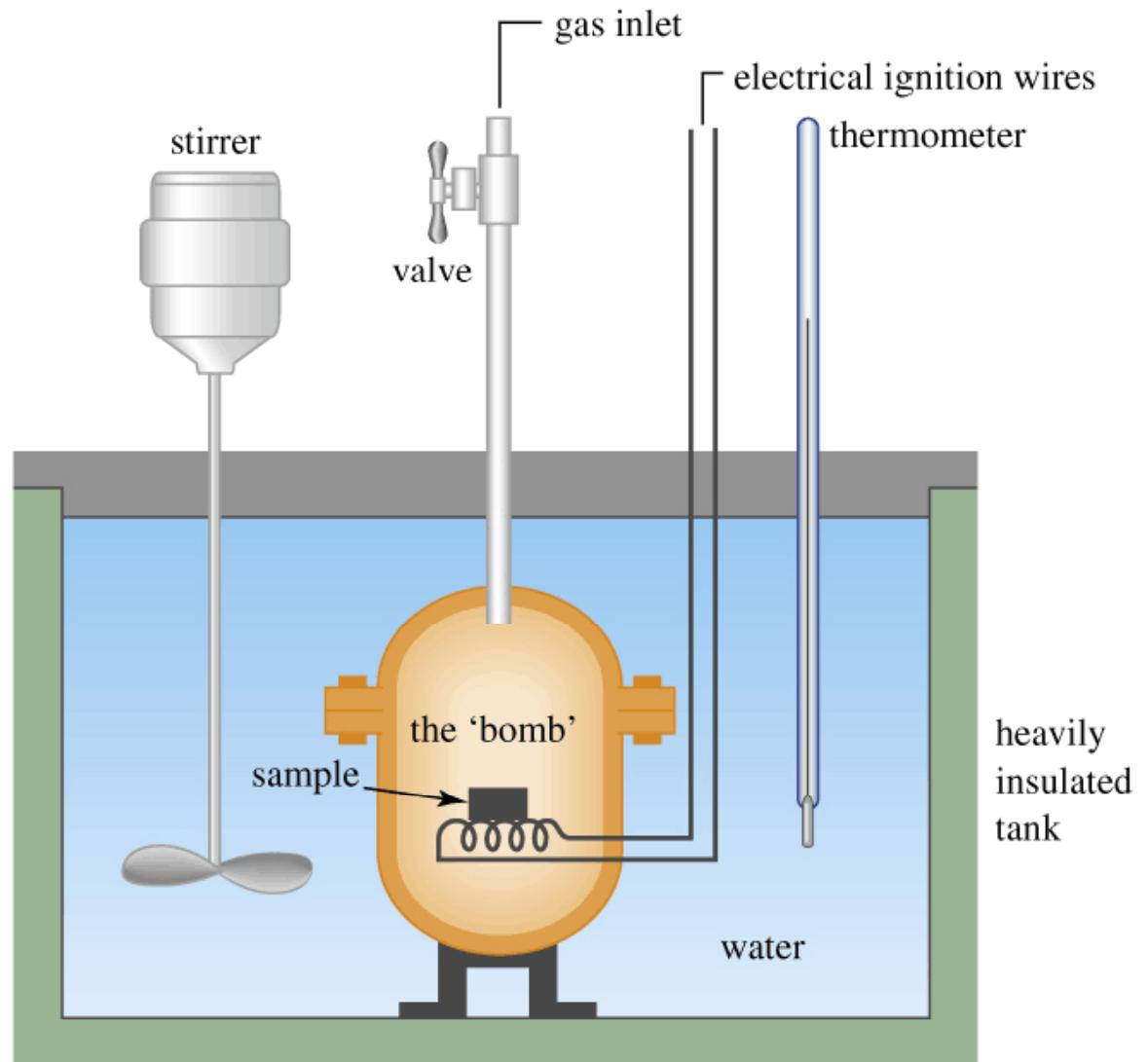
- Say we have a chemical reaction in dilute aqueous solution generating nitrogen gas where we collect the gas in a balloon. Our 1 L of water increases in temperature from 17 °C to 21 °C and we collect 5 L of nitrogen gas. **What is the total energy change in this reaction?**
- Heat capacity of water = $4.18 \text{ Jg}^{-1}\text{K}^{-1}$
- $q = -mc\Delta T = -1000 \text{ g} \times 4.18 \text{ Jg}^{-1}\text{K}^{-1} \times 4 \text{ K} = -1.67 \times 10^4 \text{ J}$
- $w = -p\Delta V = -10^5 \text{ Pa} \times 5 \text{ L}$
 $= -10^5 \text{ Nm}^{-2} \times 5 \times 10^{-3} \text{ m}^3 = -500 \text{ Nm} = -500 \text{ J}$
- $\Delta U = q + w = -1.72 \times 10^4 \text{ J}$
- This is the amount of energy that has come out of the system into the surroundings

Specific Heat

• Lead	0.128	1 kg of iron at 400 °C is added to 1 kg of water at 15 °C. What is the final T of the water?
• Gold	0.129	$q_{\text{out}}(\text{iron}) = q_{\text{in}}(\text{water})$
• Silver	0.235	$m_{\text{Fe}} c_{\text{Fe}} \Delta T_{\text{Fe}} = m_{\text{H}_2\text{O}} c_{\text{H}_2\text{O}} \Delta T_{\text{H}_2\text{O}}$
• Copper	0.387	$1 \times 0.450 \times \Delta T_{\text{Fe}} = 1 \times 4.18 \times \Delta T_{\text{H}_2\text{O}}$
• Iron	0.450	$0.450 \times (385 - \Delta T_{\text{H}_2\text{O}}) = 4.18 \times \Delta T_{\text{H}_2\text{O}}$
• Nitrogen (gas)	1.04	$173.25 - 0.450\Delta T_{\text{H}_2\text{O}} = 4.18 \Delta T_{\text{H}_2\text{O}}$
• Ethanol	2.45	$173.25 = 4.63\Delta T_{\text{H}_2\text{O}}$
• Water (liquid)	4.18	$37.4 = \Delta T_{\text{H}_2\text{O}}$
		$T_{\text{H}_2\text{O}} = 15 + 37.4 = 52.4 \text{ }^{\circ}\text{C}$
		The temperature of the iron will be the same as the water.

Calorimetry

- To measure the heat generated in a reaction
- All* heat from the reaction is transferred to something with a known heat capacity



* onto

Calorimetry



This 250 kcal (1050 kJ) means:



Calorimetry

- Doughnut + O₂ → CO₂ + H₂O
- If we burned the doughnut in a calorimeter and transferred the heat generated to 10 kg of water, for example, the temperature might go up 25.1°C:

$$q = m c \Delta T$$

$$q = 10 \text{ kg} \times 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1} \times 25.1 \text{ K}$$

$$q = 1050 \text{ kJ}$$

- This temperature rise of 25.1 °C tells us the energy released in the oxidation of the doughnut is 1050 kJ.

Enthalpy

- We can do a process at constant volume

$$\Delta U = q_v$$

q_v = heat of reaction at constant volume

- Or at constant pressure

$$\Delta U = q_p + p\Delta V$$

q_p = heat of reaction at constant pressure

= enthalpy change, ΔH

Standard Enthalpy Change

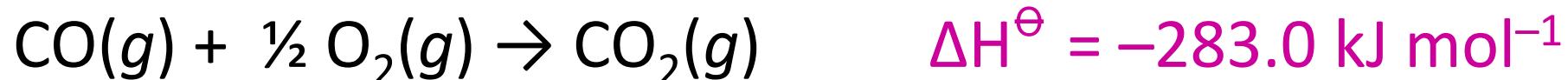
- Standard enthalpy changes (ΔH^Θ) are reported at a pressure of 10^5 Pa: or for reactions in solution, at a concentration of 1 M.



If ΔH is negative, the reaction is **exothermic (releases heat)**

If ΔH is positive, the reaction is **endothermic (absorbs heat)**

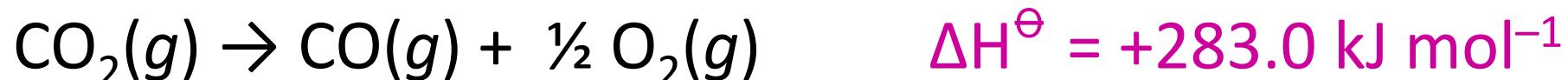
Enthalpies of Reaction



These enthalpies are state functions

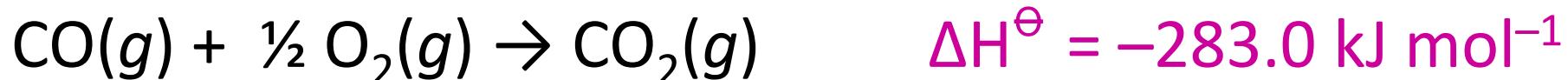
So we can add and subtract these equations like they were mathematical equations.

For instance, reversing the sign of everything:



You do remember what a state function is, don't you?

Enthalpies of Reaction

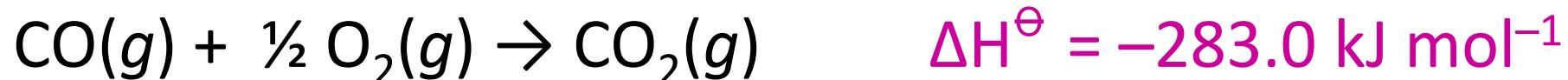


These enthalpies are **state functions**

So we can add and subtract these equations like they were mathematical equations:



Hess's Law



These enthalpies are state functions

So we can add and subtract these equations like they were mathematical equations:



This is a reaction where it is nigh-impossible to determine enthalpy of reaction directly

Hess's Law

- The overall enthalpy change for a particular chemical reaction is constant, regardless of how the reaction is carried out
- $8\text{Fe} + 6\text{NO}_2 \rightarrow 4\text{Fe}_2\text{O}_3 + 3\text{N}_2 \quad \Delta H^\ominus = ?$
- $6\text{NO}_2 \rightarrow 6\text{O}_2 + 3\text{N}_2$
- $8\text{Fe} + 4\text{NO}_2 \rightarrow 8\text{FeO} + 4\text{NO}$
- $6\text{O}_2 + 8\text{Fe} \rightarrow 4\text{Fe}_2\text{O}_3$
- $2\text{NO}_2 + 4\text{NO} \rightarrow 4\text{O}_2 + 3\text{N}_2$
- $4\text{O}_2 + 8\text{FeO} \rightarrow 4\text{Fe}_2\text{O}_3$

This is a reaction that I had some slides about when I was doing the gases lectures.

Standard Enthalpy of Formation

- The systematic way to figure out enthalpy of unknown reactions from known reactions is to use enthalpies of formation, ΔH_f^Θ
- ΔH_f^Θ = Enthalpy of reaction where the compound is formed from its elements in their standard state

- $\frac{1}{2} N_2(g) + O_2(g) \rightarrow NO_2(g)$ $\Delta H_f^\Theta = 33.8 \text{ kJ mol}^{-1}$
- $2Fe(s) + \frac{3}{2}O_2(g) \rightarrow Fe_2O_3(s)$ $\Delta H_f^\Theta = -822.3 \text{ kJ mol}^{-1}$
- $Fe(s) \rightarrow Fe(s)$ $\Delta H_f^\Theta = 0 \text{ kJ mol}^{-1}$
- $N_2(g) \rightarrow N_2(g)$ $\Delta H_f^\Theta = 0 \text{ kJ mol}^{-1}$

Hess's Law

- $8\text{Fe} + 6\text{NO}_2 \rightarrow 4\text{Fe}_2\text{O}_3 + 3\text{N}_2$
- $\Delta H^\ominus = \sum \Delta H_f^\ominus \text{products} - \sum \Delta H_f^\ominus \text{reactants}$
$$= (4 \times -822.3 + 0) - (6 \times 33.8 + 0) \text{ kJ mol}^{-1}$$
$$= -3289.2 - 202.8 \text{ kJ mol}^{-1}$$
$$= -3492.0 \text{ kJ mol}^{-1}$$
- $\frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H_f^\ominus = 33.8 \text{ kJ mol}^{-1}$
- $2\text{Fe}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) \quad \Delta H_f^\ominus = -822.3 \text{ kJ mol}^{-1}$
- $\text{Fe}(\text{s}) \rightarrow \text{Fe}(\text{s}) \quad \Delta H_f^\ominus = 0 \text{ kJ mol}^{-1}$
- $\text{N}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) \quad \Delta H_f^\ominus = 0 \text{ kJ mol}^{-1}$

Hess's Law

- $8\text{Fe} + 6\text{NO}_2 \rightarrow 4\text{Fe}_2\text{O}_3 + 3\text{N}_2$
- $\Delta H^\Theta = \sum \Delta H_f^\Theta \text{ products} - \sum \Delta H_f^\Theta \text{ reactants}$
$$= (4 \times -822.3 + 0) - (6 \times 33.8 + 0) \text{ kJ mol}^{-1}$$
$$= -3289.2 - 202.8 \text{ kJ mol}^{-1}$$
$$= \mathbf{-3492.0 \text{ kJ mol}^{-1}}$$
- $\frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H_f^\Theta = 33.8 \text{ kJ mol}^{-1}$
- $2\text{Fe}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) \quad \Delta H_f^\Theta = -822.3 \text{ kJ mol}^{-1}$
- $\text{Fe}(\text{s}) \rightarrow \text{Fe}(\text{s}) \quad \Delta H_f^\Theta = 0 \text{ kJ mol}^{-1}$
- $\text{N}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) \quad \Delta H_f^\Theta = 0 \text{ kJ mol}^{-1}$

We can burn ethanol or diamonds –
for the same amount of energy, which
generates more CO₂?

- C(s, diamond) + O₂(g) → CO₂(g)
- $\Delta H^\Theta = \sum \Delta H_f^\Theta \text{products} - \sum \Delta H_f^\Theta \text{reactants}$
 $= (-393.5) - (1.9 + 0) \text{ kJ mol}^{-1}$
 $= -395.4 \text{ kJ mol}^{-1} \text{ per CO}_2$
- CH₃COOH(l) + 2O₂(g) → 2CO₂(g) + 2H₂O(l)
- $\Delta H^\Theta = \sum \Delta H_f^\Theta \text{products} - \sum \Delta H_f^\Theta \text{reactants}$
 $= (2 \times -393.5 + 2 \times -285.9) - (-487.0 + 0) \text{ kJ mol}^{-1}$
 $= -871.8 \text{ kJ mol}^{-1} \text{ per } 2 \text{ CO}_2$
 $= -435.9 \text{ kJ mol}^{-1} \text{ per CO}_2$

Things to remember about ΔH_f° values:

For any pure element, $\Delta H_f^\ominus = 0$

Most values are negative

- reaction to form product is exothermic
- usually favourable to form product from its elements

The miracle of Hess's Law allows us to add and subtract them at whim to get any reaction we are interested in!

Generally, the more negative the ΔH^\ominus value of a reaction, the more stable the compound

Bond Enthalpies

- Most chemical reactions involve the making and breaking of bonds
- The energy involved in breaking a C-C bond, for instance, is pretty much the same wherever it is:
- $\text{H}_3\text{C}-\text{CH}_3 \rightarrow 2\text{CH}_3$ ΔH^\ominus about 348 kJ mol⁻¹
- $\text{CF}_3\text{H}_2\text{C}-\text{CH}_3 \rightarrow \text{CF}_3\text{H}_2\text{C} + \text{CH}_3$ ΔH^\ominus about 348 kJ mol⁻¹

Bond Enthalpies

- The energy needed to **break** a bond – so a positive number

	kJ mol ⁻¹		kJ mol ⁻¹
• C-C	348	H-H	436
• C=C	612	H-O	463
• C≡C	960	H-F	565
• C-H	412	H-Cl	431
• C-O	360	C-N	305
• C=O	743	O=O	495

Bond Enthalpies

- $\text{CH}_3\text{COOH(l)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$
- Need to break:
 - 3 C-H bonds, 1 C-C bond, 1 C-O bond, 2 O=O bonds
412 348 360 495
- Need to make: 3 C=O bonds, 3 O-H bonds
743 463
- $\Delta H^\Theta = \sum \text{reactant bond enthalpies} - \sum \text{product bond enthalpies}$
$$= (3 \times 412 + 348 + 360 + 2 \times 495) - (3 \times 743 + 3 \times 463) \text{ kJ mol}^{-1}$$
$$= (1236 + 348 + 360 + 990) - (2229 + 1389) \text{ kJ mol}^{-1}$$
$$= 2934 - 3618 = \mathbf{-684 \text{ kJ mol}^{-1}}$$

Entropy

- If a process absorbs or releases heat, but no change in temperature occurs in the system, we account for it by a change in the **entropy** of the system
- e.g., water melting
 - Before: 1 kg ice (0°C) + 10 kg chloroform (-30°C)
 - After: 1 kg water (0°C) + 10 kg chloroform (0°C)
- Where did the energy to heat this chloroform come from?

Entropy

- $\Delta S = q/T$

ΔS = change in entropy

q = heat transferred to the system

T = constant temperature

For 1 kg of ice melting:

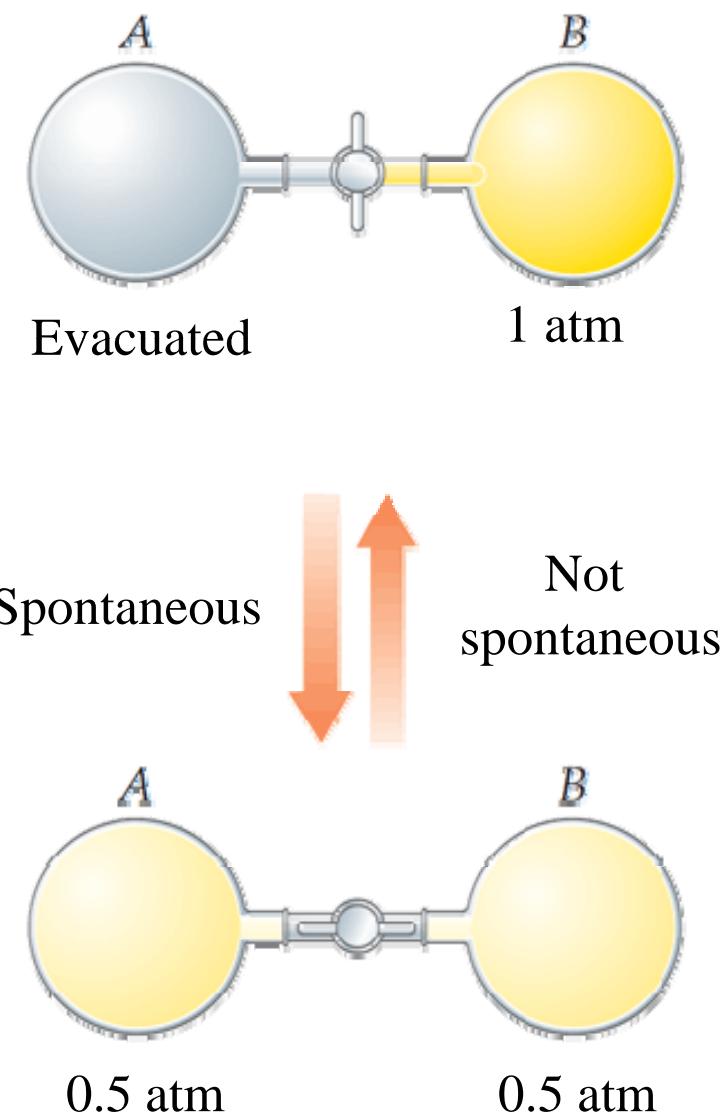
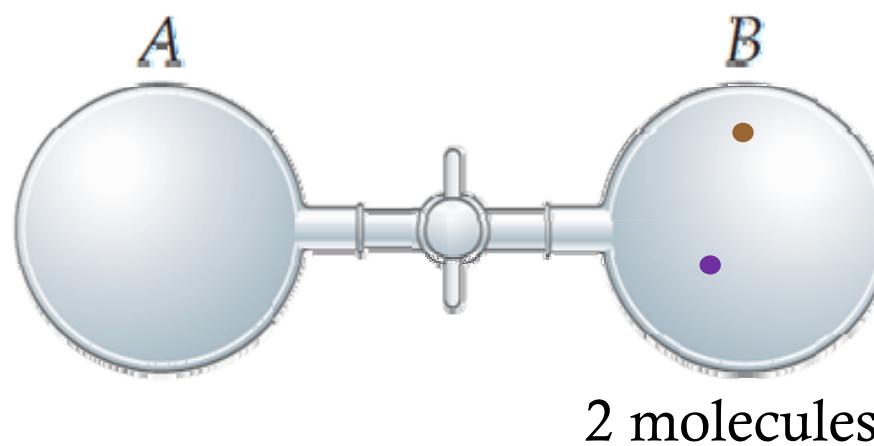
$$q = 331 \text{ kJ}$$

$$T = 273.15 \text{ K}$$

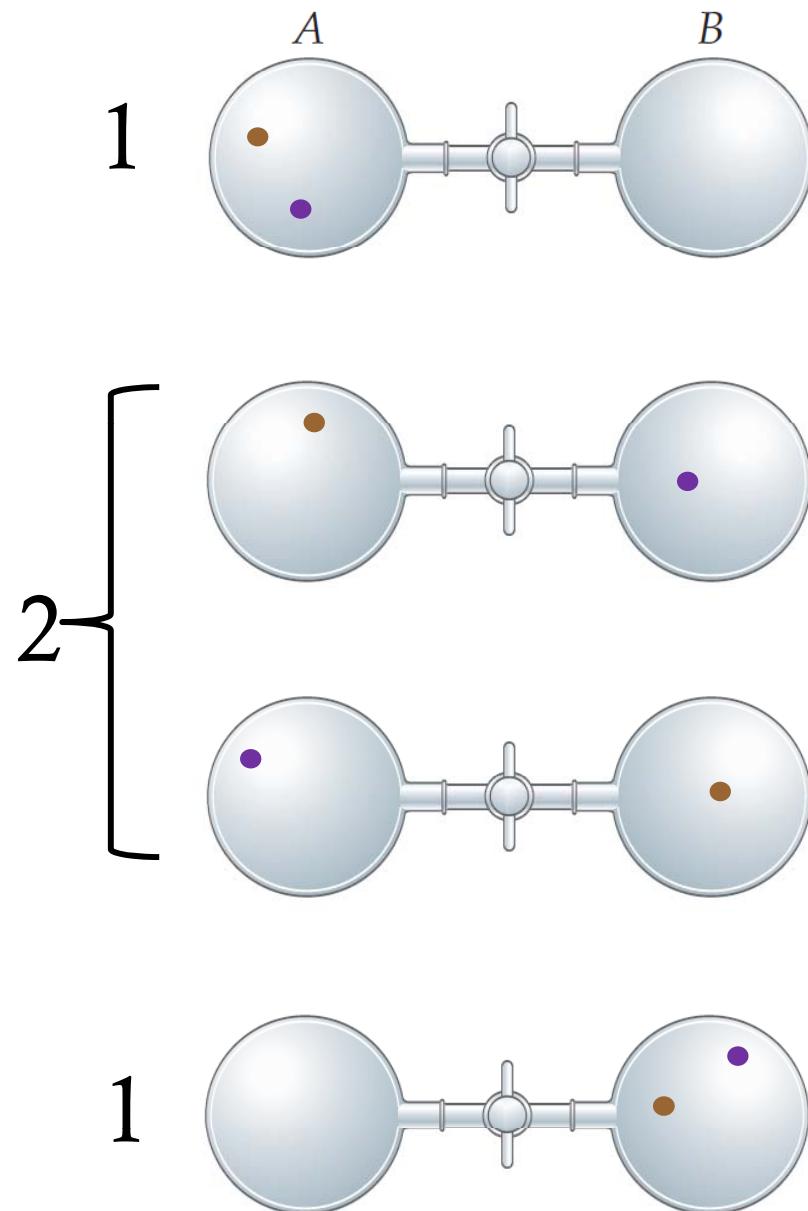
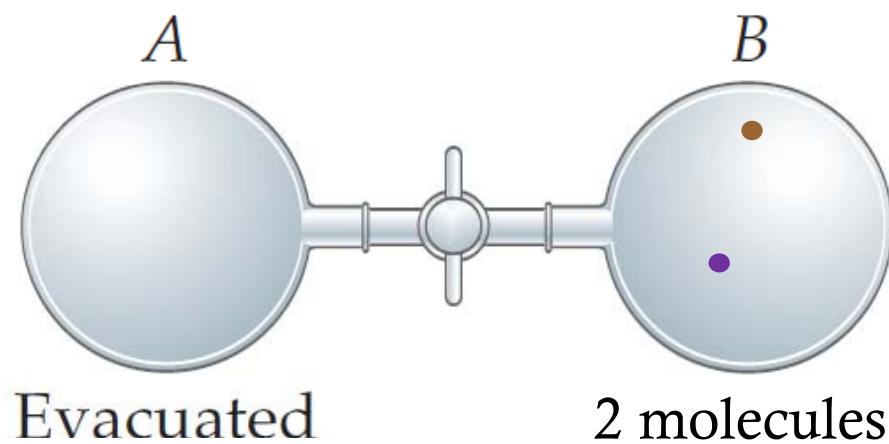
- $\Delta S = 1210 \text{ J K}^{-1}$

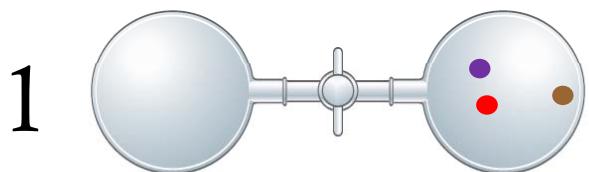
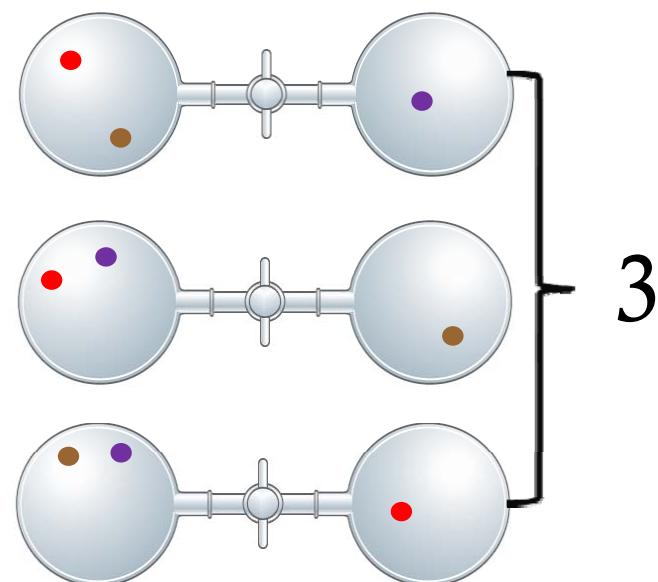
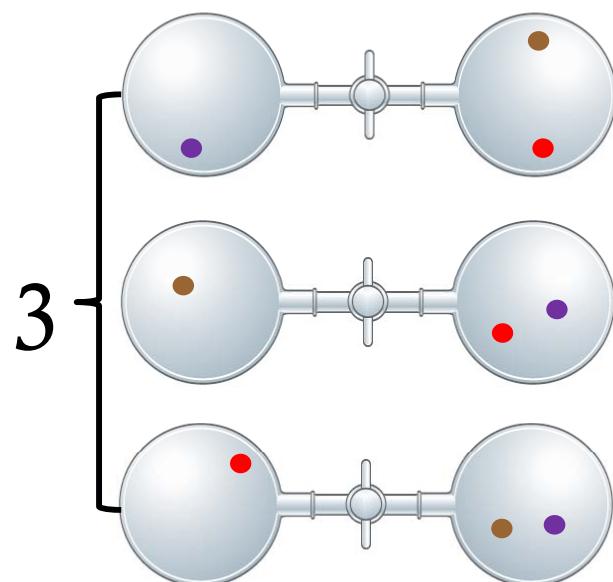
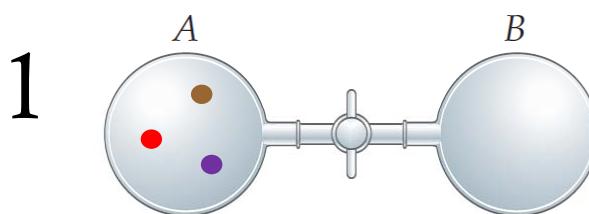
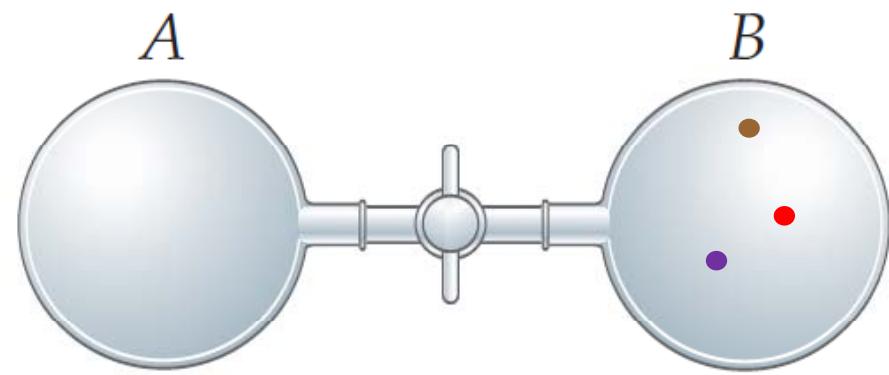


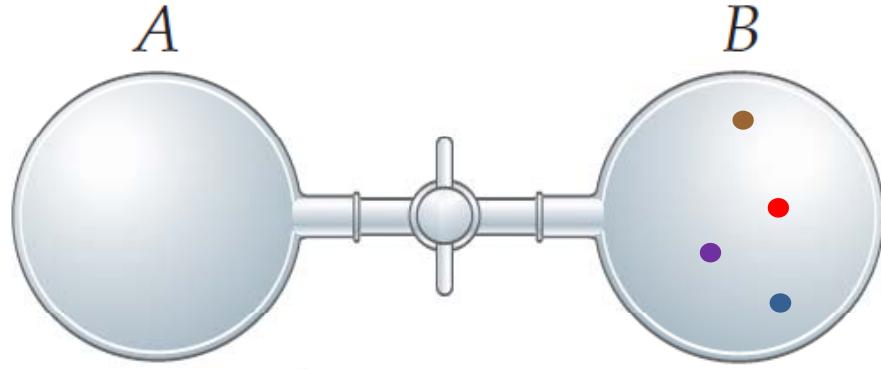
Statistical Definition of Entropy



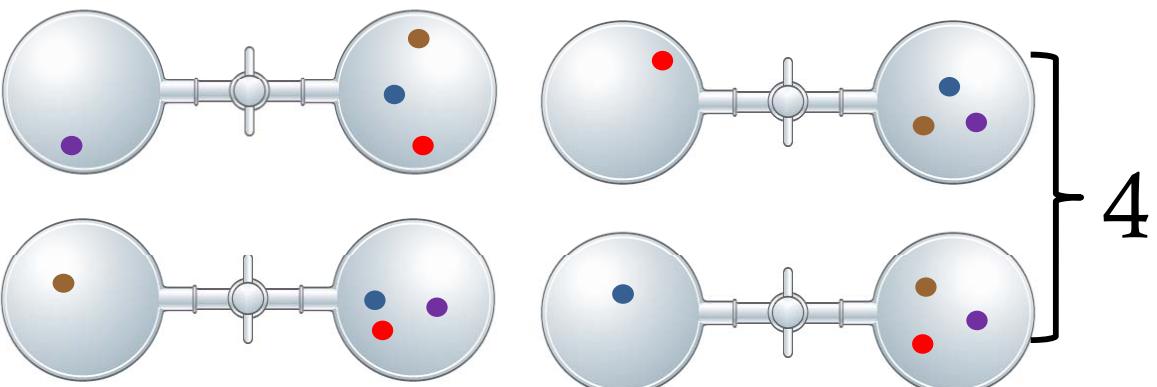
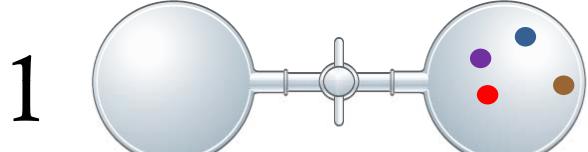
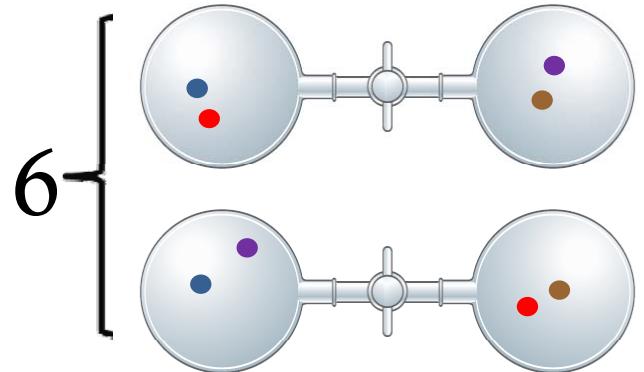
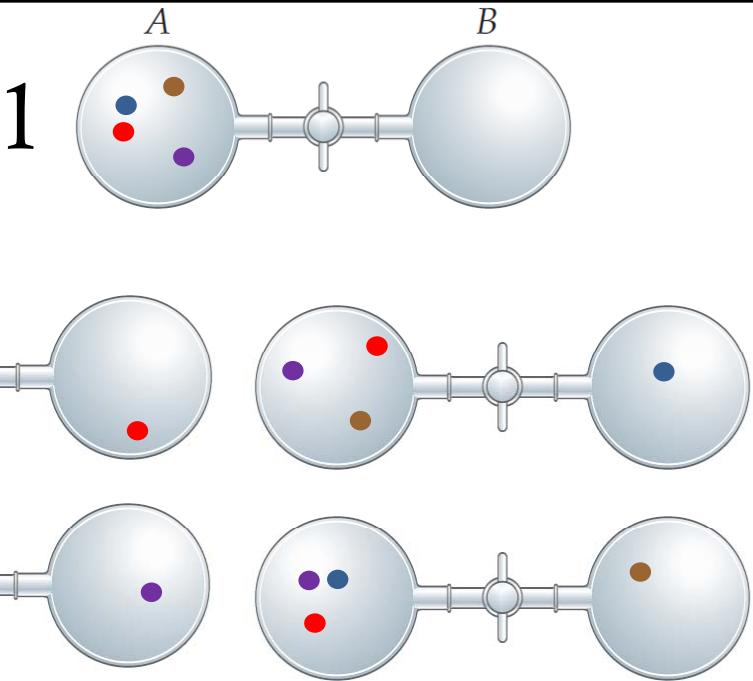
Statistical Definition of Entropy



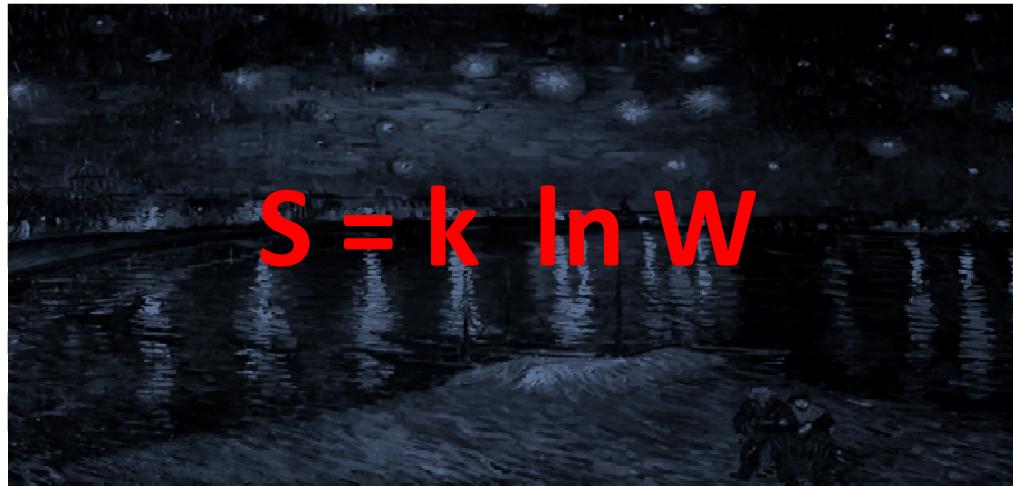




4 molecules



Boltzmann's Equation



W = number of microstates

$\ln W$ = natural log of W

R = ideal gas constant, $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$

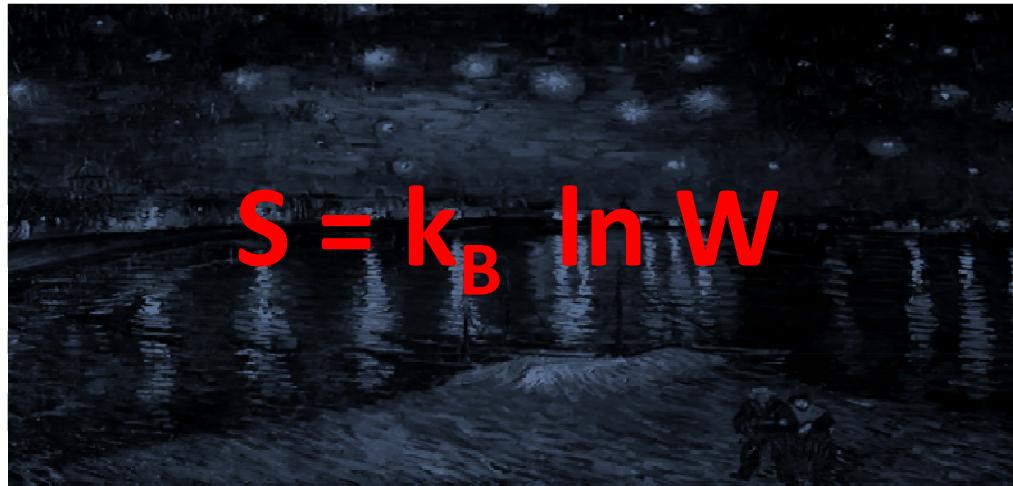
N_A = Avogadro's Number, 6.022×10^{23}

k = Boltzmann's constant (R/N_A)

\ln = logarithm to base e
 $= \log_{10} \times 2.30259\dots$

NB: 'k' is what it says in the textbook;
I like ' k_B '

Boltzmann's Equation



W = number of microstates

$\ln W$ = natural log of W

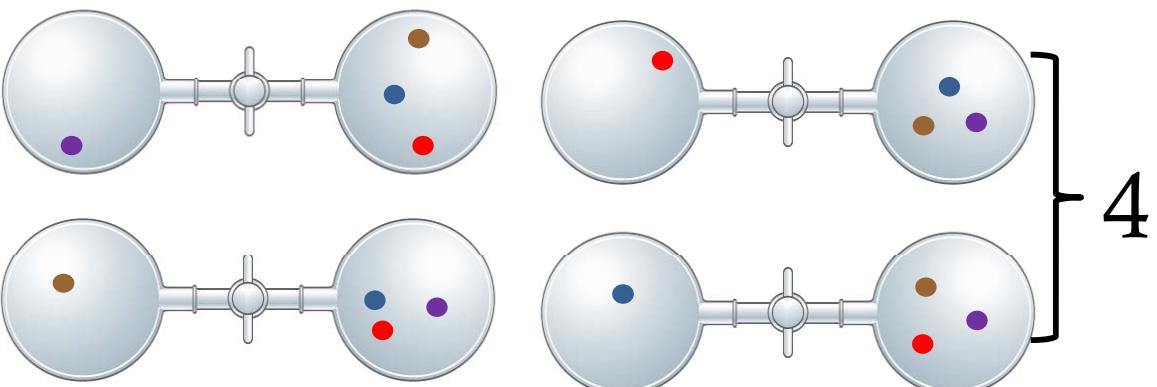
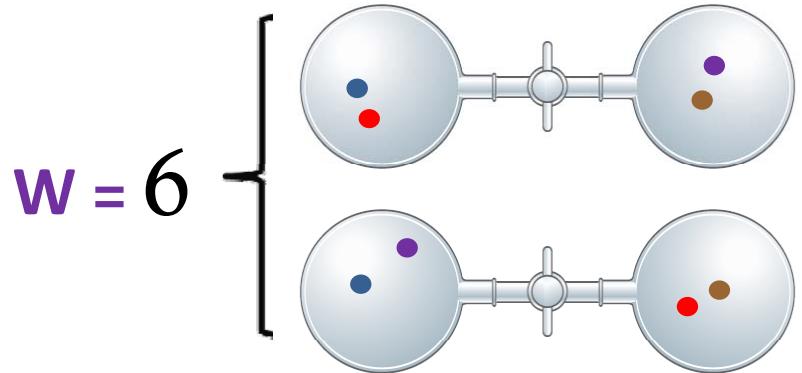
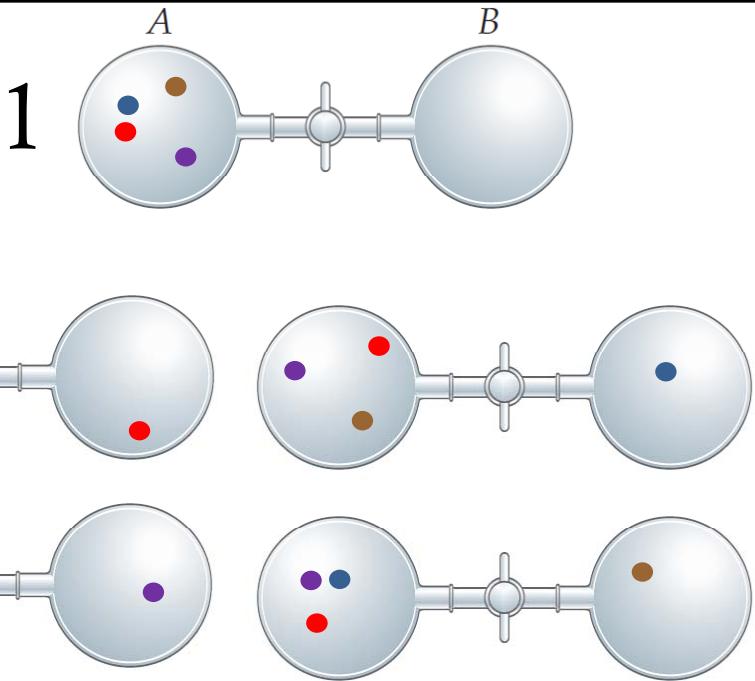
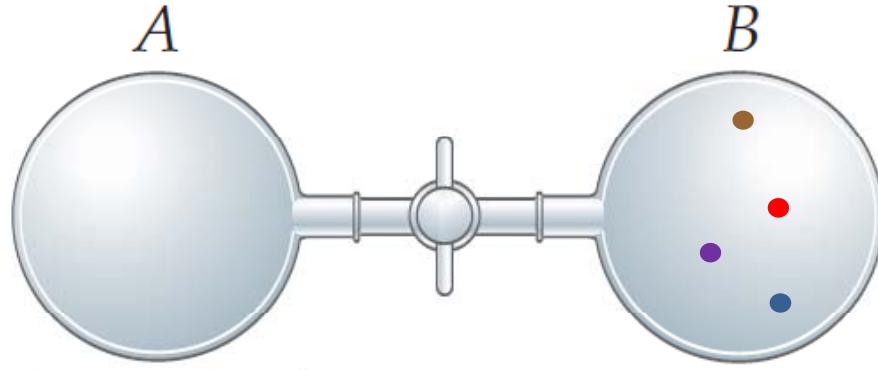
R = ideal gas constant, $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$

N_A = Avogadro's Number, 6.022×10^{23}

k_B = Boltzmann's constant (R/N_A)

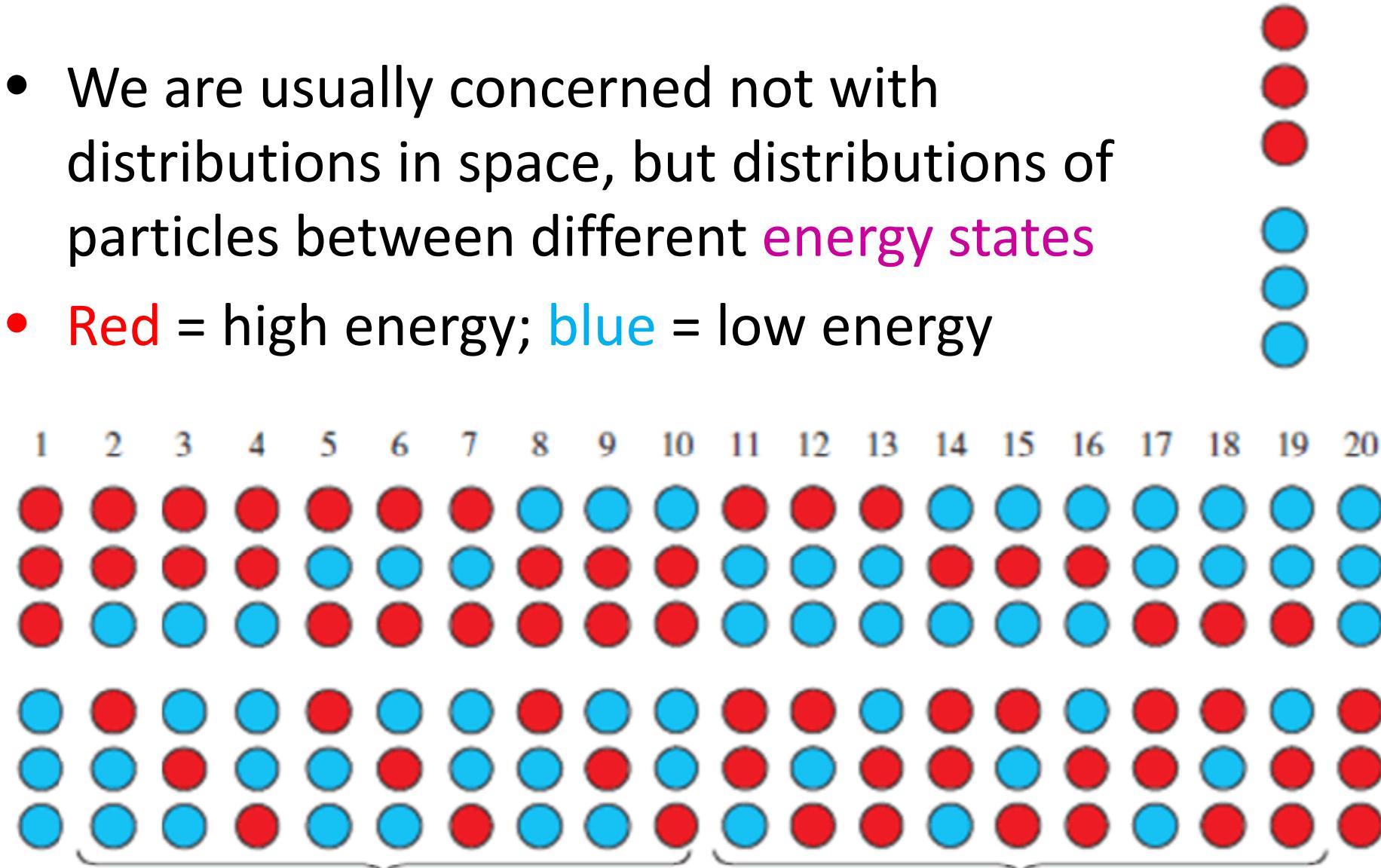
NB: 'k' is what it says in the textbook;
I like ' k_B '

You might need to remember this... in 2014.



Statistical Definition of Entropy

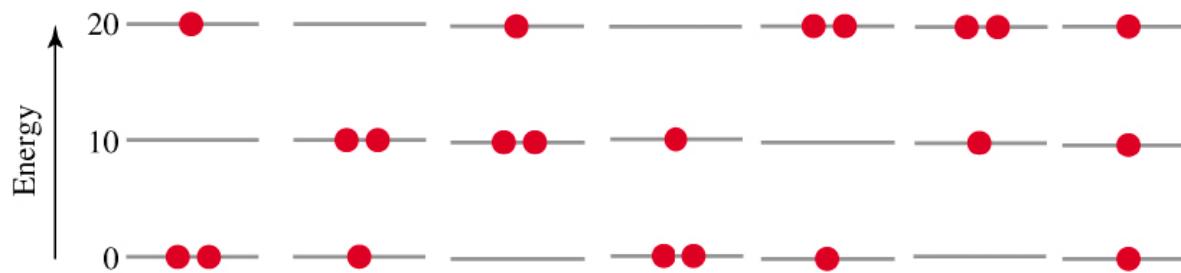
- We are usually concerned not with distributions in space, but distributions of particles between different **energy states**
- Red = high energy; blue = low energy



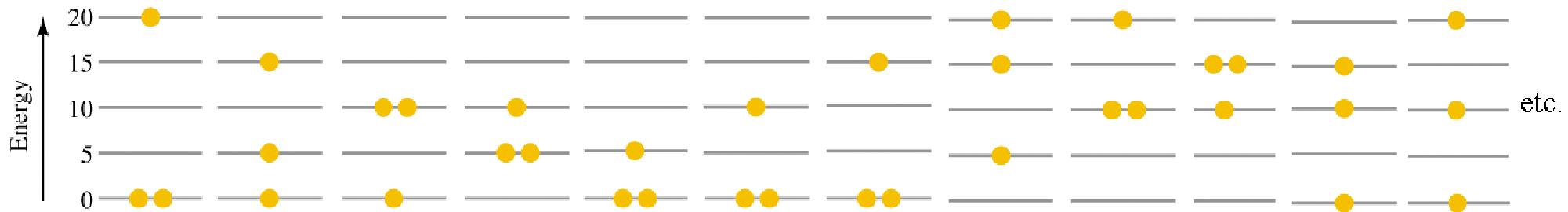
Entropy and Entropy Change

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

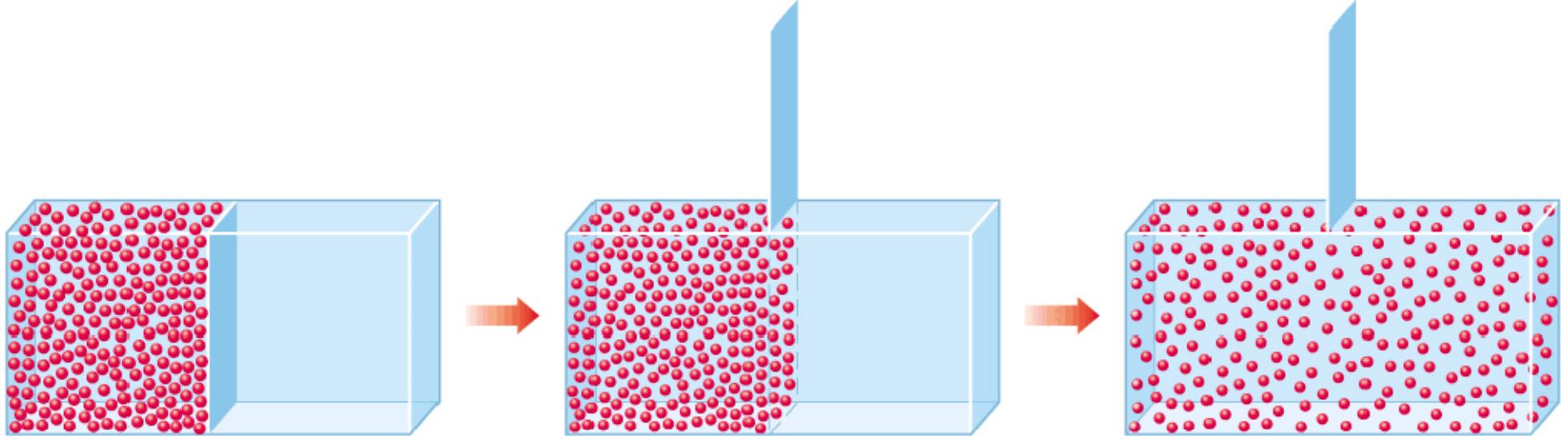
- **Low entropy** = few ways to distribute energy



- **High entropy** = many ways to distribute energy



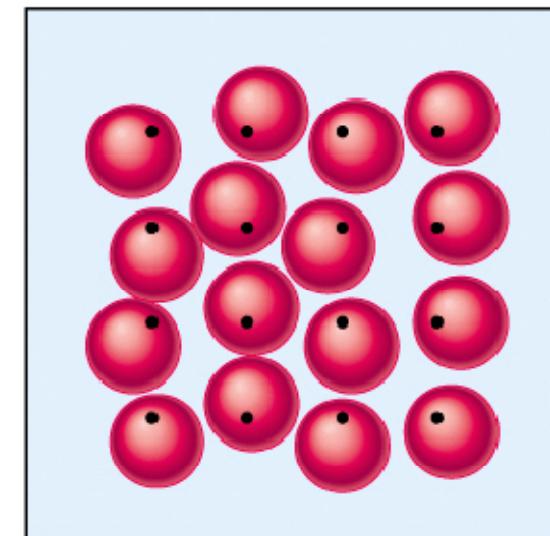
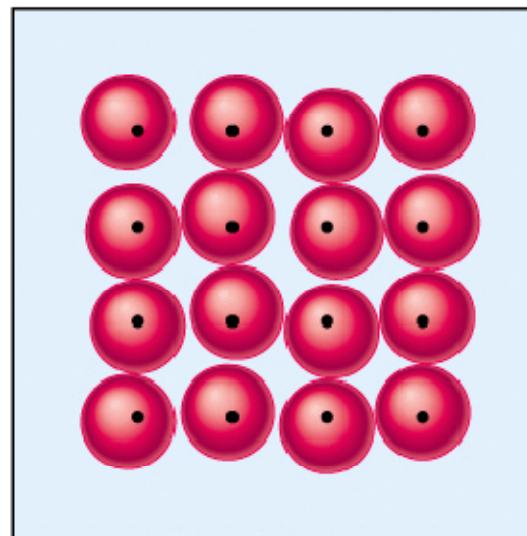
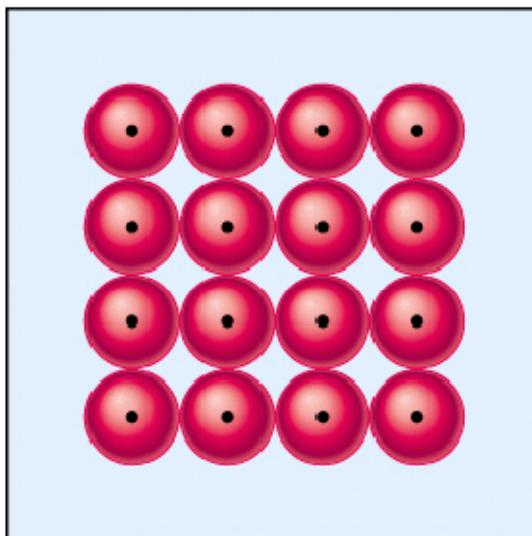
Volume



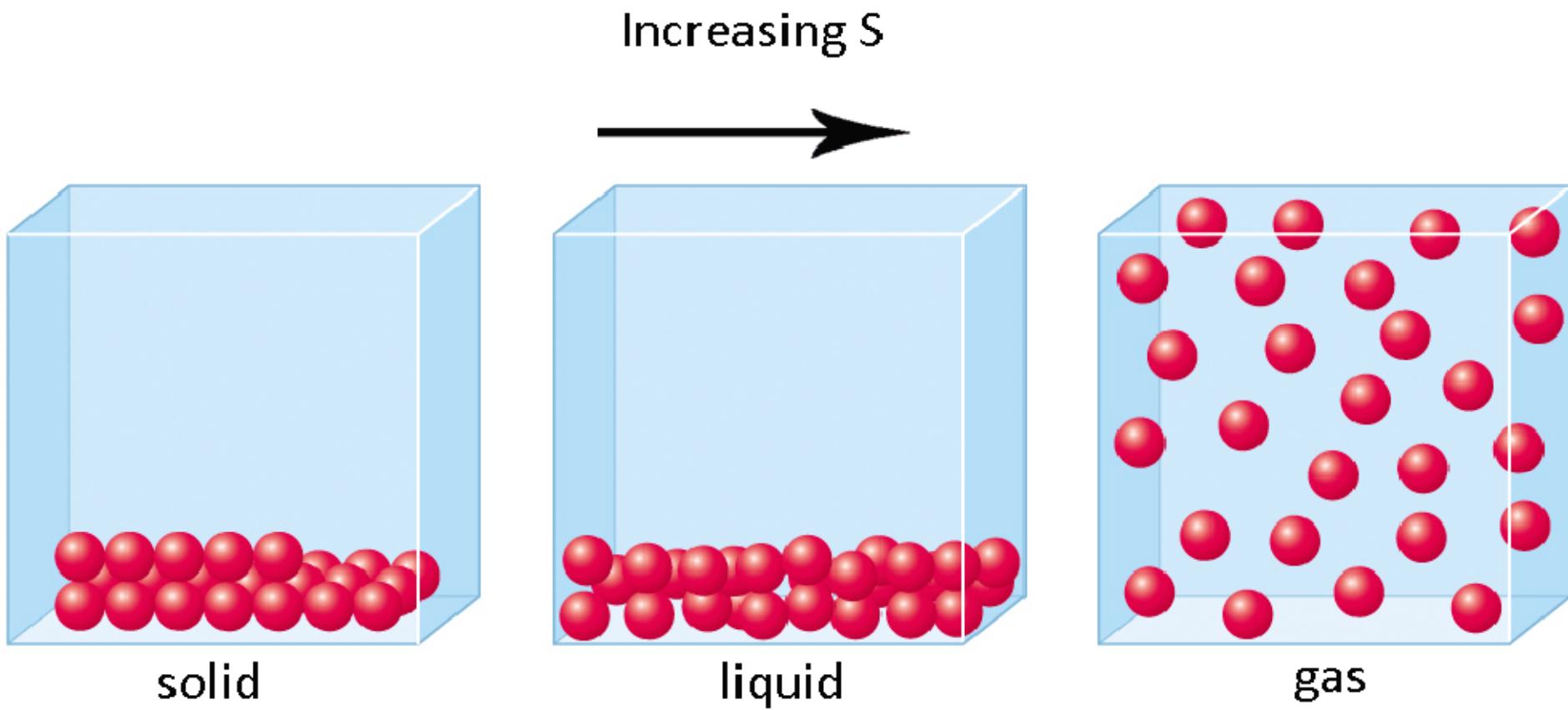
- The temperature has gone down, but no energy has escaped from the system
- So the entropy must have **increased**
- In a larger volume there are more ways to arrange the kinetic energy of the particles

Temperature

Increasing T and S

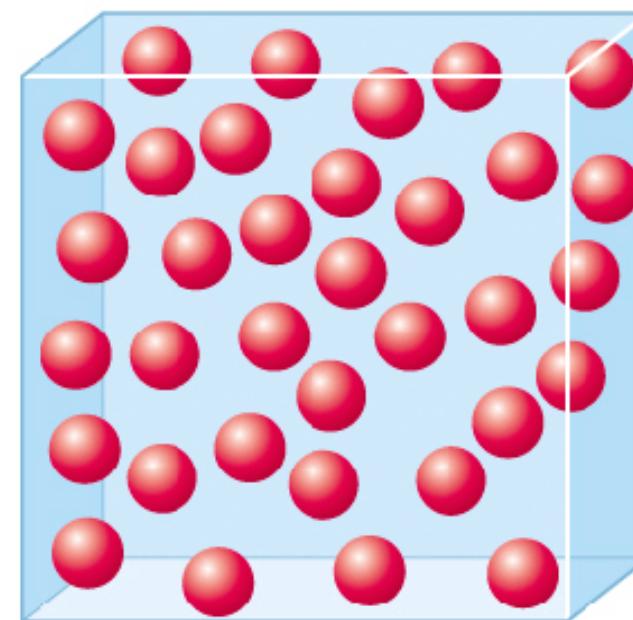
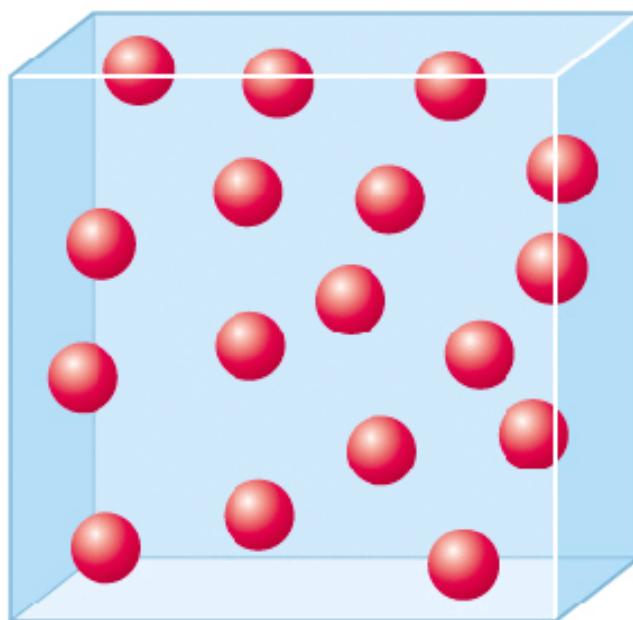


State



Number of Particles

Increasing S



The Second Law

- For *anything* to happen, the entropy of the universe must increase

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

The entropy of the universe is always increasing

You can't win

You can only break even at T = 0 K

You can't reach T = 0 K

The law that entropy always increases - the second law of thermodynamics -- holds I think, the supreme position among the laws of Nature.

If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations - then so much worse for Maxwell's equations.

If it is found to be contradicted by observation - well these experimentalists do bungle things sometimes.

But if your theory is found to be against the second law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Sir Arthur Stanley Eddington



The Third Law

- If $W = 1$, then $S = 0$
- If there is only one possible way of arranging the energy in a system, $S = 0$
- This is true for a *perfectly ordered crystalline substance at $T = 0\text{ K}$*

Standard Molar Entropy, S^\ominus

Jmol $^{-1}$ K $^{-1}$

• Lead	64.8
• Gold	47.7
• Silver	42.6
• Copper	33.2
• Iron	27
• Nitrogen (gas)	191.5
• Ethanol	161
• Water (liquid)	69.96

- Because there is a zero for entropy, every substance has a clearly defined **standard entropy per mole**

- Normally tabulated at 25 °C

Using S^\ominus

- We can calculate the entropy of a reaction in exactly the same way as we calculated the enthalpy of a reaction
- $\Delta S^\ominus = \sum S^\ominus \text{products} - \sum S^\ominus \text{reactants}$
- $\text{NO}_2(g) \quad S^\ominus = 240.5 \text{ JK}^{-1}\text{mol}^{-1}$
- $\text{Fe}_2\text{O}_3(s) \quad S^\ominus = 90 \text{ JK}^{-1}\text{mol}^{-1}$
- $\text{Fe}(s) \quad S^\ominus = 27 \text{ JK}^{-1}\text{mol}^{-1}$
- $\text{N}_2(g) \quad S^\ominus = 192 \text{ JK}^{-1}\text{mol}^{-1}$

Using S^\ominus

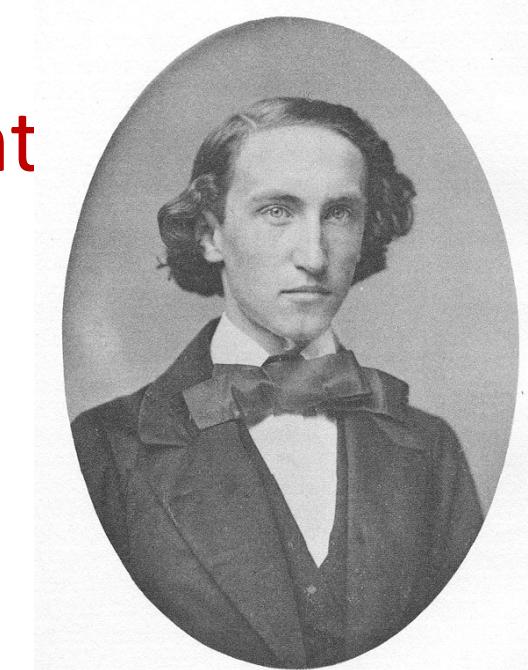
- $8\text{Fe} + 6\text{NO}_2 \rightarrow 4\text{Fe}_2\text{O}_3 + 3\text{N}_2$
- $\Delta S^\ominus = \sum S^\ominus \text{products} - \sum S^\ominus \text{reactants}$
 $= (4 \times 90 + 3 \times 192) - (8 \times 27 + 6 \times 240.5) \text{ JK}^{-1}\text{mol}^{-1}$
 $= 936 - 1659 \text{ JK}^{-1}\text{mol}^{-1}$
 $= - 723 \text{ JK}^{-1}\text{mol}^{-1}$
- $\text{NO}_2(\text{g}) \quad S^\ominus = 240.5 \text{ JK}^{-1}\text{mol}^{-1}$
- $\text{Fe}_2\text{O}_3(\text{s}) \quad S^\ominus = 90 \text{ JK}^{-1}\text{mol}^{-1}$
- $\text{Fe}(\text{s}) \quad S^\ominus = 27 \text{ JK}^{-1}\text{mol}^{-1}$
- $\text{N}_2(\text{g}) \quad S^\ominus = 192 \text{ JK}^{-1}\text{mol}^{-1}$

Gibbs Energy

- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- It would be good to have a handy function for $\Delta S_{\text{universe}}$ in terms of what the system is doing.
- $\Delta S_{\text{surroundings}} = q_{\text{surroundings}}/T$
- $\Delta S_{\text{surroundings}} = -q_{\text{system}}/T$
- $\Delta S_{\text{surroundings}} = -\Delta H_{\text{system}}/T$
- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta H_{\text{system}}/T$
- $T\Delta S_{\text{universe}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}}$
- $\Delta H_{\text{system}} - T\Delta S_{\text{system}} = -T\Delta S_{\text{universe}}$
- $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} = -T\Delta S_{\text{universe}}$

Gibbs Energy

- Named after Josiah Willard Gibbs, Jr.
- Tells you whether a process is spontaneous (if ΔG is negative) or non-spontaneous (if ΔG is positive)
- As usual, we can define a standard Gibbs energy change, ΔG^Θ , at 10^5 Pa
- $\Delta G^\Theta = \sum \Delta G_f^\Theta \text{ products} - \sum \Delta G_f^\Theta \text{ reactant}$
- $\text{C(s, diamond)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
$$\begin{aligned}\Delta G^\Theta &= \sum \Delta G_f^\Theta \text{ products} - \sum \Delta G_f^\Theta \text{ reactants} \\ &= -394.4 - (2.9 + 0) \text{ kJmol}^{-1} \\ &= -397.3 \text{ kJmol}^{-1}\end{aligned}$$



Josiah Willard Gibbs, Jr.

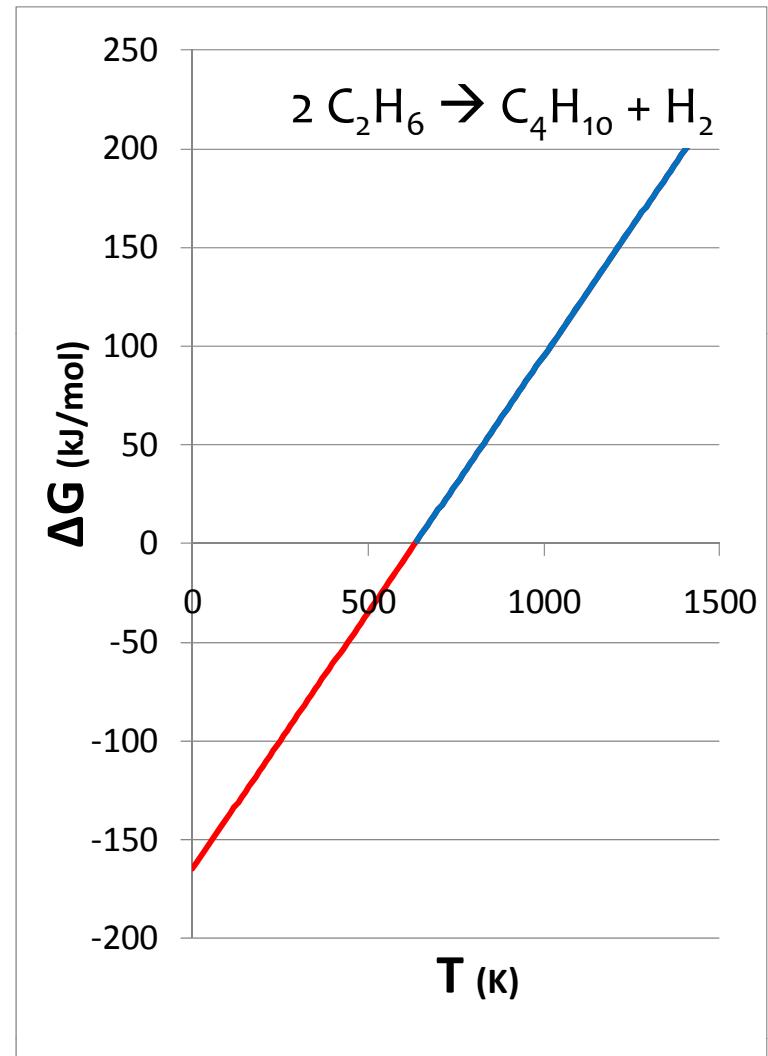
Gibbs Energy and Spontaneity

non-spontaneous, reactant-favoured

$$\Delta G^\theta_{\text{system}} = \Delta H^\theta_{\text{system}} - T\Delta S^\theta_{\text{system}} > 0$$

spontaneous, product favoured

$$\Delta G^\theta_{\text{system}} = \Delta H^\theta_{\text{system}} - T\Delta S^\theta_{\text{system}} < 0$$



Gibbs Energy and Spontaneity

- Some reactions are favoured only above, or only below, a certain temperature
- If $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, then the reaction will be spontaneous **below** $T = \Delta H^\circ / \Delta S^\circ$, and non-spontaneous above.
- If $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$, then the reaction will be spontaneous **above** $T = \Delta H^\circ / \Delta S^\circ$, and non-spontaneous below.

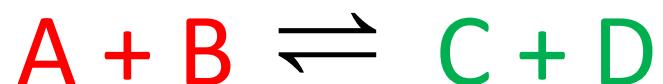
Everyone's brain starts to go fuzzy looking at big slabs of text like this, so...

Gibbs Energy and Spontaneity

	ΔH^\ominus -ve	ΔH^\ominus +ve
S^\ominus +ve	Spontaneous at all T	Spontaneous only at high T
S^\ominus -ve	Spontaneous only at low T	Non-spontaneous at all T

Gibbs Energy and Equilibrium

- There is not just spontaneous and non-spontaneous
- All reactions have some probability of going in each direction:



- If, once you can't see anything more happening:
- $[\text{C}][\text{D}] > [\text{A}][\text{B}]$, the reaction is spontaneous
- $[\text{A}][\text{B}] > [\text{C}][\text{D}]$, the reaction is non-spontaneous