

Welcome to Chemistry 154!

Chemistry for Engineering

Based on this cat scale....how do you feel today?





Reminders

- **Worksheet: Unit 8**
- Due Nov. 27th at 11:59pm

- **Achieve Assignment #8**
- Due Nov. 27th at 11:59pm

Instructor Office Hours

Monday and Friday 7-8pm via Zoom (All Lectures Site)



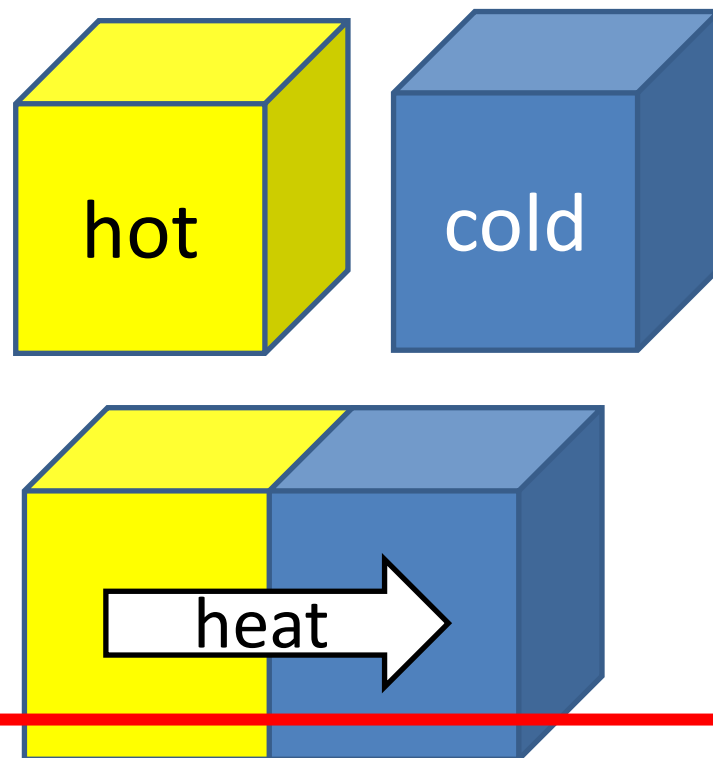
MIDTERM Exam

November 17th 6:30 – 7:30 pm

- Please bring your UBC card and a basic calculator to the exam.
- You may also bring molecular model kits (if desired).
CHEM154 Equation Sheet will be provided.
- Please arrive to your exam location at 6:00pm, students will be invited into the exam rooms approximately 15-20 minutes before the start of the exam
- Exam locations can be found on the All Lectures Canvas Site
→ Exam Information

Heat (q)

- Heat is the energy transferred between the system and surroundings which cannot be attributed to work.
- Example: energy transfer from a hot object to a cold object.



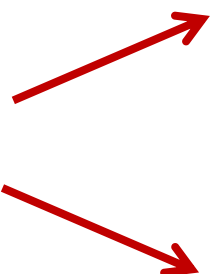
Sign convention:

Positive for heat flow from surroundings to system (endothermic)

Negative for heat flow from system to surroundings (exothermic)

Work in a Chemical Reaction: PV work

$$w = -P_{\text{ext}} \Delta V$$



If ΔV is positive
expansion = -ve work

If ΔV is negative
contraction = +ve work

- This equation valid at ***constant pressure!***
- Expansion is work by system (negative)
- Contraction is work on system (positive)
- Chemists sign convention is always positive if **system** gains energy and negative if **system** loses energy (be it heat or work)

1st Law of Thermodynamics (for closed system)

$$\Delta U = q + w$$

$$\Delta U = U_{final} - U_{initial}$$

ΔU = Change in Internal Energy

q = heat

w = work

The 1st Law is always a mathematical expression for the conservation of energy.

Because heat and work account for all energy exchange between the system and surroundings, this energy change must equal the change in total energy of the system.

State functions

- A state function has a unique value for each equilibrium state which means the difference in a state function between two equilibrium states does not depend upon the path or process used to produce them.

T - Temperature

P - Pressure

V - Volume

U – Internal Energy

H - Enthalpy

S - Entropy

G – Gibb's Energy

For a one-component closed system, if 2 of the values are fixed, you can determine any of the remaining variables.

In general, capitalized variables are usually state functions.

- Constant Volume Process:

$$\Delta U = q + w \quad \rightarrow \quad \Delta U = q = q_v$$

- Constant Pressure Process:

$$\Delta U = q_p + w = q_p - P\Delta V$$

$$q_p = \Delta U + P\Delta V = \Delta H$$



Exothermic: $\Delta H < 0$ (Heat flows from the system to its surroundings)

Endothermic: $\Delta H > 0$ (Heat flows from the surroundings to the system)

Heat and matter – Phase changes

During phase changes:

- heat is required to overcome IMFs, or
- heat is released upon the formation of IMFs

This heat is called ‘latent heat’

$$\Delta H = n \cdot \Delta H_{\text{phase change}}$$

n = number of moles of substance

$\Delta H_{\text{phase change}}$ = enthalpy of phase change

REMINDER: ΔH is an EXTENSIVE property. Therefore it scales with size/quantity/extent.

Standard Enthalpy of Formation

$$\Delta H_{rxn}^0 = \sum v_p \cdot \Delta H_f^0(\text{products}) - \sum v_r \cdot \Delta H_f^0(\text{reactants})$$

ΔH_f^0 = Enthalpy of formation for each product / reactant

v = Stoichiometric coefficient from reaction equation

If we know ΔH_f^0 for products and reactants, we can use Hess' law to determine enthalpy change.

ΔH_f^0 : Enthalpy change in a reaction where 1 mole of substance is formed from elements in their standard states.

Standard Enthalpy of Formation

What is standard state?

Gases	1 bar pressure
Pure solids + liquids	Pure substance
Solutions	1 M solution

1. $\Delta H_f^\circ = 0$ for elements in standard state.
2. Need to select one allotrope of element as reference form.

C_{graphite} vs. C_{diamond} vs. C_{60}

S_{rhombic} vs. $S_{\text{monoclinic}}$

3. ΔH_f° varies *slightly* with temperature...we use 298 K as default.

Bond Enthalpies

$$\Delta H_{rxn}^{\circ} = \sum E_{bond}(reactants) - \sum E_{bond}(products)$$

Bonds Broken
(Energy input) Bonds Formed
(Energy output)

Bond enthalpies can be used to get approximate values for enthalpies of reactions

Not ALL bond enthalpies are made equal – they are averaged over MANY compounds.

Clicker Question

An exothermic reaction is always spontaneous, and an endothermic process is always non-spontaneous.

A) True

B) False

A reaction can be spontaneous regardless of the sign of ΔH



**Ice melting process at
room temperature is
endothermic, but it is
spontaneous**

Note: spontaneity does not indicate rate of a reaction

Unit 8

Entropy and the Second and Third Laws of Thermodynamics

Learning Objectives

- After mastering this unit you will be able to:
- Explain the concept of entropy in your own words.
 - Deduce the sign of ΔS for many chemical reactions by examining the physical states of the reactants and products.
 - State the second law of thermodynamics in words and equations and use it to predict spontaneity.
 - State the third law of thermodynamics.
 - Use tabulated data to calculate the entropy change in a chemical reaction.

Entropy (S)

New State Function (units: J/K)

Entropy is often associated with the randomness of the system. Entropy is a measure of energy dispersal. *entropy increases when energy is dispersed*

$\Delta S > 0$: Increase in disorder of a system.

$\Delta S < 0$: Decrease in disorder of a system.

Clicker Question

Which process below would have a negative ΔS ?

A. The evaporation of a liquid

☒ B. The freezing of a liquid

C. The melting of a solid

D. The sublimation of a solid

Some examples of entropy increase

Entropy Increases:

1. Volume increase.
2. phases changes- $s \rightarrow l \rightarrow g$
3. A solid dissolves
4. # of moles of gas increases.
5. complexity of the molecular structure increases.

Entropy (S)

$$dS = \frac{dq_{rev}}{T}$$

Heat flow and temperature affect entropy.

The “rev” means this relation can only be used for **reversible** processes.

For an isothermal process this becomes

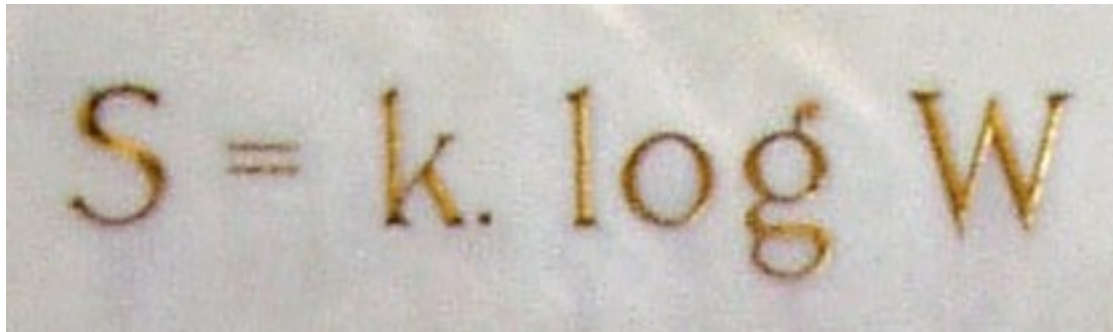
$$\Delta S = \frac{q_{rev}}{T}$$

Probabilistic Interpretation of Entropy

$$S = k \ln W$$

$k = R / N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$ = Boltzmann constant

W = number of equivalent microscopic arrangements of the system



Engraved on Boltzmann's Gravestone!

How many ways are there to arrange the letters in the alphabet?

① In the order of $A \rightarrow Z$? ①

② Without order? Random Arrangement.

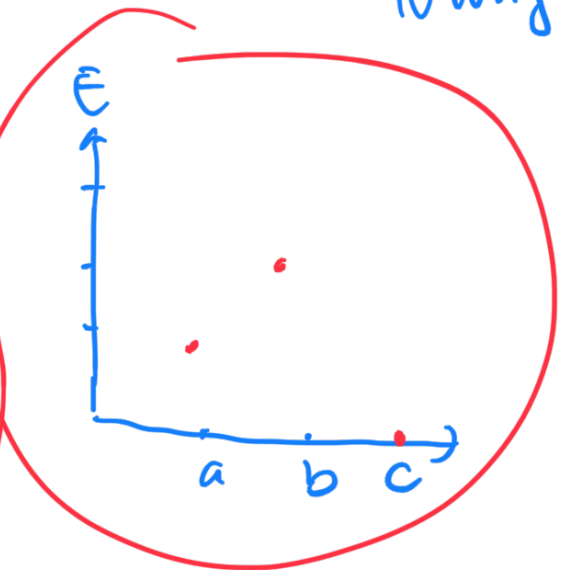
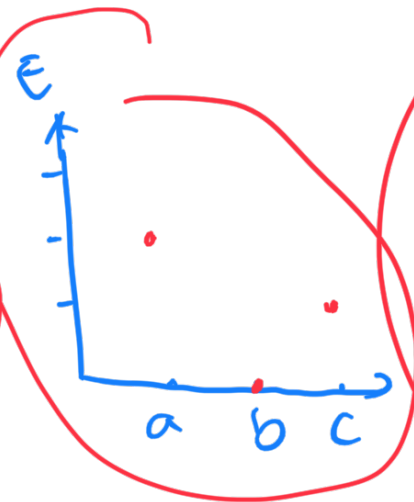
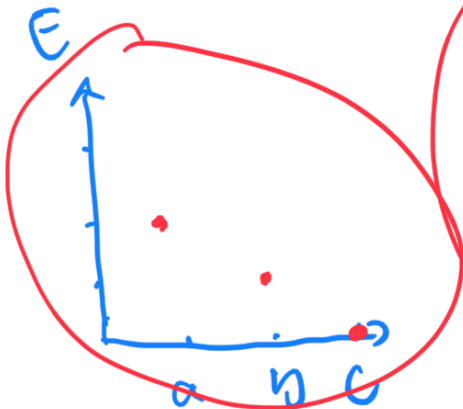
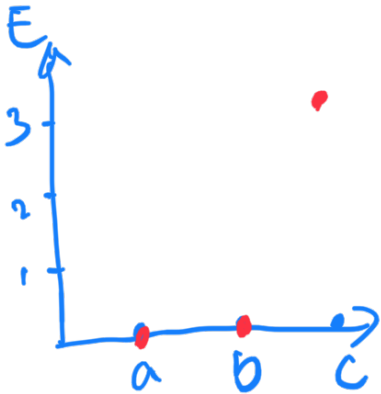
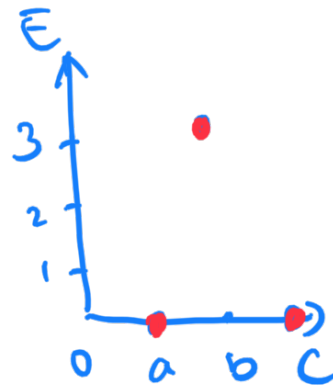
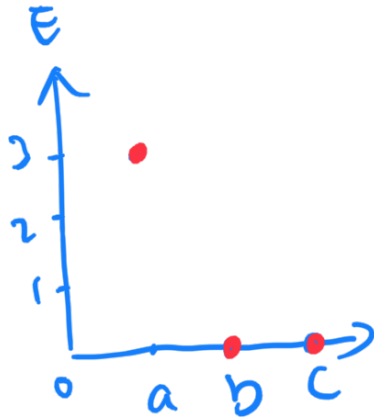
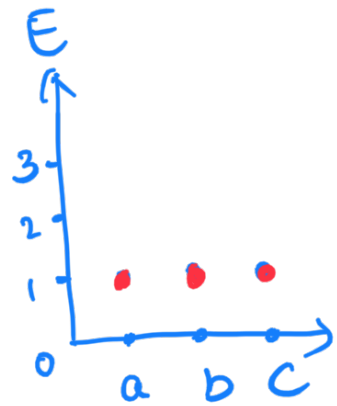
$26!$ ways.

$$26 \times (26-1) \times (26-2) \times (26-3) \dots \dots 3 \times 2 \times 1$$

a b c

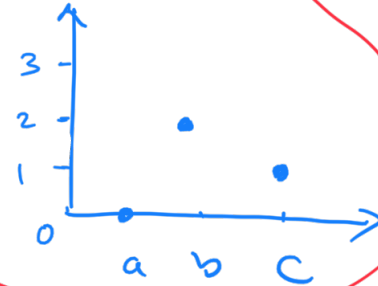
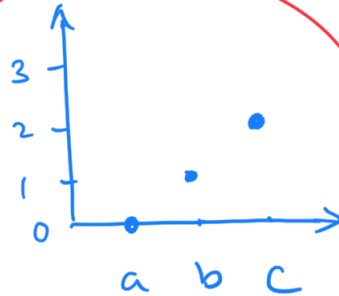
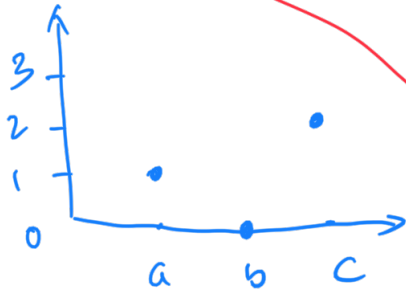
three molecules
with 3 units of
total energy.

How many ways are
there to distribute
the energy?
10 ways.



$(0, 1, 2)$ 6/10

Continued:



Total: 10 ways.

\therefore Probability of finding the system with energy distribution of (0, 1, 2) is $6/10$

Worksheet Question #1

- Find/borrow a coin – any coin!
- Decide which side will be “heads” vs “tails”
- Flip the coin 4 times and keep track of **how many times the flip lands “heads” up.**
- Click in your result:
 - A. 0 times
 - B. 1 time
 - ☒ C. 2 times
 - D. 3 times
 - E. 4 times

$$S = K \ln \frac{W}{4}$$

A. 0 times

(t, t, t, t)

$$W = 1$$

B. 1 time

(h, t, t, t)

(t, h, t, t)

$$W = 4$$

(t, t, h, t)

(t, t, t, h)

C. 2 times.

(t, t, h, h)

(t, h, h, t)

(h, h, t, t)

(h, t, t, h)

(t, h, t, h)

(h, t, h, t)

$$W = 6$$

Worksheet Question #1 (Reprise)

- Find/borrow a coin – any coin!
- Decide which side will be “heads” vs “tails”
- Flip the coin 4 times and keep track of **how many times the flip lands “heads” up.**
- Click in your result:

- | | | |
|----|---------|-------------------|
| A. | 0 times | $W = 1$ (t,t,t,t) |
| B. | 1 time | $W = 4$ |
| C. | 2 times | $W = 6$ |
| D. | 3 times | $W = 4$ |
| E. | 4 times | $W = 1$ (h,h,h,h) |

Worksheet Question #2 – Good Question

If all students in the class flip a coin four times, calculate the entropy associated with the MOST and LEAST likely outcomes. ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$).

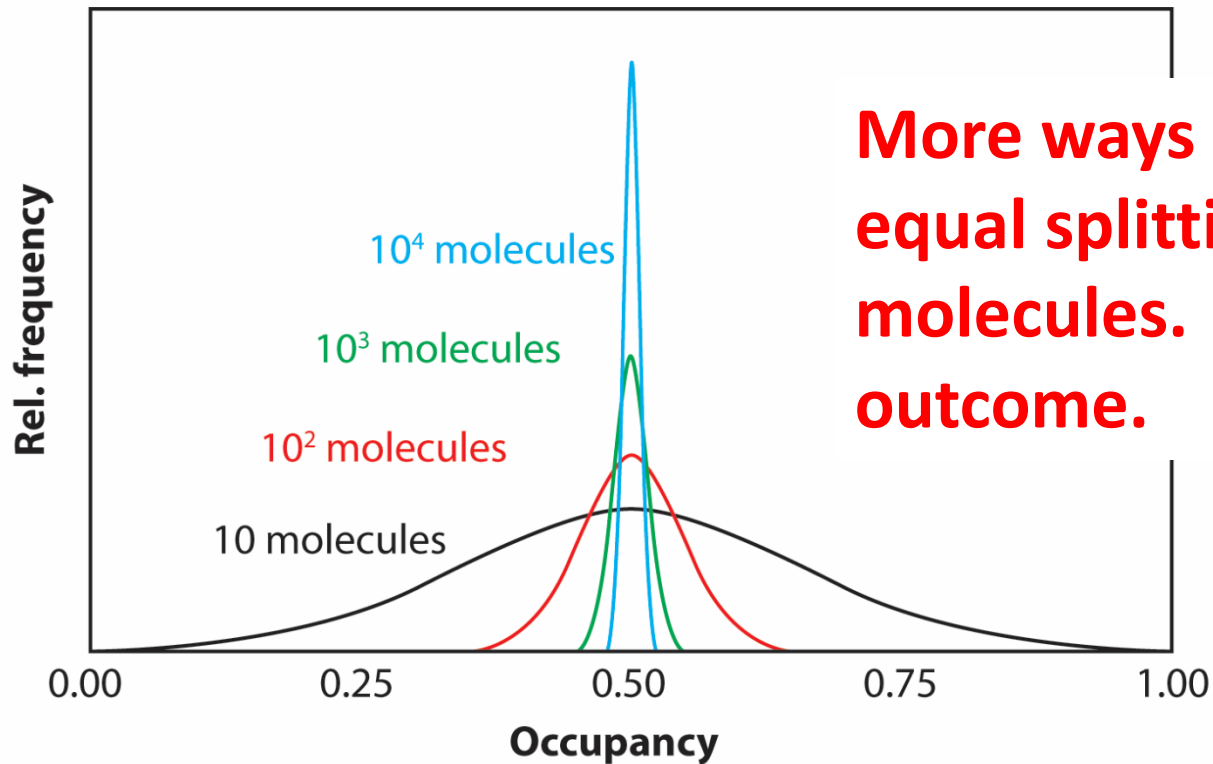
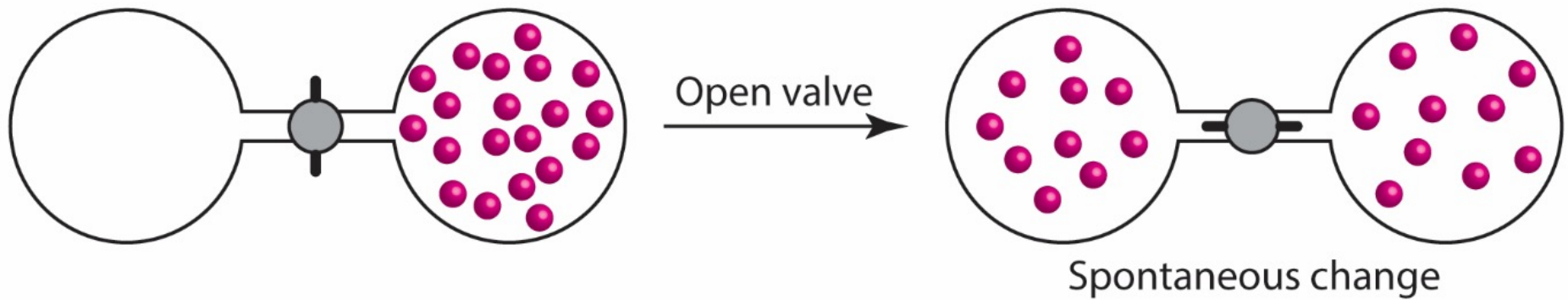
$$S = K \ln W(E)$$



Degeneracy / Number of microstates.

number of ways a system can be arranged
at a fixed E .

Matter Dispersal



More ways to describe the equal splitting with 10^4 molecules. More probable outcome.

Second Law of thermodynamics

Many formulations of the Second Law exist.

The one involving the entropy of the universe (system and surroundings) is

$$\Delta S_{universe} = \Delta S_{surr} + \Delta S \geq 0$$

ΔS can be positive or negative but ΔS_{surr} must compensate so that $\Delta S_{universe}$ is **never** negative.

$\Delta S_{universe} = 0$, only if **all** processes are reversible.

Entropy Video

<https://www.youtube.com/watch?v=uQSoaiubuA0>



DEMO TIME

