



C.A.R.E. PHYS 213 Final Exam Review Session





C.A.R.E. PHYS 213 Quiz 1

Review Session

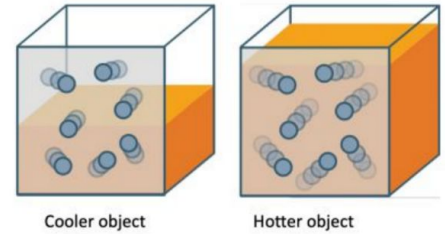


Units for the Exam

- Internal Energy
- Temperature
- Heat Capacity
- Entropy

Internal Energy

- Total energy is **ALWAYS** conserved



- **Positive work on a system increases the system's internal energy**
- **Higher temperature → More Internal Energy**

- First law of thermodynamics:

$$\Delta U = W_{on} + Q$$

Change in
internal
energy

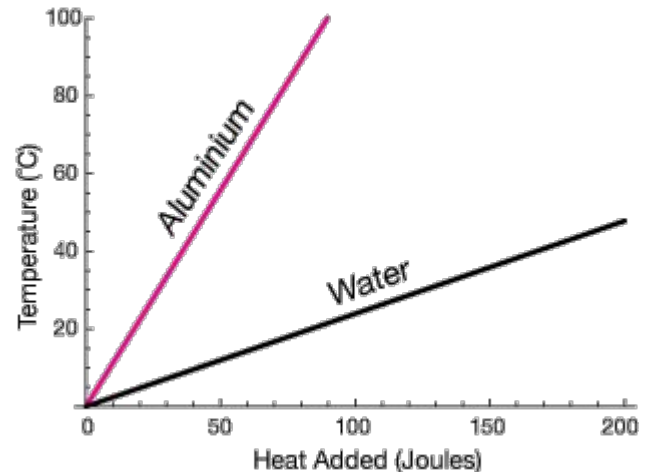
Work done
on the
system

Heat added
to the
system

Temperature & Heat Capacity

- **Heat Capacity (C)** - how much energy it takes to **increase** the temperature of a substance by $1 \text{ K}/^\circ\text{C}$
 - Units of J/K
- **Larger C** → **More energy** is required to **increase the temperature** of the object

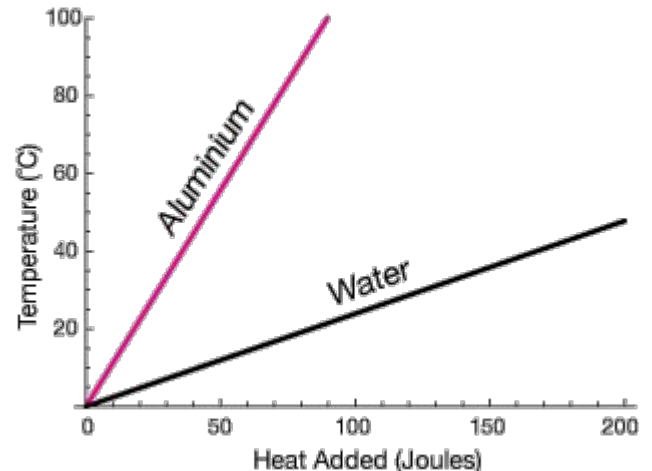
$$C = dQ/dT$$



Temperature & Heat Capacity

- **Heat Capacity (C)** - how much energy it takes to **increase** the temperature of a substance by $1 \text{ K}/^\circ\text{C}$
 - Units of J/K
- **Larger C \rightarrow More energy** is required to **increase the temperature** of the object
- Water has a larger heat capacity than Aluminum

$$C = dQ/dT$$

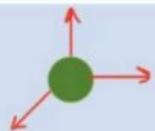


Types of Heat Capacity

- **Molar Heat Capacity [J/mol K]:** The amount of heat required to raise the temperature of **1 mole** of a substance by 1 K/°C
 - $c_M = C/n$, where n is the number of moles
- **Specific Heat Capacity [J/kg K]:** The amount of heat required to raise the temperature of **1 kg** of a substance by 1 K/°C
 - $c = C/m$, where m is the mass [kg]
- **Heat Capacity at a Constant Volume and Constant Pressure:**
 - $C_v = dU/dT$
 - $C_p = dU/dT + p dV/dT$

Equipartition

Monatomic:
DOF = 3

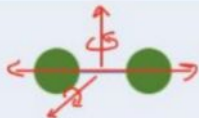


$N_{\text{DOF}} = 3$
x, y, z momentum

$$U = \frac{3}{2} NkT$$

$$C_v = \frac{3}{2} Nk$$

Diatomic:
DOF = 5

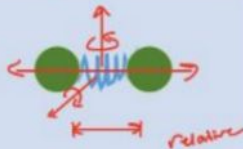


$N_{\text{DOF}} = 5$
x, y, z momentum
2 rotation axes

$$U = \frac{(3+2)}{2} NkT$$

$$C_v = \frac{5}{2} Nk$$

Vibrational:
DOF = 7

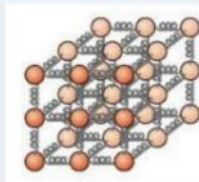


x, y, z momentum
2 rotation axes
vibration mode
(momentum+potential)
 $N_{\text{DOF}} = 7$

$$U = \frac{(3+2+2)}{2} NkT$$

$$C_v = \frac{7}{2} Nk$$

Solid:
DOF = 6



x, y, z momentum
x, y, z spring modes

$$U = \frac{(3+3)}{2} NkT$$

$$C_v = 3Nk$$

Equipartition & Heat Capacity

- Only need to memorize DOFs for monatomic gas, diatomic gas, and solids (3, 5, and 6, respectively)
- For substances under the **equipartition assumption**:

$$U = \frac{N_{\text{DOF}}}{2} NkT \implies C = \frac{dU}{dT} = \frac{N_{\text{DOF}}}{2} Nk$$

$$*Nk = nR$$

$$R = 8.314 \text{ J}/(\text{mol K})$$

$$R = 0.08206 \text{ L atm}/(\text{mol K})$$

Entropy

- Microstate vs Macrostate:
 - Microstate: individual, **specific** arrangement
 - Macrostate: property that arises from the microstates
 - **Many microstates can lead to the same macrostate**
 - Two people have the same weight (macrostate), but the distribution of the weight can be different (microstate)



Entropy (Cont.)

- Entropy (S) is a measure of the degree of 'diversity' associated with a macrostate
 - $S = k \ln(\Omega)$, where Ω is the number of microstates
 - **Second Law of Thermodynamics: $\Delta S \geq 0$**
- Equilibrium
 - Occurs when the macrostate of the system ceases to change
 - The **most probable macrostate** is the one with the **highest entropy (most microstates)**
 - **Equilibrium** is achieved when **S, entropy, is maximized**

Binomial Coefficient

If I have **N coins** and I am looking for the macrostate with **q heads**, the number of microstates:

$$\binom{N}{q} = \frac{N!}{q!(N-q)!}$$

Example: If I have **20 coins**, how many microstates are associated with the macrostate of getting **7 heads**?

Answer:

Binomial Coefficient

If I have **N coins** and I am looking for the macrostate with **q heads**, the number of microstates:

$$\binom{N}{q} = \frac{N!}{q!(N-q)!}$$













Example: If I have **20 coins**, how many microstates are associated with the macrostate of getting **7 heads**?

Answer:

$$\binom{20}{7} = \frac{20!}{7!(20-7)!} = 77520$$













Entropy (Cont.) - Dice Example

- **Microstate:**
- **Macrostate:**
- What is the most likely macrostate?
 -
- What is the macrostate with the highest entropy?
 -
- **Entropy of a macrostate is simply a measure of the number of microstates associated with it**
- **More microstates → Higher Entropy, Higher Probability**

						
	2	3	4	5	6	7
	3	4	5	6	7	8
	4	5	6	7	8	9
	5	6	7	8	9	10
	6	7	8	9	10	11
	7	8	9	10	11	12

Entropy (Cont.) - Dice Example

- **Microstate:** set of individual die values
- **Macrostate:**
- What is the most likely macrostate?
 -
 -
- What is the macrostate with the highest entropy?
 -
- Entropy of a macrostate is simply a measure of the number of microstates associated with it
- More microstates → Higher Entropy, Higher Probability

						
	2	3	4	5	6	7
	3	4	5	6	7	8
	4	5	6	7	8	9
	5	6	7	8	9	10
	6	7	8	9	10	11
	7	8	9	10	11	12

Entropy (Cont.) - Dice Example

- **Microstate:** set of individual die values
- **Macrostate:** sum of die values
- What is the most likely macrostate?













○

○

- What is the macrostate with the highest entropy?

○

- Entropy of a macrostate is simply a measure of the number of microstates associated with it
- More microstates → Higher Entropy, Higher Probability

						
	2	3	4	5	6	7
	3	4	5	6	7	8
	4	5	6	7	8	9
	5	6	7	8	9	10
	6	7	8	9	10	11
	7	8	9	10	11	12

Entropy (Cont.) - Dice Example

- **Microstate:** set of individual die values
- **Macrostate:** sum of die values
- What is the most likely macrostate?
 - 7: has the largest number of microstates associated with it
 - Probability = $6/36 = 0.167$
- What is the macrostate with the highest entropy?
 -
- Entropy of a macrostate is simply a measure of the number of microstates associated with it
- More microstates → Higher Entropy, Higher Probability

	1	2	3	4	5	6
1	2	3	4	5	6	7
2	3	4	5	6	7	8
3	4	5	6	7	8	9
4	5	6	7	8	9	10
5	6	7	8	9	10	11
6	7	8	9	10	11	12

Entropy (Cont.) - Dice Example

- **Microstate:** set of individual die values
- **Macrostate:** sum of die values
- What is the most likely macrostate?
 - 7: has the largest number of microstates associated with it
 - Probability = $6/36 = 0.167$
- What is the macrostate with the highest entropy?
 - Again, 7: has the largest number of microstates associated with it
- **Entropy of a macrostate is simply a measure of the number of microstates associated with it**
- **More microstates → Higher Entropy, Higher Probability**

	1	2	3	4	5	6
1	2	3	4	5	6	7
2	3	4	5	6	7	8
3	4	5	6	7	8	9
4	5	6	7	8	9	10
5	6	7	8	9	10	11
6	7	8	9	10	11	12

Important Equations

Start with the definition
of temperature

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{V,N}$$

multiply by dU

$$\frac{1}{T} dU = dS$$

integrate

$$\Delta S = \int_{U_i}^{U_f} \frac{1}{T} dU$$

plug dU into ΔS

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V(T)}{T} dT$$

Or the definition of
heat capacity

$$C_V = \left(\frac{dQ}{dT} \right)_{V,N}$$

at constant volume
 $dQ = dU$

$$C_V = \left(\frac{dU}{dT} \right)_{V,N}$$

multiply by dT

$$C_V dT = dU$$

multiply by dT

$$C_V dT = dQ$$

integrate

$$\Delta U = \int_{T_i}^{T_f} C_V(T) dT$$

Differential Manipulation

- Know these tricks!

$$C = \frac{\partial U}{\partial T} \implies \Delta U = \int_{T_i}^{T_f} C dT$$

- Heat Capacity is the link between dU and dT

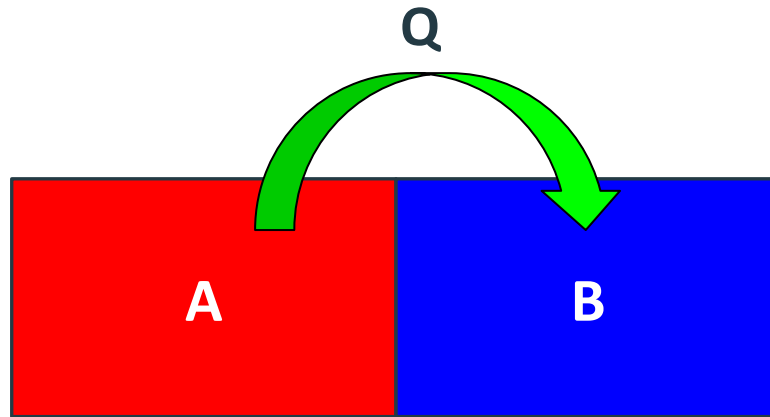
$$\frac{\partial S}{\partial U} = \frac{1}{T} \implies \Delta S = \int \frac{dU}{T} = \int_{T_i}^{T_f} \frac{C dT}{T}$$

- **If you know the heat capacity and the temperature change, you can find the change in internal energy and the change in entropy**

Entropy of Two Blocks in Thermal Contact - Example

Two blocks A and B, are in thermal contact and insulated from surroundings. Initially, block A is at a higher temperature than block B. **Each block has a temperature-dependent heat capacity given by $C = pT^2$.**

Determine the entropy change for each block



Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

$$C = \frac{dQ}{dT}$$

Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

$$C = \frac{dQ}{dT}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C dT}{T}$$

Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

$$C = \frac{dQ}{dT}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{pT^2}{T} dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C dT}{T}$$

Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

$$C = \frac{dQ}{dT}$$

$$\begin{aligned}\Delta S &= \int_{T_i}^{T_f} \frac{pT^2}{T} dT \\ &= \int_{T_i}^{T_f} pT dT\end{aligned}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C dT}{T}$$

Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

$$C = \frac{dQ}{dT}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C dT}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{pT^2}{T} dT$$

$$= \int_{T_i}^{T_f} pT dT$$

$$= p \frac{T_f^2}{2} - p \frac{T_i^2}{2} = \frac{p}{2} [T_f^2 - T_i^2]$$

Entropy of Two Blocks in Thermal Contact - Example (Cont.)

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

$$C = \frac{dQ}{dT}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C dT}{T}$$

$$\begin{aligned} \Delta S &= \int_{T_i}^{T_f} \frac{pT^2}{T} dT \\ &= \int_{T_i}^{T_f} pT dT \end{aligned}$$

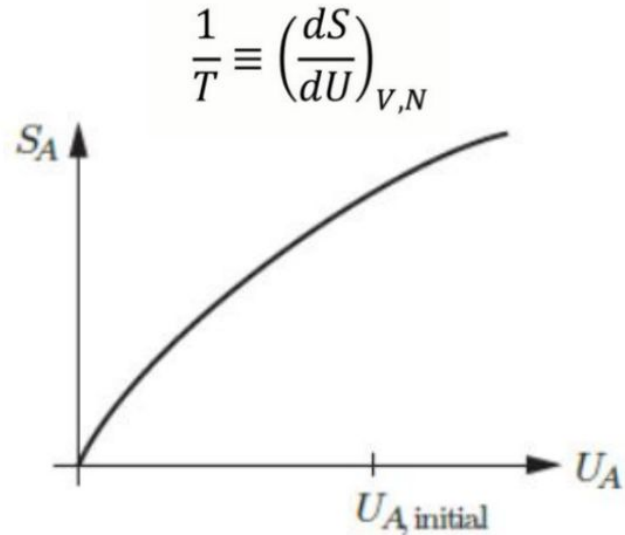
$$= p \frac{T_f^2}{2} - p \frac{T_i^2}{2} = \frac{p}{2} [T_f^2 - T_i^2]$$

$$\Delta S_A = \frac{p}{2} [T_{A,f}^2 - T_{A,i}^2]$$

$$\Delta S_B = \frac{p}{2} [T_{B,f}^2 - T_{B,i}^2]$$

Entropy (S) vs. Internal Energy (U)

- Since slope is always positive, temperature is always positive
- **More energy = greater entropy**
- **Diminishing returns:** it gets harder and harder to increase the entropy as internal energy increases
- **Decreasing slope = increasing temperature**
 - **More energy means greater temperature**



Units for the Exam

- Kinetic Theory of Ideal Gases
- Quasistatic Processes
- Thermodynamic Cycles
- Gibbs Free Energy

Ideal gas and Equipartition

- Ideal Gas: Approximation of particles as points with no interactions:

- Follows **ideal gas law**: $pV = NkT = nRT$

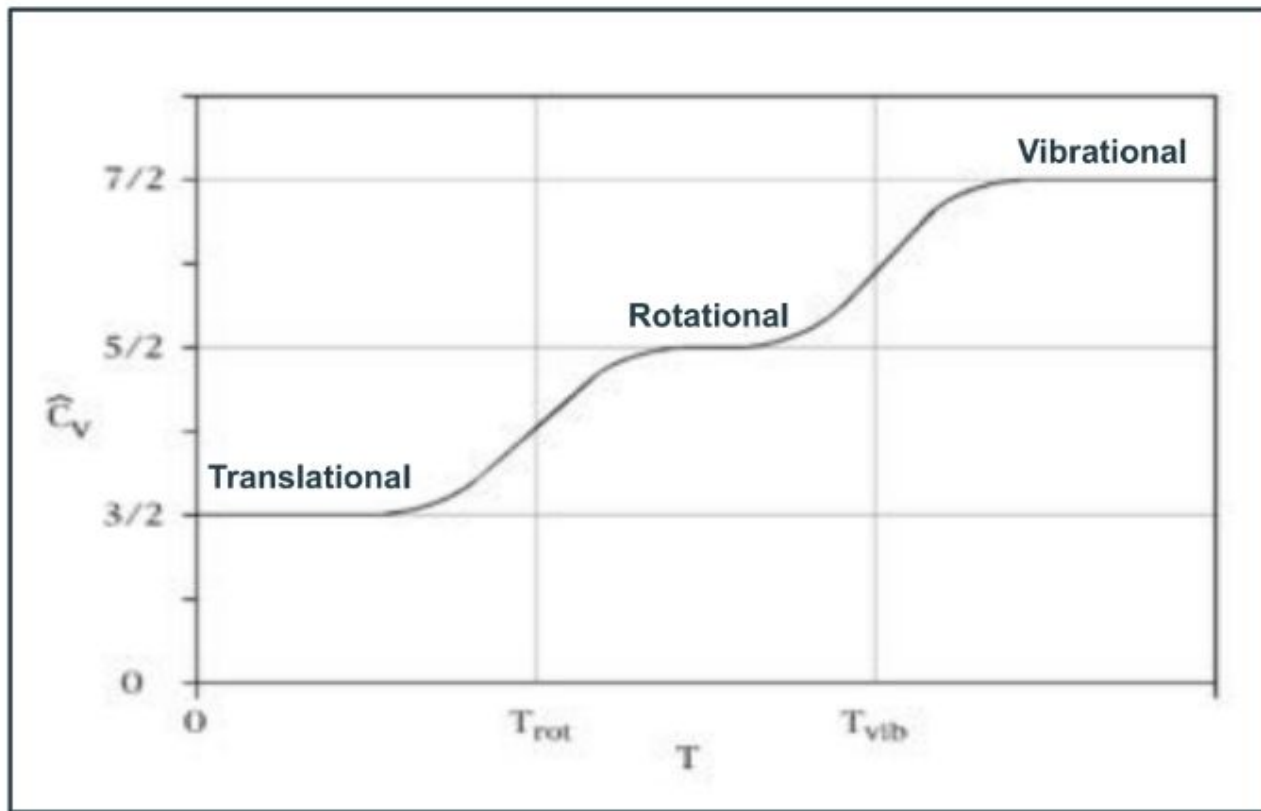
- **Equipartition**: each degree of freedom contributes $\frac{1}{2} kT$ of energy

- Internal energy in each particle:

- $U = (N_{DOF}/2)kT$

- Molar heat capacity:

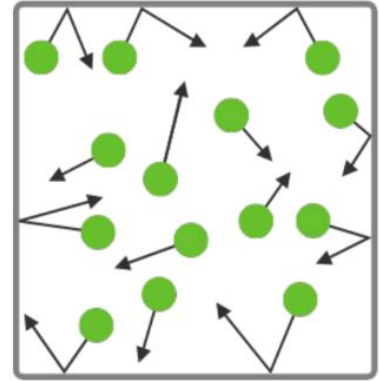
- $c_M = (N_{DOF}/2)kN_A$



Root-Mean-Square Velocity

- v_{rms} : Average (**translational**) velocity of gas particles
- Translational Kinetic Energy: $KE_{translational} = 1/2 m (v_{rms})^2$
- Relationship to temperature:

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT$$



- This only applies to **ONE PARTICLE**
- **Notice:** this does **NOT** depend on the number of DOFs; it's **ALWAYS** $(3/2)kT$
 - Why? Translational KE only depends on the translational modes motion (there are only 3 translational modes: v_x, v_y, v_z)

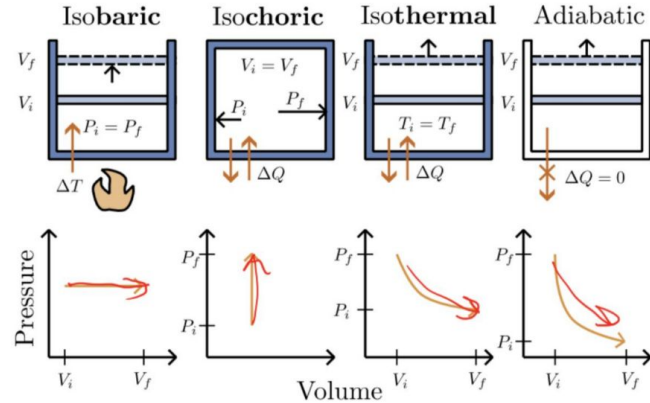
Thermodynamic Processes

- Isochoric or Isovolumetric
 - Constant VOLUME

- Isobaric
 - Constant PRESSURE

- Isothermal
 - Constant TEMPERATURE, REVERSIBLE

- Adiabatic
 - Constant HEAT ($dQ = 0$), REVERSIBLE



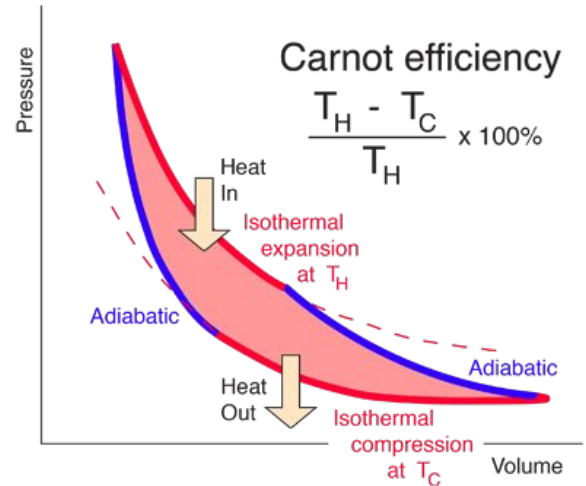
$$(\Delta S_{total} = 0, \Delta U = 0)$$

$$(\Delta S_{total} = 0, \Delta Q = 0)$$

Reversible Processes

- Isothermal + Adiabatic processes are REVERSIBLE

- $\Delta S_{total} = 0$ (no change in entropy)
- For isothermal processes:
 - $PV = \text{constant}$
- For adiabatic processes:
 - $PV^\gamma = \text{constant}$
 - $\gamma = (2/N_{DOF}) + 1$ (given on equation sheet)



Example Problem - Adiabatic Process

- Assume we have a gas undergoing an adiabatic process, determine the work done given the following parameters:
 - $V_i = 10 \text{ m}^3$, $p_i = 10 \text{ kPa}$
 - $V_f = 4 \text{ m}^3$, $N_{\text{DOF}} = 3$

1. Calculate γ

2. Find pV^γ

3. Calculate W

4. Calculate W

Example Problem - Adiabatic Process

- Assume we have a gas undergoing an adiabatic process, determine the work done given the following parameters:
 - $V_i = 10 \text{ m}^3$, $p_i = 10 \text{ kPa}$
 - $V_f = 4 \text{ m}^3$, $N_{\text{DOF}} = 3$

$$\gamma = \frac{2}{N_{\text{DOF}}} + 1 = \frac{2}{3} + 1 = \frac{5}{3}$$

2. Find pV^γ

3. Calculate W

4. Calculate W

Example Problem - Adiabatic Process

- Assume we have a gas undergoing an adiabatic process, determine the work done given the following parameters:

- $V_i = 10 \text{ m}^3$, $p_i = 10 \text{ kPa}$
- $V_f = 4 \text{ m}^3$, $N_{\text{DOF}} = 3$

$$\gamma = \frac{2}{N_{\text{DOF}}} + 1 = \frac{2}{3} + 1 = \frac{5}{3}$$

$$pV^\gamma = \text{Constant} = p_i V_i^\gamma = (1000)(10)^{\frac{5}{3}} = 464158.88$$

3. Calculate W

4. Calculate W

Example Problem - Adiabatic Process

- Assume we have a gas undergoing an adiabatic process, determine the work done given the following parameters:

- $V_i = 10 \text{ m}^3$, $p_i = 10 \text{ kPa}$
- $V_f = 4 \text{ m}^3$, $N_{\text{DOF}} = 3$

$$\gamma = \frac{2}{N_{\text{DOF}}} + 1 = \frac{2}{3} + 1 = \frac{5}{3}$$

$$pV^\gamma = \text{Constant} = p_i V_i^\gamma = (1000)(10)^{\frac{5}{3}} = 464158.88$$

$$W = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{C}{V_i^\gamma} dV = \left[C \frac{V_f^{(-\frac{5}{3}+1)}}{-\frac{5}{3}+1} \right] - \left[C \frac{V_i^{(-\frac{5}{3}+1)}}{-\frac{5}{3}+1} \right]$$

4. Calculate W

Example Problem - Adiabatic Process

- Assume we have a gas undergoing an adiabatic process, determine the work done given the following parameters:

- $V_i = 10 \text{ m}^3$, $p_i = 10 \text{ kPa}$
- $V_f = 4 \text{ m}^3$, $N_{\text{DOF}} = 3$

$$\gamma = \frac{2}{N_{\text{DOF}}} + 1 = \frac{2}{3} + 1 = \frac{5}{3}$$

$$pV^\gamma = \text{Constant} = p_i V_i^\gamma = (1000)(10)^{\frac{5}{3}} = 464158.88$$

$$W = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{C}{V_i^\gamma} dV = \left[C \frac{V_f^{(-\frac{5}{3}+1)}}{-\frac{5}{3}+1} \right] - \left[C \frac{V_i^{(-\frac{5}{3}+1)}}{-\frac{5}{3}+1} \right]$$

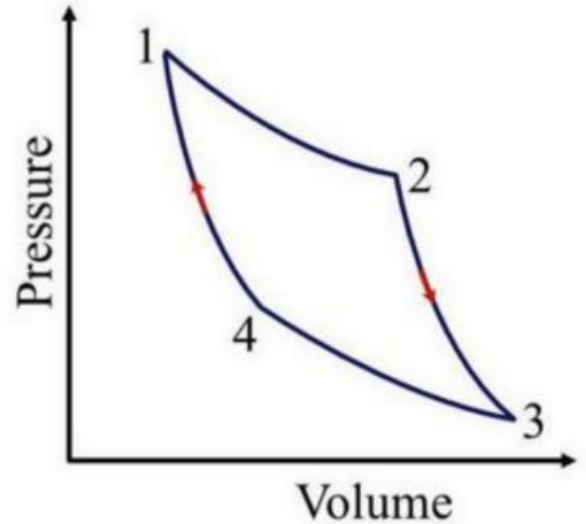
$$W = \left[(464158.88) \frac{4^{(-\frac{5}{3}+1)}}{-\frac{5}{3}+1} \right] - \left[(464158.88) \frac{10^{(-\frac{5}{3}+1)}}{-\frac{5}{3}+1} \right] \approx -126.30 \text{ kJ}$$

$$W \approx -126.30 \text{ kJ}$$

p-V Diagrams

- Used to visualize thermodynamic cycles
- Area enclosed in the curve is equal to the work per cycle
 - **Clockwise direction: work is positive** (engine did work)
 - **Counterclockwise direction: work is negative** (work done on engine)

$$W_{\text{by}} = \int_{V_i}^{V_f} p \, dV$$



Heat Engines

- Cycles of Thermodynamic processes are used to make **engines**, **heat pumps**, and **refrigerators**

- **Efficiency of engines:**

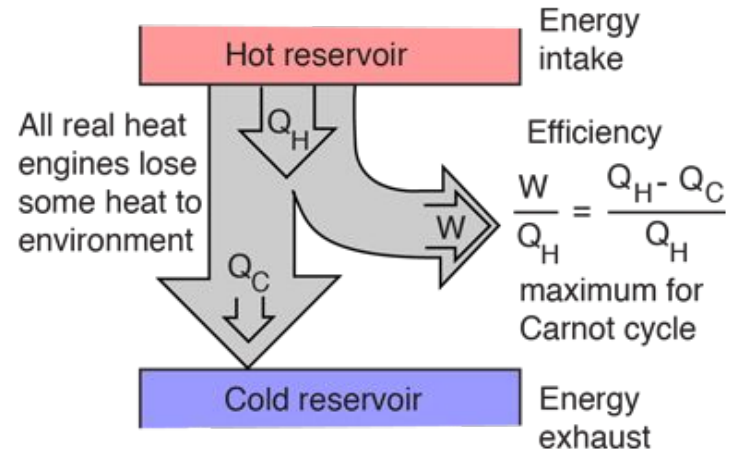
$$\varepsilon = \frac{W_{by}}{Q_H} \leq 1 - \frac{T_C}{T_H}$$

- **COP of pumps and refrigerators:**

- **Heat pump:** $\text{COP} = \frac{Q_H}{W_{on}} \leq \frac{1}{1 - \frac{T_C}{T_H}}$

- **Refrigerator:** $\text{COP} = \frac{Q_C}{W_{on}} \leq \frac{1}{\frac{T_H}{T_C} - 1}$

Efficiency/COP can be thought of as
“what you get out” divided by
“what you put in.”



Example Problem: Engine/Heat Pump COP

Given a hot reservoir at a temperature of $T_h = 373K$
and a cold reservoir at a temperature of $T_c = 293K$,
calculate the maximum efficiency ϵ of an engine
and the maximum COP of a heat pump between the
two reservoirs.

Heat Engine Efficiency:

Heat Pump COP:

Example Problem: Engine/Heat Pump COP

Given a hot reservoir at a temperature of $T_h = 373K$
and a cold reservoir at a temperature of $T_c = 293K$,
calculate the maximum efficiency ϵ of an engine
and the maximum COP of a heat pump between the
two reservoirs.

Heat Engine Efficiency:

$$\epsilon = 1 - \frac{T_c}{T_h} \approx 0.21$$

Heat Pump COP:

Example Problem: Engine/Heat Pump COP

Given a hot reservoir at a temperature of $T_h = 373K$
and a cold reservoir at a temperature of $T_c = 293K$,
calculate the maximum efficiency ϵ of an engine
and the maximum COP of a heat pump between the
two reservoirs.

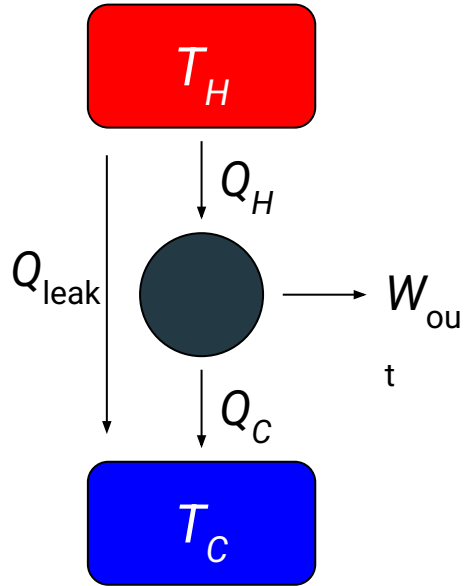
Heat Engine Efficiency:

$$\epsilon = 1 - \frac{T_c}{T_h} \approx 0.21$$

Heat Pump COP:

$$COP = \frac{1}{1 - T_c/T_h} \approx 4.7$$

Engine, Pump, and Refrigerator Diagrams



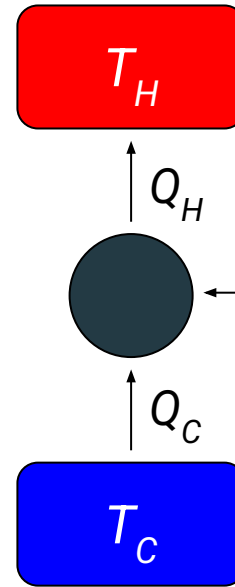
Heat Engine Diagram

In a leaky engine, the heat we put in is $Q_H + Q_{leak}$, which affects the efficiency.

$$Q_H = W_{out} + Q_C$$

$$\epsilon = W_{out} / (Q_H + Q_{leak})$$

$$\epsilon_C = 1 - (T_C / T_H)$$



Heat Pump/Refrigerator Diagram

A heat pump or fridge is just a heat engine run in reverse.

$$Q_H = W_{in} + Q_C$$

Gibbs Free Energy

- Useful when temperature and pressure are fixed

$$G = U - T_{env}S + pV$$

- **Minimizing Gibbs of a system will maximize total (system + environment) Entropy**
 - As a system approaches equilibrium, free energy will decrease to a minimum
- **Fundamental Thermodynamic Relation in Equilibrium:**
 - $TdS = dU + pdV - \mu dN$
 - $\mu = (dG/dN) \rightarrow \mu N = G$ (at fixed temperature and pressure)
 - Equilibrium favors lowest μ



C.A.R.E. PHYS 213 Final Exam Review Session



CARE / CARE PHYS 213 Exam Review Session

No location specified

Enable notifications

Open Queue

Delete All Questions

Show staff message

This affects anyone using this queue



On-Duty Staff

No on-duty staff

Join

Queue

Welcome

Tutorials

Tuesday

Workshop

Slides

Solutions

Also, here

install

Jupyter

Good luck



session!

during these times:

in the test. If you do not have a Jupyter Notebook environment, try this suggestion for this coding example!

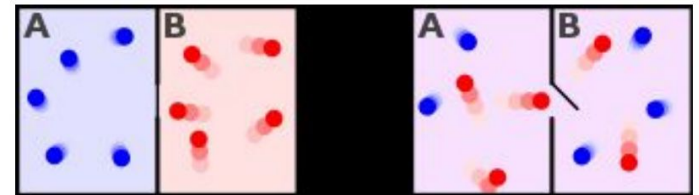
This queue is closed. Check back later!

New Units for the Exam

- Chemical Potential and Phase Diagrams
- Ideal Solutions
- Boltzmann Factors
- Semiconductors

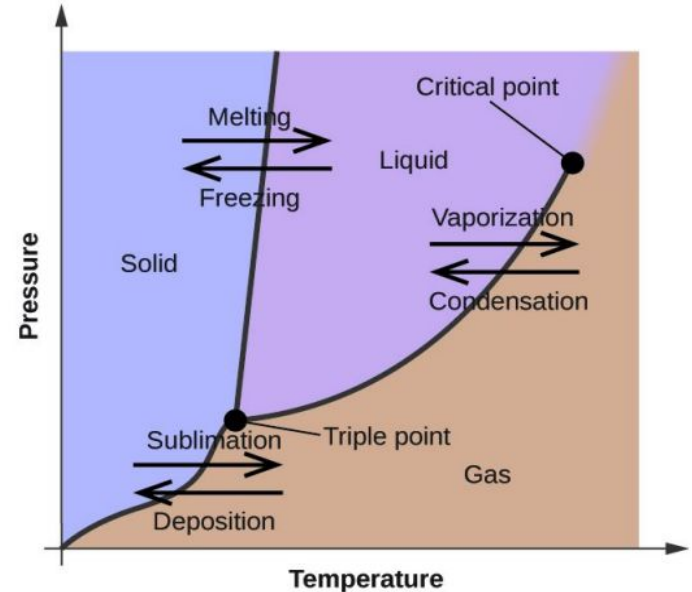
Chemical Potential

- Chemical Potential μ describes which way particles in a system will go:
 - Temperature is to heat as chemical potential is to number of particles
 - Particles go from **high μ to low μ**
 - When μ 's are equal, the system is in **equilibrium**
- $\mu = (dG/dN) \rightarrow \mu N = G$ (at fixed temperature and pressure)
- **Equilibrium favors lowest μ**
 - Important concept with phase diagrams



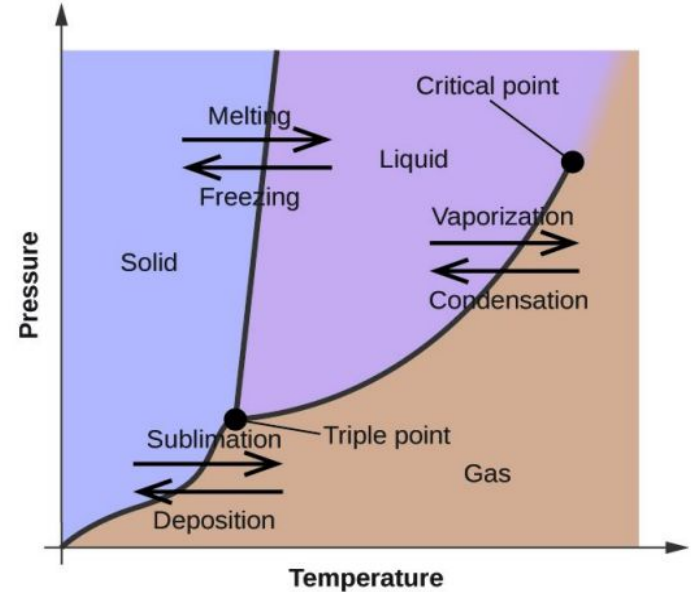
Phases

- Phases coexist at equal chemical potentials
- Higher pressure phase → Higher density
- Higher temperature phase → Higher entropy
- Using the phase diagram:
 - Rank the phases from **highest to lowest density**
 -
 - Rank the phases from **highest to lowest entropy**
 -



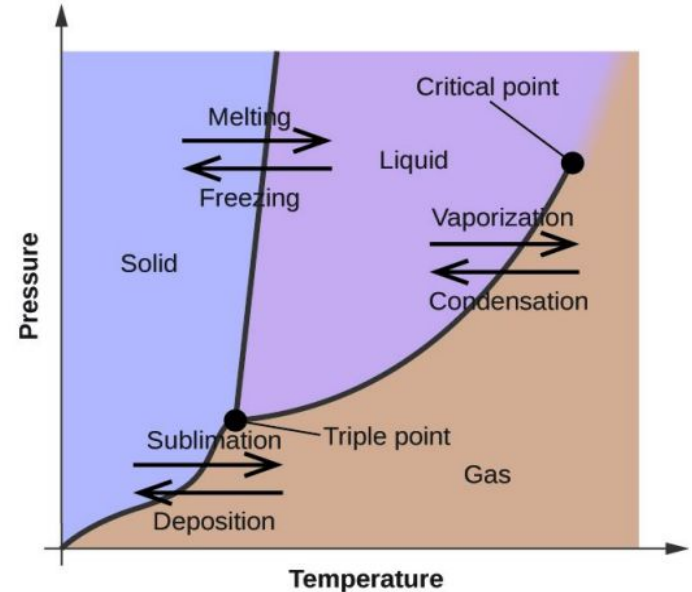
Phases

- Phases coexist at equal chemical potentials
- Higher pressure phase → Higher density
- Higher temperature phase → Higher entropy
- Using the phase diagram:
 - Rank the phases from **highest to lowest density**
 - Solid → Liquid → Gas
 - Rank the phases from **highest to lowest entropy**
 -



Phases

- Phases coexist at equal chemical potentials
- Higher pressure phase → Higher density
- Higher temperature phase → Higher entropy
- Using the phase diagram:
 - Rank the phases from **highest to lowest density**
 - Solid → Liquid → Gas
 - Rank the phases from **highest to lowest entropy**
 - Gas → Liquid → Solid

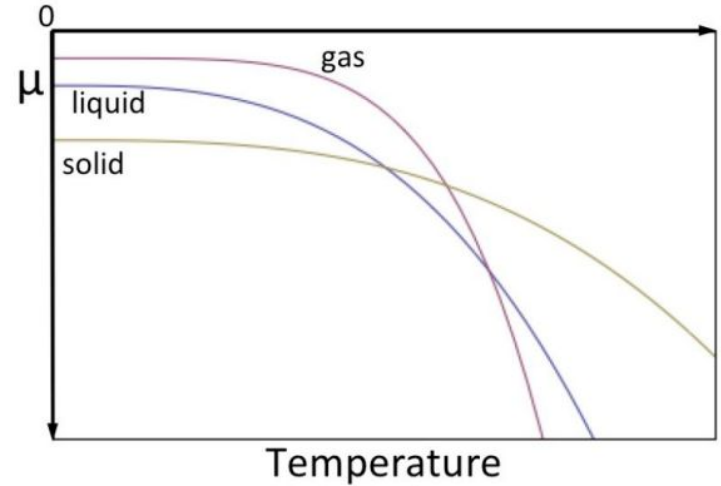


Phases (Cont.) - Latent Heat

- **Latent Heat:** the amount of heat required to perform a phase change
 - Heat of vaporization: boiling/condensing
 - Heat of fusion: melting/freezing
- **Relation to Entropy:** $L = T\Delta S$
- **Relation to Enthalpy:** $L = \Delta H$, where $H = U + pV$
 - **At constant pressure:** $L = \Delta U + p\Delta V$
- **WATCH YOUR UNITS!**
 - L is often given in **units** of **J/kg** or **J/g**
 - Sometimes you will have to find the **change in entropy per particle**, not per kg
 - Use **molar mass** and/or **Avogadro's Number** to perform unit conversions

Phases (Cont.) - μ vs. T Diagrams

- The substance exists in the phase with the **lowest chemical potential** at a particular temperature
- Adding solute lowers the chemical potential curve of the liquid phase which:
 - **Lowers the melting point**
 - **Raises the boiling point**
- **Applications to real life:**
 - Salting in icy road lowers the freezing point, causing the ice to melt
 - Adding salt to boiling water will cause the water to boil at a higher temperature (cooking your food faster)



Boltzmann Factors - Equations

- Formula: $f_i = e^{\frac{-E_i}{kT}}$
- Represents a likelihood of being in a particular microstate with energy E
 - Lower energy states will ALWAYS have a greater likelihood
- **Normalization** with the partition function (Z) gives us **probability**:

$$Z = \sum_i f_i$$

- Probability of state i : $P(E_i) = \frac{e^{\frac{-E_i}{kT}}}{Z}$

Boltzmann Factors - Equations (Cont.)

- To determine the ratio of probabilities:

$$\frac{P(E_1)}{P(E_2)} = \frac{e^{-E_1/kT}}{e^{-E_2/kT}} = e^{-(E_1-E_2)/kT}$$

*Notice how the partition function (Z) is not needed

Useful when not all f_i 's are known

- To determine the average energy of the system:

$$E_{\text{avg}} = \sum_i E_i P(E_i)$$

Boltzmann Factors - Concepts

- When temperature is very low (close to 0K), ALL of the Boltzmann factors become very small
 - The ground state becomes the most likely, with a probability approaching 1

- When temperature is very large, all of the Boltzmann factors approach 1
 - All microstates become EQUALLY LIKELY (same probability)

$$T \rightarrow 0 \implies e^{-E_i/kT} \rightarrow 0$$
$$P(\text{ground state}) \approx 1, P(\text{excited}) \approx 0$$

$$T \rightarrow \infty \implies e^{-E_i/kT} \rightarrow 1$$

Likelihood of each state ≈ 1

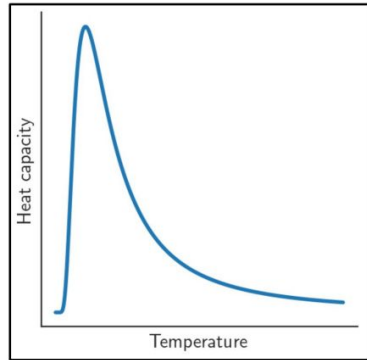
*Remember: Entropy from microstates

$$S = k \ln(\Omega)$$

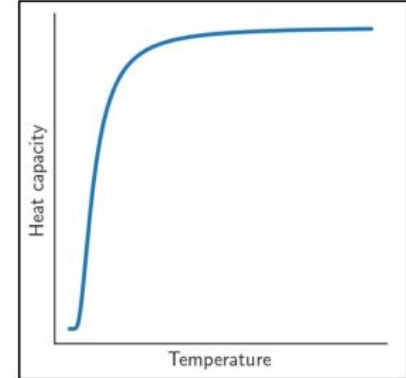
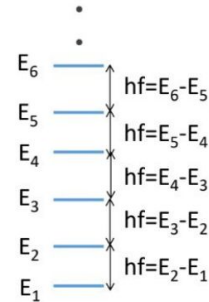
Boltzmann Factors - Quantum Systems

- Looking at two specific quantum systems and their heat capacity:

Two-State System:



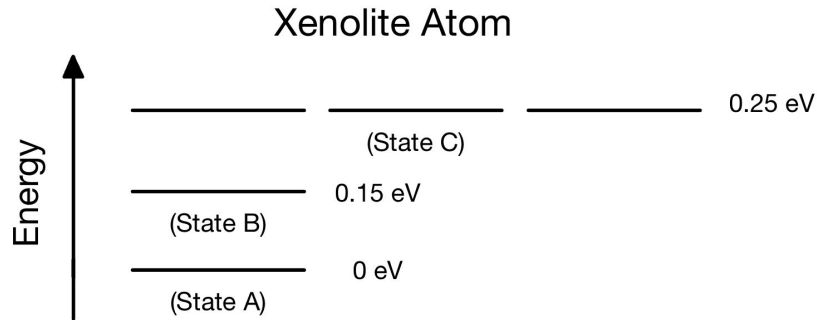
Harmonic Oscillators:



Boltzmann Factors - Example Problem

A fictional atom 'Xenolite' can occupy three different quantum states:

- The ground state (**State A**), energy = 0 eV
 - An excited state (**State B**), energy = 0.15 eV
 - And a second excited state with 3 levels (**State C**), energy = 0.25 eV
- **At 1200 K, what is the probability that the atom is in State C? (use k in eV)**



Boltzmann Factors - Example Problem (Cont.)

1. Equation for Probability

2. Boltzmann Factor of f_A

3. Boltzmann Factor of f_B

4. Boltzmann Factor of f_C

5. Calculate Z

6. Calculate $P(E_C)$ using step 1

Boltzmann Factors - Example Problem (Cont.)

$$P(E_C) = \frac{f_C}{Z} = \frac{f_C}{f_A + f_B + f_C}$$

2. Boltzmann Factor of f_A

3. Boltzmann Factor of f_B

4. Boltzmann Factor of f_C

5. Calculate Z

6. Calculate $P(E_C)$ using step 1

Boltzmann Factors - Example Problem (Cont.)

$$P(E_C) = \frac{f_C}{Z} = \frac{f_C}{f_A + f_B + f_C}$$

$$f_A = e^{\frac{-E_A}{kT}} = e^{\frac{-0}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 1$$

3. Boltzmann Factor of f_B

4. Boltzmann Factor of f_C

5. Calculate Z

6. Calculate $P(E_C)$ using step 1

Boltzmann Factors - Example Problem (Cont.)

$$P(E_C) = \frac{f_C}{Z} = \frac{f_C}{f_A + f_B + f_C}$$

$$f_A = e^{\frac{-E_A}{kT}} = e^{\frac{-0}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 1$$

$$f_B = e^{\frac{-E_B}{kT}} = e^{\frac{-0.15}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 0.234$$

4. Boltzmann Factor of f_C

5. Calculate Z

6. Calculate $P(E_C)$ using step 1

Boltzmann Factors - Example Problem (Cont.)

$$P(E_C) = \frac{f_C}{Z} = \frac{f_C}{f_A + f_B + f_C}$$

$$f_A = e^{\frac{-E_A}{kT}} = e^{\frac{-0}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 1$$

$$f_B = e^{\frac{-E_B}{kT}} = e^{\frac{-0.15}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 0.234$$

$$f_C = 3 * e^{\frac{-E_C}{kT}} = 3 * e^{\frac{-0.25}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 0.267$$

5. Calculate Z

6. Calculate $P(E_C)$ using step 1

Boltzmann Factors - Example Problem (Cont.)

$$P(E_C) = \frac{f_C}{Z} = \frac{f_C}{f_A + f_B + f_C}$$

$$f_A = e^{\frac{-E_A}{kT}} = e^{\frac{-0}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 1$$

$$f_B = e^{\frac{-E_B}{kT}} = e^{\frac{-0.15}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 0.234$$

$$f_C = 3 * e^{\frac{-E_C}{kT}} = 3 * e^{\frac{-0.25}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 0.267$$

$$Z = f_A + f_B + f_C = 1 + 0.234 + 0.267 = 1.502$$

6. Calculate $P(E_C)$ using step 1

Boltzmann Factors - Example Problem (Cont.)

$$P(E_C) = \frac{f_C}{Z} = \frac{f_C}{f_A + f_B + f_C}$$

$$f_A = e^{\frac{-E_A}{kT}} = e^{\frac{-0}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 1$$

$$f_B = e^{\frac{-E_B}{kT}} = e^{\frac{-0.15}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 0.234$$

$$f_C = 3 * e^{\frac{-E_C}{kT}} = 3 * e^{\frac{-0.25}{(8.617 \cdot 10^{-5}) \cdot 1200}} = 0.267$$

$$Z = f_A + f_B + f_C = 1 + 0.234 + 0.267 = 1.502$$

$$P(E_C) = \frac{0.267}{1.502} = 0.178$$

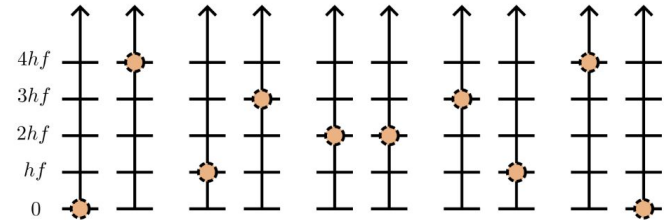
Quantum Harmonic Oscillators (QHO)

- A Quantum Harmonic Oscillator has **discrete energy levels**
 - A collection of these oscillators have a **finite amount of energy (quanta)**

For N oscillators with q quanta

$$\Omega = \binom{N - 1 + q}{q}$$

- For a single oscillator in an array:
 - Thermodynamically favorable to be in a **lower energy state**
 - Leads to **greater number of microstates** for the other QHOs and thus **greater entropy**



Semiconductors

- Resistivity (ρ) is directly proportional to Resistance

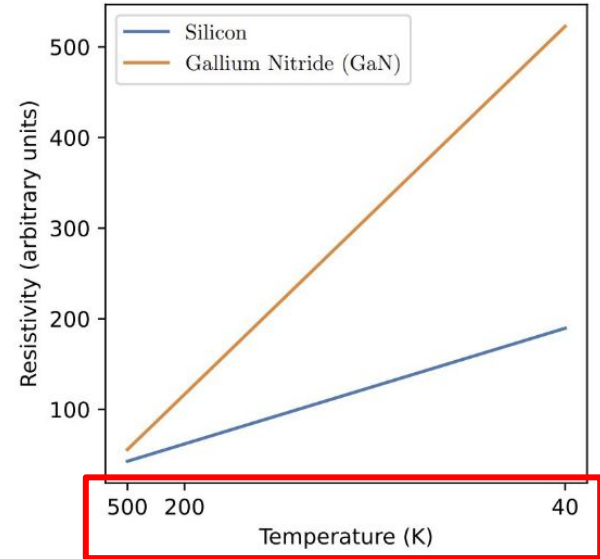
$$\rho = Ce^{\frac{\Delta}{2kT}}$$

- Conductivity (σ):

$$\sigma = \frac{1}{\rho} = Ce^{\frac{-\Delta}{2kT}}$$

- Denominator is $2kT$ NOT kT
- Conductivity given on formula sheet

Arrhenius Plot



$$\ln \rho = \ln C + \frac{\Delta}{2kT}$$

Larger Slope = Larger Energy Gap (Δ)

Good luck!

Feel free to ask any questions you may have.

You got this!

