Two fundamental thermodynamic driving forces: **minimize energy (enthalpy)** and **maximize multiplicity (entropy).** 1st **Law of Thermodynamics (Conservation of Energy)**: Energy can neither be created nor destroyed during a process; it can only change forms. 2nd **Law of Thermodynamics (Increase in Entropy)**: Isolated systems tend towards their states of maximum entropy. Change in 'free energy' **$\Delta G=\Delta H-T\Delta S$**. The enthalpic term ΔH changes in bonding, i.e., interaction energy, between molecules (Van der Waals forces, hydrogen bonding, electric charge interactions), and physical work done by the system/on the system. The entropic term: $T\Delta S$ (or just ΔS) changes in the arrangement of the molecules of the system, reflects the degrees of freedom ('multiplicity'), rotational and translational changes, and increases linearly with absolute temp, T. **Thermodynamic system**: a collection of matter in any form, delineated from its surroundings by real or imaginary boundaries. Systems can contain subsystems. Boundaries can be fixed or movable. **Open system $\Delta U= Q+W+\Delta E_{mass}$**: a system that can exchange energy, volume, and matter with its surroundings. For the change of energy in an open system, we must also consider the energy contained in the matter entering and exiting the system. ΔE_{mass} is energy carried with the net mass flow into the system. **Closed system $\Delta U=Q+W$**: a system that can exchange energy, but not matter, with its surroundings. Positive for work on the heat going into the system and negative for leaving the system. The change in the internal energy of a closed system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings. **Isolated system $\Delta E=\Delta U=0$**: neither energy nor matter can be exchanged with its surroundings; volume cannot change; boundaries do not move. For an isolated system, the total energy is constant. $\Delta U=0$ because no change in internal energy. **Thermal Energy $E_{thermal}=mcT$.** **Semipermeable membrane**: a boundary that restricts the exchange of some types of particles, but not others. **Adiabatic boundary**: a boundary that does not allow heat to flow between the system and its surroundings. **Phase**: a homogeneous part of a system that can be mechanically separated from the rest of the system. Homogeneous means that the pressure, temperature, and concentration are uniform, or continuous, functions of position within a phase. **Simple system**: a system consisting of a homogeneous, single-phase, uncharged, with no electric, magnetic, gravitational, or surface effects. **System/state properties**: the state of a system is defined by its properties. **Properties include pressure, volume, temperature, mass, internal energy, enthalpy, entropy, number of particles, density, etc.** Note that not all properties are independent! Thermodynamic equations/equations of state describe relationships, e.g., **$S = S(U, V, N)$ or $U = U(S, V, N)$**. Changing any one of the properties results in a different state! **Extensive properties**: property scales with system size (mass, number of particles, volume, internal energy (entropy S, enthalpy H)). **Intensive properties**: independent of the size of the system (temperature, pressure, density, concentration). For simple systems, the state of the system is fully defined by two independent intensive properties. **Heat transfer**: Energy transfer resulting from a temperature difference between the system and its surrounding. Heat transfer into a system increases its internal energy (e.g., the movement of the molecules inside the system). **Work transfer**: An energy transfer that is not caused by a temperature difference between a system and its surroundings. This can include mechanical work (i.e., force acting on a distance) as well as other work (e.g., electrical work, magnetic work). **Mass flow**: When mass enters a system, the energy of the system increases by the energy carried in the mass; when mass leaves the system, it carries energy with it. This can include thermal energy, kinetic energy, chemical energy, etc. Energy, Heat, Work. Systems possess energies but not heat or work. Cannot tell where the internal energy came from. Heat and work are associated with a process, not a state. **Heat and work are path functions, i.e., their magnitude and direction depend on the path followed during a process as well as the end states.** Heat and work are only recognized as they cross the boundaries of a system. **Heat and work can be applied to a system (+) or done by a system (−)**, changing the energy of the system. The internal energy, U, of a system is described by the sum of all of the microscopic energies of the molecular components of the system. The portion of the internal energy of a system associated with the kinetic energies of the molecules is called **sensible energy**. The internal energy of a system associated with the phase of a system (intermolecular interactions) is called the **latent energy**. The internal energy associated with the atomic bonds in a molecule is called the **chemical energy**. Outcomes A, B are **mutually exclusive** if the occurrence of each one of them precludes the occurrence of all others. Outcomes A, B are **collectively exhaustive** if they constitute the entire set of possibilities, and no other outcomes are possible. Events A1, A2 are **independent** if the outcome of each one is unrelated to (or not correlated with) the outcome of any other. The **multiplicity** of events, W, is the total number of ways in which different outcomes can possibly occur. If outcomes A and B are **mutually exclusive**, the probability p(A or B) of observing either outcome A or outcome B is: **$p(A \text{ or } B) = p_A + p_B$**. Ex: p(sf)=p(sf/h)(h)+p(sf/h*)p(h*). If outcomes A and B are **mutually exclusive and independent** of each other, then the probability p(A and B) of observing both outcome A and outcome B is: $p(A \text{ and } B) = p_A \times p_B$. The **conditional probability** $p(B|A)$ is the probability of event B, given that some other event A has occurred. The **joint probability** of events A and B is the probability that both events A and B occur. It is expressed as: p(A and B) or p(AB). If outcomes A and B occur with probabilities p(A) and p(B), the joint probability of events A and B is: **$p(AB) = p(B|A)\,p(A) = p(A|B)\,p(B)$. $p(A|B)=(p(B|A)p(A))/p(B)$.** If events A and B are independent, the precondition A has no influence on the probability of B. Then, $p(B|A) = p(B)$, and: **$p(AB) = p(B|A)\,p(A) = p(B)\,p(A)$**. If events A and B are not mutually exclusive, the probability of event A or event B is: $p(A \text{ or } B) = p(A \cup B) = p(A) + p(B) - p(A \cap B)$ If events A and B are mutually exclusive, then $p(A \cap B) = 0$. The behavior of individual elements of the system (**microstate**), which we cannot measure, relates to measurable properties of the system (**macrostate**). For a **binary event** with probability p for one outcome (A), and probability 1-p for the other outcome (B), the probability P(n, N) to obtain outcome A exactly n-times in N trials is: **$P(n, N)=p^n(1-p)^{N-n}N!/(n!(N-n)!)$. $W(n, N)=N!/(n!(N-n)!)$.** Entropy is always positive! Equations to calculate entropy: **Multiplicity form: $S=k_B\ln W$. Probability form: $S=-k_B\sum p_i\ln p_i$.** $k_B=1.38*10^{-23}\,m^2kgs^{-2}K^{-1}$. Entropy: **$dS=(\partial S/\partial U)dU+(\partial S/\partial V)dV+\sum^M_{j=1}(\partial S/\partial N_j)dN_j$**. Energy: **$dU= (\partial U/\partial S)dS+ (\partial U/\partial V)dV+ \sum^M_{j=1}(\partial U/\partial N_j)dN_j$**. 1/T is the slope of S as a function of U for both systems A and B. At thermal equilibrium, both systems have the same temperature T (and slope 1/T), but not necessarily the same energy U or entropy S. Block B is hotter than Block A. At the initial temperature, look at the slope of the U vs S graph. If the slope at the initial state is larger, it has a higher temperature. $T_B>T_A$, $1/T_B<1/T_A$. At equilibrium, find the point where they have the same slope. $T_B=T_A$, $1/T_B=1/T_A$. In the fundamental thermodynamic equation for internal energy, $dU=TdS-PdV$, the natural (independent) variables of internal energy U are entropy S, volume V, and number of particles (they are extensive), not temperature T or pressure P. For very small values of x, the natural logarithm function $f=\ln(1-x)$ can be approximated using a Taylor series expansion about x=0: $\ln(1-x)= -x-x^2/2-x^3/3-x^4/4\ldots$So, for very small x, the higher-order terms become negligible, and we can write the first-order approximation: $\ln(1-x)\approx-x$. **Fundamental thermodynamics equations (FTE) are valid anywhere, anytime. $dS=1/T\,dU+p/T\,dV-\sum^M_{j=1}(\mu_j/T)dN_j$.** $p=-(\partial U/\partial V)$. **Equations of state** are valid only for a specific thermodynamic system. Ideal gas law: **$pV=nN_Ak_BT=nRT$**. $S=k_B(M!/((N!(M-N)!)$. **Premises for the four basic ideal gas thermodynamic processes**: **Ideal gas** (Particles are very dilute, do not interact with each other), **the processes are quasi-static** (A quasi-static process is sufficiently slow so that we can neglect any time or speed-dependent effects. The system is at/near equilibrium during the entire process), **the processes are reversible** (A process is reversible if returning the system to its initial condition also returns the surroundings to their initial condition. Characteristics: slow (quasi-static); no friction; no turbulence; no leakage; no diffusion; no energy dissipation), **closed system, can describe work in a quasi-static process** as $\partial W=-p_{ext}dV$ (system performs work when $dV>0$), and **can describe heat capacity for a system with constant volume** ($C_V=(\partial U/\partial T)_V$). For an ideal gas: **$(\partial U/\partial V)_T=0 \rightarrow dU=(\partial U/\partial T)_V dT=C_V dT \rightarrow C_V=(\partial U/\partial T)_V \rightarrow \Delta U=\int^{T_2}_{T_1}C_V dT=C_V(T_2-T_1)$**. Assuming that the heat capacity C_V is constant over the temperature range. **Reversible**: Well-insulated piston, piston in water bath, i.e., heat (and entropy) are exchanged with local surroundings only and can be fully recovered. **Irreversible**: Piston with friction, balloon with a hole, stirring water, burning wood. **P-V diagram: Isochoric (constant volume):** Since volume doesn't change, $\Delta V=0 \rightarrow$ no work is done **$(W=0)$, $\Delta U=Q$, $Q=C_V(T_2-T_1)=C_V V/Nk\,(P_2-P_1)$, $\Delta S=C_V\ln(T_2/T_1)$. On a PV diagram, the process is represented by a vertical line.** As pressure changes, volume stays fixed. If pressure increases, the line moves upward; if it decreases, downward. On a TS diagram, a sloped upward line (starting lower than isobaric). Example: Heating a gas in a rigid container. **Isobaric (constant pressure): $W=P\Delta V=P(V2-V1)$, $\Delta U=Q+W=C_V(T_2-T_1)=C_V P/Nk\,(V_2-V_1)$, $Q=(C_V/(Nk)+1)p(V_2-V_1)=((CV+R)/Nk)p(V_2-V_1)$, $\Delta S=(C_V+R)\ln(T_2/T_1)=C_p\ln(T_2/T_1)$.** On a PV diagram, the process is represented by a horizontal line. Volume changes while pressure remains the same. On a TS diagram, a sloped upward line. Example: Heating a gas in a piston that can move freely. **Isothermal (constant temperature): $W=-Q=NkT_0\ln(V_2/V_1)=NkT_0\ln(P_1/P_2)$, $\Delta U=Q+W=C_V(T_2-T_1)=0$, $\Delta S=Q/T_0=Nk\ln(V_2/V_1)=Nk\ln(p_1/p_2)$. On a PV diagram, a downward curve since $P\propto1/V$.** Area within the rectangle with height P_1 and width V_1 is equal to the area within the rectangle with height P_2 and width V_2. The same would be true for any points along the PV curve. On the TS diagram, a straight horizontal line (T constant). Example: Slow expansion or compression of an ideal gas with thermal contact (heat exchange allowed). **Adiabatic (no heat exchange, no change in entropy): $\Delta U=W=C_V dT=-pdV$. , $Q=0$, $\Delta S=Q/T_0=0$, $T_2/T_1=(V_1/V_2)^{Nk/C_V}$. On a PV diagram, the curve looks similar to an isothermal curve, but steeper.** As the gas expands, it cools and pressure drops more rapidly than in an isothermal process. On a TS diagram, a vertical line. Example: Rapid compression or expansion (no time for heat transfer). A thermodynamic **pathway** is a particular sequence of processes. A thermodynamic **cycle** is a set of processes that begin in one state, pass through other states, and then return to the initial state. **Every state function sums to zero around a cycle**. If all steps of a cycle are reversible, the whole cycle is reversible. **Carnot cycle on a P-V diagram: Isothermal Expansion (A to B)**: The gas expands slowly at a constant high temperature T_H. It absorbs heat Q_H from the hot reservoir. Pressure decreases as volume increases. The curve is a hyperbola (because $PV=nRT_H$). **Adiabatic Expansion (B to C)**: The gas continues to expand but without heat exchange. The temperature drops from T_H to T_C. Pressure and temperature both decrease. The curve is steeper than the isothermal one. **Isothermal Compression (C to D)**: The gas is compressed at a constant low temperature T_C. It releases heat Q_C to the cold reservoir. Pressure increases as volume decreases. This curve is another hyperbola. **Adiabatic Compression (D to A)**: The gas is compressed without heat exchange. The temp rises back from T_C to T_H. Pressure and temperature both increase. The curve is steeper than the isothermal compression. The area inside the loop represents the net work done by the engine. **T-S Diagram (Temperature vs Entropy): Isothermal Expansion (A to B)**: Temp is constant at T_H. Entropy increases as the system absorbs heat. The line is horizontal. **Adiabatic Expansion (B to C):** Temp drops from T_H to T_C. Entropy remains constant (no heat exchange). The line is vertical. **Isothermal Compression (C to D):** Temp is constant at T_C. Entropy decreases as heat is released. The line is horizontal again. **Adiabatic Compression (D to A)**: Temperature rises from T_C to T_H. Entropy is constant. The line is vertical. The area enclosed by the rectangle on the T-S diagram represents the work done per cycle. **Gibbs free energy $G=H-TS$ (T and P constant). Helmholtz free energy $F=U-TS$ (T, V, # of particles N constant). Enthalpically driven if TS term is negligible. Entropically driven if TS term is larger and negative.** $F_{dimer}=-\varepsilon-kT\ln(V)$. $F_{monomer}=-kT\ln(V^2/2)$. On the TF graph, the monomer starts at 0 with a bigger negative slope, and the dimer starts as $-\varepsilon$ with a slower negative slope. Equilibrium (F has a minimum) depends on temperature T, binding energy, and volume, V. At high temp, monomers are favored (maximizing entropy dominates). At low temperatures, dimers are favored (minimizing internal energy dominates). An increase in volume will favor monomers because there will be a larger space, so entropy increases. **If $U=-\varepsilon$, it means that it takes energy (ε) to break the bond.** If two indistinguishable molecules are held together by a bond, the multicity is V-1. At very low temperatures, the system will be more likely to be in the dimer state since it has the lower free energy. Increasing volume will increase the entropy more for the monomer than than the dimer, thus favoring the monomer state. The dimer state is the ground state because the dimer has the lower energy level U. The ground state is set to have zero energy: $\varepsilon_1=0$ thus, we need to shift the energy so that ε_{dimer} becomes 0. **DNA Melting Temperature:** DNA strands are held together by hydrogen bonds between complementary bases: A-T pairs have 2 hydrogen bonds and G-C pairs have 3 hydrogen bonds. The more G-C pairs a DNA molecule has, the more hydrogen bonds there are holding the two strands together. In addition, G-C pairs have stronger base-stacking interactions (hydrophobic interactions between adjacent bases) than A-T pairs, which further stabilize the double helix. As a result, more energy (higher temperature) is required to break these bonds and separate the strands, meaning a higher melting temp. Increasing the length of the DNA means there are more base pairs holding the two strands together. Even if the average GC-content stays the same, a longer DNA molecule has more total hydrogen bonds and base- stacking interactions, which requires more energy to denature completely. As the length increases, the melting temperature increases. A combined system consisting of the test tube and the water bath in an isolated system. 1. $dS_{combined}=dS_{system}+dS_{bath}\geq 0$ 2. $dU_{combined}=dU_{system}+dU_{bath}=0$ 3. $dS=1/TdU$. $dS_{system}-1/TdU_{system}\geq 0 \rightarrow dU_{system}-TdS_{system}\leq 0$. $F=U-TS$. $dF=dU-TdS \rightarrow dF_{system}\leq 0$. A system held at constant temperature and volume reaches equilibrium where the free energy F has a minimum. **Three ways to think about enthalpy**: Change in internal energy + work performed by volume change at constant pressure ('create space'), Heat released by the system (e.g., chemical reaction), $G=H-TdS$ has a minimum at equilibrium for T,p,N=constant. Methane CH_4 , Ethane C_2H_6 , Propane C_3H_8 , Methanol CH_3OH , Ethanol C_2H_5OH , Butane → $C_4H_1\ 0$. **ΔH=-Q. ΔH<0 exothermic reaction, releases heat. ΔH>0 endothermic reaction, requires heat**. The lowest energy level (ground state) has energy = 0. Energy in ATP is stored in high-energy phosphoanhydride bonds between its phosphate groups. When ATP is hydrolyzed to ADP+P, these bonds are broken and replaced with more stable bonds to water, releasing free energy (ΔG<0) that the cell uses to drive other reactions. The **Boltzmann distribution** describes the population distribution (i.e., probability) at each (internal) energy level as a function of the energy level and temperature. Probability to find a system in a microstate with internal energy level E_j (i.e., fraction of population in that microstate with energy at level with energy E_j) for a system with j = 1...t. $P_j=(W(E_j)e^{-E_j/kT})/(\sum_{j=1}^{t}W(E_j)e^{-E_j/kT})=e^{-E_j/kT}/q$= Boltzmann factor/Parition function. **W(E): Density of state with Energy E_j; ie, number of microstates with energy level E_j.** The energy levels E_j are determined by the microscopic/ quantum properties of the system and are independent of temperature. Their occupancy changes with temperature. At low temperatures, most particles will have low energy, and few particles will have high energy. At very high temperatures, or if all energy levels are very low, the distribution approaches a flat distribution. **The Boltzmann Distribution and partition function provide information on the number of states that are effectively accessible to a system at a given temperature, rather than the total number of states.** System consisting of N independent, identical, **distinguishable** particles: $Q=q^N$. System consisting of N independent, identical, **indistinguishable** particles: $Q=q^N/N!$. **Q: partition function of total system. q: partition function of particle (subsystem).** Ex: $\varepsilon_1=0$ (ground state): compact configuration, 1 microstate. $\varepsilon_2=\varepsilon$: 4 microstates. $q=\sum_{j}^{t}e^{-E_j/kT}=e^{-0/kT}+e^{-\varepsilon/kT}+e^{-\varepsilon/kT}+e^{-\varepsilon/kT}+e^{-\varepsilon/kT}$. $q=1+4e^{-\varepsilon/kT}$. $W(E_1=0)=1$. $W(E_2=\varepsilon)=4$. $P_j=(W(E_j)e^{-E_j/kT})/(\sum_{j=1}^{t}W(E_j)e^{-E_j/kT})=e^{-E_j/kT}/q$. **Compact state (ground state)**: $P_c=e^{-E_j/kT}/q=e^{-0/kT}/q=1/(1+4e^{-\varepsilon/kT})$. **Open configuration (excited state)**: $P_o=4e^{-\varepsilon_2/kT}/q=4e^{-\varepsilon/kT}/(1+4e^{-\varepsilon/kT})$. Total energy of a single molecule: $\boldsymbol{\varepsilon_{total}=\varepsilon_{translation}+\varepsilon_{roration}+\varepsilon_{vibration}+\varepsilon_{electronic}}$. Total partition function for a single molecule: $\boldsymbol{q_{total}=q_{translation}q_{roration}q_{vibration}q_{electronic}}$. For nuclear energy, since nuclear transitions involve extremely high energies compared to k_BT at ordinary temperatures, essentially all nuclei are in their ground nuclear energy state at normal temperatures. $q_{nulear}=1$. **Translational energy partition function**: $q_{translation}=((2\pi mkT)/(h^2))^{3/2}V$ [m: mass of particle, h: **Plank constant (6.626×10^{-34} m^2kg/s)**, V: volume]. **Rotational energy partition function (linear molecule)**: $q_{rotation}=(8\pi^2IkT)/(\sigma h^2)$ [I: moment of inertia, σ: number of equivalent rotations, h: Planck constant]. **Rotational energy partition function (non-linear molecule)**: $q_{rotation}=((\pi I_aI_bI_c)^{1/2}/(\sigma))((8\pi^2kT/h^2)^{3/2})$. **Vibrational energy partition function**: $q_{vibration}=1/(1-e^{-hv/kT})$ [v: vibrational frequency of particle]. **Electronic excitation partition function electronic**: $g_0+g_1e^{-\Delta\varepsilon_1/kT}+g_2e^{-\Delta\varepsilon_2/kT}+\ldots$ [$\Delta\varepsilon_i$= electronic excited state energy, g= electronic degeneracies. $\boldsymbol{\varepsilon_{translational}<\varepsilon_{rotation}=\varepsilon_{vibration}<<\varepsilon_{electronic}}$. If humans were made entirely of water, they would see blue or blue-green lights transmitted through their tissue. This is because water's molecular vibrational energy levels absorb red and infrared light, allowing only higher energy (shorter wavelengths) blue light to penetrate – consistent with the energy-level structure and the thermodynamic partitioning of states in water. HW 1: Sealed tube in a hot water bath. **Closed system. No mass transfer→no energy associated w/ mass.** System is stationary+has rigid walls→ assumes no work. ΔU=Q. Cell placed in a hypotonic solution, water enters the cell, causing it to swell. **Open system. Mass can pass through and enter the system.** Because the system (cell) and surroundings (solution) are at the same temperature, there is no heat transfer. As the cell swells, the volume of the system increases, and the system is doing work on the surroundings. ΔU=W+Emass. $\Delta U=p\Delta V+mc_pT$. Dialysis. **Open system. Mass and energy can enter and exit the system.** Boundaries are rigid and the system is stationary, so no work. Assume all fluids entering and exiting the system are at the same temperature, so no heat. ΔU=Emass. ΔU=mcT. Fan in the room. Well insulated, so Q=0. Closed system, electricity enters to power the fan, no mass transport. ΔU=W. W=PΔT. Hot water heater. Open system. Assume no work. Steady state, so ΔU=0. ΔU=Q+Emass=0. $m_{out}C_pT_{out}-m_{in}C_pT_{in}=Q=P$. Bioreactor. An open system because mass crosses the boundary (two inflows and one outflow) as well as energy via heat and work. Rate of mass in kg/s. Add them. The temp in the mix is the rate of mass times temp for each divide total mass rate. The change in temp is desired minus the average temp in. The $Q_f=mc_p\Delta T$. Q_c is Q fluid minus pump work. The answer seems reasonable because the pump's contribution is small relative to the heating load, so the coil dominates the heating requirement. No change. Stage I's steady-state energy balance depends only on its own mass flow and inlet/outlet conditions. Changing stage II volumes does not affect Stage I flows or inlet temperature, so the power required to maintain T_{out} remains identical. The temp will decrease. Mass flow doubles, but coil power is unchanged. The heating per unit mass is halved, so the achievable temperature rise decreases by ½. With $Q_c=0$, $W_p+m_1C_pT_1+m_2C_pT_2=mc_pT_{out}$. Without the heater, the outlet settles near the weighted average of the inlet plus a negligible 0.1 degrees Celsius from the pump's heat input. The coil's absence makes the outlet much cooler than desired. HW 2: 4 bases A,C,T,G with equal likelihood in a DNA sequence of 9 monomers. Probability of finding the sequence AAATCGAGT is $(1/4)^9$. Probability of finding 4 A,2 T,2 G, 1 C is $W=9!/4!2!2!1!$, $W_{total}=4^9$, $P=W/W_{total}$. Probability of finding CATCAG anywhere in the genome with 3.2×10^9 base pairs in the human genome is P(no seq)=1-p(seq)=$1-(1/4)^6$. P(no seq in genome)≈$(1-(1/4)^6)^{3.2\times10^9}$≈0. P(seq in genome)=1-p(no seq in genome)≈1-0≈1. Dipolar molecules. The system became less disordered when the electric field was applied because entropy decreased. When we apply the field, we lose the flat distribution (max entropy) and cause one state to become favored. This means the system is less random and more "ordered" with the field than without. Lattice model. State A particles cannot cross the barrier, so two independent events $W_A=W_MW_N=M!/m!(M-m)!\times N!/n!(N-n)!$. Particles can cross the barrier. No longer independent. $W=(M+N)!/(m!n!(N+M-n-m)!)$. ΔS negative means that the entropy of state B is greater than the entropy of state A. This makes sense because the particles in state A are constrained by the barrier between the lattices and therefore have fewer potential configurations than state B. The total probability for each should equal 1. $P_2/P_1=e^{-(E2-E1)/(RT)}$. $E_2-E_1=-RTln(P_2/P_1)$. We choose the ground state to be the macrostate with the lowest energy. From the probabilities, that is, microstate 1, so $E_1=0$. If macrostate 2 actually has two microstates, it would be 2e instead. Having two microstates (higher degeneracy) increases the probability of occupying macrostate 2 for a given energy; therefore, to keep observed P_2, the energy of macrostate 2 must be raised (so the Boltzmann suppression offsets the larger degeneracy). At very high temp, energy differences become negligible in the Boltzmann factors, so the probability becomes proportional to degeneracy. As T approaches 0, only the ground state level is populated. Since we defined the ground macrostate to be macrostate 1 ($E_1=0$) and states 2 and 3 have higher energies, in the low temperature limit, all population goes to state 1. HW3: **Irreversible if material cannot return to its original state and energy is lost in order to break the bond.** Adiabatic-derived P_2/P_1 as a function of V_1/V_2. $T_2/T_1=(V_1/V_2)^{\gamma-1}$. $\gamma=C_p/C_V$, $C_p=C_V+R$, $R=N_Ak_B$. $\gamma=1+R/C_V=1+(N_Ak_B)/C_V$. $P=nRT/V$. $P\propto T/V$. $P_2/P_1=(T_2/T_1)/(V_2/V_1)=(V_1/V_2)^{\gamma-1}(V_1/V_2)=(V_1/V_2)^{\gamma}$. $\gamma=1+(N_Ak_B)/C_V$. $P_2/P_1=(V_1/V_2)^{1+(NAkB)/CV}$. **Isothermal: $P_2V_2=P_1V_1$. $P_2=P_1(V_1/V_2)$. Adiabatic: $P_2/P_1=(V_1/V_2)^{Nk/Cv+1}$. $P_2=P_1(V_1/V_2)^{Nk/Cv+1}$. Equations with higher exponents are steeper, so the adiabatic PV curve is steeper. Van der Waals gas**: $p=(RT/V-b)-(a/V^2)$. W_{by}=integral V1 to V2 of pdV. W_{on}=-integral V_1 to V_2 of p(V)dV. W=-integral V1 to V2 of $(RT/V-b)-(a/V^2)$ dV. W=-RT integral V_1 to V_2 dV/V-b + a integral V_1 to V_2 dV/V^2. Integral V_1 to V_2 dV/V-b = $ln|V_2-b/V_1-b|$. Integral V_1 to V_2 $dV/V^2=[-1/V]$ V_1 to V_2 $=-1/V_2+1/V_1$. $W=-RTln|V_2-b/V_1-b|+a(-1/V_2+1/V_1)$. $W_{on}=RTln|V_1-b/V_2-b|-a(1/V_2-1/V_1)$. Less work is required in the low-density limit (for large volumes). Internal attractive energy aids compression (not bumping since farther apart). More work is required in high-density limits (small volumes). Stronger repulsion due to dispersion (bumping). More work to compress. HW4: If -TS>H, the system would be entropy driven. **Derive the expression for the internal energy change of an ideal gas.** U=U(T,V). $dU=(\partial U/\partial V)_TdV+(\partial U/\partial T)_VdT$. **For an ideal gas, internal energy depends only on temperature, does not change with volume.** $dU=(\partial U/\partial V)_TdV+(\partial U/\partial V)_VdT\rightarrow dU=(\partial U/\partial T)_VdT$. $(\partial U/\partial T)_VdT$ is the change in energy with temperature change at a constant volume→heat capacity C_V. $\boldsymbol{dU=C_VdT}$. Polymer: $F_{open}=-k_BTln4$ ($U_{open}=0$ and $S_{open}=k_Bln4$), $F_{compact}=2\varepsilon$ ($U_{compact}=2\varepsilon$ and $S_{compact}=k_Bln1=0$). ε is positive now because before we were looking at molecules that bind together via covalent or intermolecular bonds. In these cases, we have to add energy to break the bonds. Therefore, forming the bonds takes energy out of the system, and ε is negative. In this case, instead of forming bonds, we're trying to force two ends of a polymer together. These ends have the same charge and are therefore repelled by each other. Instead of bond energies. In this case, ε is the energy associated with repulsion. Because the ends are repelled by each other, we have to put energy into the system to form the compact conformation, and energy is released when they dissociate. Molecules separate ε =negative. Molecules join together ε =postive. Recitation 1: If more heat is leaving than the work going in, the final internal energy of the system should be lower than the initial. Closed system because no KE, PE, or mass change. $\Delta U=U_2-U_1=W_{in}-Q_{out}$. $U_2=W_{in}-Q_{out}+U_1$. Check/Compare: This matches my prediction, and the order of magnitude is within the expected range. The heat capacity of Styrofoam is high because it's an insulator. $m_Ic_I(T_{Ii}-T_f)=m_Sc_S(T_{Si}-T_f)$. Open system has to consider heat, work, and mass flow. **P=ΔW/T.** For a system at steady state, **ΔU/Δt=0.** Recitation 2: Arrange indistinguishable letters in Mississippi: $W=N!/(n_1!n_2!n_3!)$. Arrange the letters of the alphabet: W=N!. Draw red or blue balls out of a bag without replacement: W=N!/(n!(N-n)!). Win 13/16 games in a football season: W=N!/(n!(N-n)!). $W_{total}=2^N$. $P(n,N)=N!/(2^Nn!(N-n)!)$. Answer 10 questions in a T/F test: $W=2^N$ (independent and 2 possible outcomes). Arrange 10 identical chairs in a row: W=N!/n!. If specificity is high, we expect the answer to be greater than 50%. Recitation 3: How many arrangements are there of 15 indistinguishable lattice gas particles distributed on V=20 sites? W(N=15,V=20)=20!/15!5!. What is the probability that exactly 15 particles occupy the lattice if the lattice has N sites and each site can either be empty or occupied by one particle? $p(n,N)=W(n,N)/W_{total}$. $W_{total}=2^N$ (two outcomes for N trials). W(n, N)=N!/15!(N-15)!. $P(n,N)=N!/(2^N15!(N-15)!)$. Two independent lattices: $W_A=W_NW_M=N!/(n!(N-n)!)\times M!/(m!(M-m)!)$. Distinguishable mixed together: $W_B=(N+M)!/(n!m!(N+M-n-m)!)$. **Stirling's approximation: $x!\approx(x/e)^x$ for x>>1. E cancel outs.** State B has **greater entropy** because the particles are unconstrained and have access to the full volume **(more arrangements, higher multiplicity).** State A's particles are confined to separate lattices, limiting mixing. The salt dissolved in water has a higher entropy. In the solid crystal, the Na^+ and Cl^- ions sit on fixed lattice sites (highly ordered). When NaCl dissolves, the ions become separated and solvated by many water molecules, each ion now has translational freedom and many more possible arrangements. An increase in microscopic disorder means higher entropy. Gibbs free energy. Dissolution of NaCl in water at ordinary temp is spontaneous (ΔG<0). Because the enthalpy change ΔH for NaCl is small, the only way to get ΔG<0 is for TΔS to be positive (ΔS>0). Lowering the temp will not reverse the ordering of entropies. The dissolved state still has greater configurational and translational entropy than the ordered crystal. Only at a temp where dissolution is no longer possible or there is crystallization would phase change alter the comparison. **Use thermodynamic equations and 2nd law to show that the systems will equilibrate.** $dS_{total}=dS_A+dS_B=0$. $dS_{total}=(dS_A/dU_A)dU_A+(dS_A/dV_A)dV_A+(dS_B/dU_B)dU_B+(dS_B/dV_B)dV_B=0$. $dU_{total}=0\rightarrow dV_A=-dV_B$. $dS_{total}=[(dS_A/dU_A)-(dS_B/dU_B)]dU_A+[(dS_A/dV_A)-(dS_B/dV_B)]dV_A$. Recall: $1/T=dS/dU\rightarrow dS_A/dU_A=1/T_A$ and $dS_B/dU_B=1/T_B$. $dS/dV=P/T$. $dS_{total}=(1/T_A-1/T_B)dU_A+(P_A/T_A-P_B/T_B)dV_A$. $DS_{total}=(P_A/T_A-P_B/T_B)dV_A$. For equilibrium: $dS_{total}=0$. $P_A/T_A=P_B/T_B\rightarrow$ for $T_A=T_B$, $P_A=P_B$. Recitation 4: **efficiency=1-T_{cold}/T_{hot}.** Recitation 5: Enthalpy: (When pressure is constant, dQ=dH; H=U+pV; state function; takes into account both the internal energy of a system along with the energy associated with work done on the surroundings.) F=U-TS. $F_{unbound}=-Tkln9$ because no bond energy. $F_{bound}=U=5\varepsilon_0$ (because multiplicity=1 and ln1=0. $\Delta F_{binding}=F_{bound}-F_{unbound}=5\varepsilon_0+Tkln9$=5(-1kcal/mol)+(0.002kcal/Kmol)(300K)(ln9). At the dissociation temp, the free energy change is zero, so $5\varepsilon_0=T_dkln9$. If the flexible loop were made rigid (and in the proper configuration for ligand binding), the new ΔF* binding would be $\Delta F_{binding}$=5(-1kcal/mol) because $F_{unbound}=0$ and $F_{bound}=U=5\varepsilon_0$. If the loop is rigid, then the binding will be tighter because it does not incur the entropic penalty from the loss of the loop's conformational freedom. So the free energy is more negative in the rigid case. **Q=PΔt. Q in Joules (J). P in Watts(W) or (J/s).** In an air-filled balloon, the air inside heats up quickly, expands, and increases the internal pressure on the rubber. The rubber can't stretch enough, so it bursts. In a water-filled balloon, the water absorbs and distributes the heat much more effectively than air, keeping the balloon's rubber cooler and preventing rapid expansion. So the air-filled balloon pops first, while the water-filled balloon lasts longer because water resists temp change and heat buildup. If you have two independent systems A and B (System A has W_A microstates, System B has W_B microstates), then the combined system has $W_{total}=W_A\times W_B$. If entropy is to add (not multiply) $S_{total}=S_A+S_B$. The only mathematical function that turns multiplication into addition is the logarithm $ln(W_AW_B)=ln(W_A)+ln(W_B)$. So using lnW ensures that entropy behaves additively, as it must in thermodynamics.