

**1 Energy in Thermal Physics 1.1 Thermal Equilibrium** Temperature (theoretical and operational definition) Thermal Equilibrium Relaxation time Rounded room temperature: 300K.

**1.2 The Ideal Gas**  $PV = nRT$   $P$ =pressure,  $V$ =volume,  $n$ =number of moles of gas,  $R = 8.31 \frac{J}{mol \cdot K}$ ,  $T$ =temp. A mole of molecules = Avogadro's number of molecules =  $N_A = 6.02 \times 10^{23}$ . Number of molecules =  $N = n \times N_A$ . Boltzmann's constant =  $k = \frac{R}{N_A} = 1.381 \times 10^{-23} \frac{J}{K}$ .  $PV = NkT$  Valid in the low density limit (average space between gas molecules » size of a molecule)  $\bar{K}_{trans} = \frac{3}{2}kT$

**1.3 Equipartition of Energy** Equipartition theorem: At temperature  $T$ , the average energy of any quadratic degree of freedom is  $\frac{1}{2}kT$  Gas of monoatomic molecules:  $f=3$  (translational) Diatomic gas: any comb. of  $f=5$  (3 translational, 2 rotational not third if the axis of symmetry is down its length)  $f=6$  (3 translational, 3 rotational)  $f=8$  (3 translational, 3 rotational, 2 vibrational  $K$  and  $P$  - often don't contribute at room temp). Solid:  $f=6$  (6 vibrational - 3  $K$ , 3  $P$  - again some may be frozen out at room temperature).

**1.4 Heat and Work** 1. Law of thermodynamics (conservation of energy):  $\Delta U = Q + W$  Heat transfer: Conduction, convection, radiation

**1.5 Compression Work**  $F = PA$  = pressure of the gas  $\times$  area of piston requires assumption: as the gas is compressed it always remains in internal equilibrium so that its pressure uniform, hence well defined = compression must be slow enough so the gas has time to continually equilibrate to the changing conditions = **quasistatic**. For gas being compressed aka negative  $\Delta V$  this gives  $W = F\Delta x = P\Delta x = -P\Delta V$ .

**Application to Ideal Gas** Isothermal compression = so slow the temperature of the gas doesn't rise at all (quasistatic) Adiabatic compression = so fast no heat escapes from the gas (in practice approximate as quasistatic) Adiabatic compression:  $VT^{\frac{f}{2}}$ . The final pressure is then  $V^{\gamma}P = \text{constant}$ ,  $\gamma = \frac{f+2}{f}$ , the adiabatic exponent.

**1.6 Heat Capacities** Heat capacity = amount of heat needed to raise object's temperature per degree temperature increase  $C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$   $W = 0$  (usually means  $V = \text{constant}$  since no else there would be compression work  $-P\Delta V$ ):  $C_V = (\frac{\delta U}{\delta T})_V$

However, if object expand when heated and do work on surroundings, there is a negative  $W$ . At constant  $P$   $Q$  is unambiguous and we then have the heat capacity at constant pressure  $C_P = (\frac{\Delta U - (-P\Delta V)}{\Delta T})_P = (\frac{\delta U}{\delta T})_P + P(\frac{\delta V}{\delta T})_P = (\frac{\delta H}{\delta T})_P$

Phase transformation:  $C_V = \frac{Q}{\Delta T} = \frac{Q}{0} = \infty$  while  $L = \frac{Q}{m}$  is the heat required to accomplish the transformation divided by the mass of the substance.

Ambiguous def. since any amount of work could be done during process, but assume pressure constant and no other work done beside the usual constant-pressure expansion or compression.

How to keep track of constant-pressure work done during process. Enthalpy  $H = U + PV$ . Add the energy needed to make room for the system - pressure of surroundings  $\times$  system's volume. Then have the total  $E$  needed to create system out of nothing or extracted if system annihilated: the energy content + energy needed to make room for it. 1. law:  $\Delta U = Q + W = Q - P\Delta V + W_{other} \rightarrow \Delta H = Q + W_{other}$  (constant  $P$ ). Thus given constant  $P$  enthalpy change never caused by compression/expansion work, so don't have to think about it. And tells you the added heat if no other work.

**2 The Second Law 2.1 Two-State Systems**  $\Omega(N, n) = \frac{N!}{n!(N-n)!} = \binom{N}{n}$

**2.2 The Einstein Model of a Solid** 1 energy unit  $\hbar f = \hbar \omega$ . Multiplicity of an Einstein solid with  $N$  oscillators ( $\frac{N}{3}$  atoms) and  $q$  energy units:  $\Omega(N, q) = \binom{q+N-1}{q}$

**2.3 Interacting Systems** Two solids. Weakly coupled = exchange of energy between them much slower than the exchange of energy between atoms within each solids. Then have the (temporarily) macrostate  $U_A + U_B$  were both specified and look at the microstates for these. Later look at the (long time scale) macrostate  $U_{total}$  with all combinations  $U_A, U_B$ . Fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

Detailed balance: at the microscopic level we expect that any process that would take the system from state  $X$  to  $Y$  is reversible, so that the system can just as easily go from state  $Y$  to state  $X$ .

For a large system, the number of "accessible" microstates is usually so huge that only a minis-

cule fraction of them could possibly occur within a lifetime. Assume that the microstates that do occur, over "long" but not unthinkably long time scales, constitute a representative sample.

**2.4 Large Systems** Useful approximation given  $|x| \ll 1$  is  $\ln(x+1) \approx x$  (Taylor). Stirling's approximation:  $N! \approx N^N e^{-N} \sqrt{2\pi N}$ , accurate in the limit where  $N \gg 1$ . If  $N$  is a large number (thus  $N!$  very large) the sqrt-factor can be omitted. Usually good enough if we care about the logarithm. Then have  $\ln N! \approx N \ln N - N$ . In a large Einstein solid the case  $q \gg N$  is the "high temperature" limit.

**2.5 The Ideal Gas** For any system with only quadratic "degrees of freedom", having some many units of energy that energy quantization is unnoticable, the multiplicity is proportional to  $U^{N_f/2}$ , where  $N_f$  is the total number of degrees of freedom.

**2.6 Entropy**  $S = k \ln \Omega$  2. law of thermodynamics: Entropy tends to increase. Entropy of an Ideal Gas (Sackur-Tetrode equation):  $S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$ . Entropy of ideal gas depends on  $V$ ,  $E$ ,  $N$  - increasing any of them increase  $S$ . Gibbs paradox - if particles distinguishable, could entropy decrease? Assume all atoms of given type is distinguishable. Irreversible = processes that create new entropy. Sudden expansion: creates new entropy. Gradual compression or expansion does not by itself change entropy. Any reversible volume change must be quasistatic so that  $W = -P \Delta V$  (however a quasistatic process may still be irreversible if heat flowing in and out, or entropy created in some other way).

Can define irreversible process as one that can be reversed by changing the conditions only infinitesimally (infinitesimally change in temp when very slow heat flow between objects at nearly same temp, or a infinitesimal pressure change during a quasistatic volume change).

**3 Interactions and Implications 3.1 Temperature** Two Einstein solids:  $\frac{\delta S_A}{\delta U_A} = \frac{\delta S_B}{\delta U_B}$  at equilibrium ( $N_A, N_B$  held fixed). A steep slope corresponds to low temperature (heat flows to you, you want energy as it leads to much entropy increase) while a shallow slope corresponds to high temperature (you can lose heat, as losing energy doesn't decrease your entropy that much). Define temperature  $\frac{1}{T} = \left( \frac{\delta S}{\delta U} \right)_{N,V}$

**3.2 Entropy and Heat Capacity** Predict heat capacity of a

system: 1. Express  $\Omega$  in terms of  $U, V, N$  and other relevant variables (using Q.M. and combinatorics) 2. Find  $S = k \ln \Omega$  3. Find  $T(U, \text{other variables}) = \left( \frac{\delta S}{\delta U} \right)_{N,V}^{-1}$  4. Solve for  $U(T, \text{other variables})$  5. Find  $C_V = \left( \frac{\delta U(T)}{\delta T} \right)_{N,V}$  holding  $N, V$  and other variables constant.

3. Law of Thermodynamics: At  $T=0$  a system should settle into its unique lowest-energy state,  $\Omega = 1, S=0$ . Must have  $C_V \rightarrow 0$  as  $T \rightarrow 0$ . For this to hold for for ex. Einstein solid and Ideal gas, the degrees of freedom must freeze out at low  $T$ .

### 3.3 Paramagnetism

**3.4 Mechanical Equilibrium and Pressure**  $P = T \left( \frac{\delta S}{\delta V} \right)_{U,N}$  If any change in volume takes place quasistatically (so pressure always uniform throughout system), no other form of work done, and no other relevant variables (like  $N$ ) change, we know  $W = -P \Delta V \rightarrow Q = T \Delta S \rightarrow \Delta S = \frac{Q}{T}$  Special case: if process also adiabatic ( $Q=0$ )  $\rightarrow \Delta S = 0$ , it is isentropic. Adiabatic + quasistatic = isentropic. Finding  $\Delta S$  when  $T$  changes (fex as heat is added)

- constant  $V$ :  $(\Delta S)_V = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T} dT$  while at constant  $P$ :  $(\Delta S)_P = \int_{T_i}^{T_f} \frac{C_P}{T} dT$

**3.5 Diffusive equilibrium and Chemical Potential**  $\mu = - \left( \frac{\delta S}{\delta N} \right)_{U,V}$

**3.6 Summary and a look ahead** The thermodynamic identity (how to recover  $T, P$  and  $\mu$  from partial derivatives of  $S$ ):  $dU = T dS - P dV + \mu dN$  The formulae in table ?? apply to any large system whose macrostate is determined by  $U, V, N$ .

### 4 Engines and Refrigerators 4.1 Heat Engines

Heat engine = device that absorbs heat and converts part of that energy into work. Work produced = heat absorbed - waste heat expelled to get rid of entropy brought along by absorbed heat, in order for cycle to be able to start over. Absorb heat  $Q_h$  from hot reservoir w/  $T_h$ , waste heat  $Q_c$  dumped to cold reservoir w/  $T_c$ .  $W$  is net work done by engine. Efficiency:  $e = \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h}$  using 1. law ( $E$  conserved) in last step

Now use 2. law,  $S$  must increase, + assume engine operates in cycles=state of total system must be unchanged at the end of 1 cycle:  $S_{\text{expelled}} \geq S_{\text{absorbed}} \rightarrow \frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \rightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$  Thus:  $e \geq 1 - \frac{T_c}{T_h}$

The Carnot Cycle (max efficiency): Let the engine's working substance be a gas. Step 1: Gas absorbs  $Q_h$ . In the process  $\Delta S_R = -\frac{Q_h}{T_h}$  and

$\Delta S_{gass} = \frac{Q_h}{T_{gass}}$ . Want to not create new S that is  $\Delta S_{total} = \frac{Q_h}{T_{gass}} - \frac{Q_h}{T_h} = 0 \rightarrow T_h = T_{gass}$ . However no heat flows between objects at same T. Solution:  $T_{gass}$  slightly less than  $T_h$ . Keep  $T_{gass} = \text{constant}$  by letting  $V_{gass}$  expand as it absorbs  $Q_h$  = isothermal expansion. Step 2: How to get gass from previous  $T_{gass} = \text{constant}$  to next? Don't want heat flow at the intermediate T's  $\rightarrow$  adiabatic expansion. Step 3: Waste heat  $Q_c$  dumped from gas to reservoir. Same as step 1:  $T_{gass}$  slightly above  $T_c$ . Keep  $T_{gass} = \text{constant}$  by isothermal compression, so  $V_{gass}$  decreases, as  $Q_c$  leaves. Step 4: Change  $T_{gass} = \text{constant}$  from step 3 constant to step 1 constant without heat flow  $\rightarrow$  adiabatic compression.

**4.2 Refrigerators** Heat engine operated in reverse - switch directions - now  $Q_c$  and  $W$  enters while  $Q_h$  leaves. Efficiency now named coefficient of performance:  $COF = \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1}$ . Require again  $S_{expelled} \geq S_{absorbed} \rightarrow \frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$ . Thus  $COF \leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c}$ .

## 5 Free Energy and Chemical Thermodynamics

Processes that are not cyclic, and interaction with environment so that constant T and P, not E and V.

**5.1 Free Energy as Available Work** Environment with constant P, enthalpy: total energy to create system out of nothing = system's energy + work needed to make room for it  $\rightarrow H = U + P\Delta V = U + P(V - 0) = U + PV \rightarrow$  energy recovered if annihilating the system = system's energy + work done by the collapsing atmosphere.

Environment with constant T, a heat  $T\Delta S$  can be extracted for free, to create the system out of nothing only provide additional work needed: energy that must be provided as work to create the system (Helmholtz free energy) = total energy needed to create the system - free heat from environment  $\rightarrow F = U - T\Delta S = U - T(S - 0) = U - TS \rightarrow$  if system annihilated the energy that comes out as work, that is available/free, = system's total energy - heat dumped into the environment to get rid of system's entropy.

Environment with constant P and T: work needed to create system/work recovered when destroyed = Gibbs free energy = system's energy - heat term + atmospheric work term =  $U - TS + PV$ .

Thermodynamic potentials: U, H, F, G. Identities: H:  $dH = TdS + VdP + \mu dN$  F:  $dF = -SdT - PdV + \mu dN$  S:  $S = -(\frac{\delta F}{\delta T})_{V,N}$  P:  $P = -(\frac{\delta F}{\delta V})_{T,N}$

$\mu = (\frac{\delta F}{\delta N})_{T,V}$  G:  $dG = -SdT + VdP + \mu dN$  S:  $S = -(\frac{\delta G}{\delta T})_{P,N}$  V:  $V = (\frac{\delta G}{\delta P})_{T,N}$   $\mu = (\frac{\delta G}{\delta N})_{P,T}$

Example of **Maxwell relation**:  $(\frac{\delta}{\delta V}(\frac{\delta U}{\delta S}))_{V,N} = (\frac{\delta}{\delta S}(\frac{\delta U}{\delta V}))_{S,N} \rightarrow (\frac{\delta T}{\delta V})_{S,N} = -(\frac{\delta P}{\delta S})_{V,N}$  From the T. I. for U evaluated the partial derivatives in parantheses to obtain the nontrivial identity called a Maxwell relation.

**5.2 Free Energy as a Force toward Equilibrium** Constant N, U, V: S increase Constant N, T, V: F decrease Constant N, T, P: G decrease

Extensive: V, N, S, U, H, F, G, mass Intensive: T, P,  $\mu$ , density

## 5.3 Phase Transformations of Pure Substances The Clausius-Clapeyron Relation

Phase boundary between liquid and gass, N fixed:  $G_l = G_g \rightarrow G_l/N_l = G_g/N_g \rightarrow \mu_l = \mu_g$ . Diffusive equilibrium between liquid and gass. Use T. I. for G to solve for the slope of the phase boundary line  $dP/dT$  (gradient in a P-T diagram):  $\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{1}{T} \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T\Delta V}$  The relation applies to the slope of any phase boundary line on a PT diagram.

**The van der Waals Model** Equation of state for liquid-gas systems modifying the ideal gas model to take into account approximate molecular interactions:  $(P + \frac{aN^2}{V^2})(V - Nb) = NkT$

## 5.6 Chemical Equilibrium

**6 Boltzmann Statistics 6.1 The Boltzmann factor** System now in contact with a reservoir and we now only apply the fundamental assumption of equal probability for all microstates to the microstates of the complete system and reservoir (not the system by itself, which is no longer isolated and can exchange energy with the reservoir). Boltzmann factor =  $e^{-E(s)/kT}$  Partition function =  $\sum_s e^{-E(s)/kT}$  Boltzmann/canonical distribution:  $P(s) = \frac{1}{Z} e^{-E(s)/kT}$

**6.2 Average Values** Average of a variable X:  $\bar{X} = \sum_s X(s)P(s)$  Average energy is also  $\bar{E} = -\frac{1}{Z} \frac{\delta Z}{\delta \beta} = -\frac{\delta \ln Z}{\delta \beta}$

Example: Rotation of diatomic molecules (two rotational degrees of freedom). Rotational motion of diatomic molecule (assume isolated = low-density gas). Allowed energies  $E(j) = j(j+1)\epsilon$ ,  $j=0,1,\dots$  with degeneracy  $\Omega(j) = 2j+1$ . Then  $Z_{rot} = \sum_{j=0}^{\infty} (2j+1)e^{-E(j)/kT}$  We can approximate

this with an integral when  $kT \gg \epsilon$ :  $Z_{rot} \approx \int_0^\infty (2j+1)e^{-E(j)/kT} dj = \frac{kT}{\epsilon} \rightarrow \bar{E} = kT$  in agreement with the equipartition theorem (if atoms identical we must divide  $Z$  by 2).  $C_V = \frac{\delta \bar{E}}{\delta T} = k$ . At low  $T$   $C_V \rightarrow 0$  according to 3. law - agrees with the exact  $Z$ .

**6.3 The Equipartition Theorem** Applies to systems w/ Energy in the form of quadratic degrees of freedom:  $E(q) = cq^2$ ,  $c$  a constant,  $q$  a coordinate or momentum variable ( $x, p_x, L_x$  etc). each  $q$  corresponds to a separate, independent state, pretend they're discretely spaced, separated by small intervals  $\Delta q$ .  $Z = \sum_q e^{-\beta cq^2} \approx \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta cq^2} dq$  Approximate to integral if  $\Delta q$  small. Recognize the integrand as a Gaussian. Calc  $\bar{E} = \frac{1}{2}kT$  from this to confirm equipartition theorem. Only true in the high  $T$  limit - or when the spacing between energy levels is much less than  $kT$ .

**6.4 The Maxwell Speed Distribution** Speed  $v$  of molecules in ideal gas.  $v$  can vary continuously = infinitely small probabilities, look instead at probability for a speed in an interval  $v_1-v_2$ . Given by the area under the distribution function  $D(v)$ :  $P(v_1 \dots v_2) = \int_{v_1}^{v_2} D(v) dv$ . Derive  $D(v)$ : Space is 3D - several  $\vec{v}$  may give same  $v$ . Thus  $D(v) \propto P(\vec{v}) \times \Omega(v)$  where  $\Omega(v)$  = number of  $\vec{v}$  giving same  $v$ , must be the set of vectors that lives on a surface of a sphere (in velocity space) with radius  $v$ :  $4\pi v^2$ . Using Boltzman factor and normalizing to determine  $P(v)$  we get the Boltzman distribution for the speeds of molecules in an ideal gas:  $D(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}$

**6.5 Partition Functions and Free Energy** System in contact with reservoir, fixed  $T$ ,  $Z(T)$  analogous to  $\Omega(U)$  for isolated system, fixed  $U$ .  $F = U - TS = -kT \ln Z$   $F$  tends to decrease.  $S = -\left(\frac{\delta F}{\delta T}\right)_{V,N}$   $P = -\left(\frac{\delta F}{\delta V}\right)_{T,N}$   $\mu = \left(\frac{\delta F}{\delta N}\right)_{V,T}$

**6.6 Partition Functions for Composite Systems** Noninteracting, distinguishable particles:  $Z_{total} = Z_1 Z_2 \dots Z_N$  Noninteracting, indistinguishable particles:  $Z_{total} = \frac{1}{N!} Z_1^N$  where  $N!$  = the number of ways to interchange  $N$  particles with each other. OBS: this assumes no particles in the same state - assumption OK for low density systems. Single-particle state = state of individual particle, system state = state of the entire system.

**6.7 Ideal Gas Revisited**  $E(s) = E_{tr}(s) + E_{int}(s)$ .  $E_{tr}$  = molecule's translational KE.  $E_{int}$  = internal (see

sec 2.6), may be rotational, vibrational.. (these states can again have various electronic states).  $Z_1 = Z_{tr} Z_{int}$  Find  $Z_{tr}$ : Count the independent definite  $E$  wavefunctions - start with molecule confined to 1D box. Allowed standing wave patterns limited to wavelengths  $\lambda_n = \frac{2L}{n}$ ,  $n=1,2,\dots$  de Broglie gives  $p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$  Then for nonrelativistic particle  $E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2}$  Then  $Z_{1d} = \sum_n e^{-E_n/kT} \approx \int_0^\infty e^{-h^2 n^2 / 8mL^2 kT} dn = \frac{L}{l_Q}$  (Approximate to integral in limit where neither  $L$  nor  $T$  extremely small.) Where  $l_Q = \frac{h}{\sqrt{2\pi mkT}}$  is the quantum length, aside from  $\pi$  factor the de Broglie w.l. of particle w/mass  $m$ , KE  $kT \rightarrow \frac{L}{l_Q}$  is ca number of de Broglie wavelengths to fit inside the box. In 3D:  $E_{tr} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$ . Since  $n$ 's for the 3 p components can be chosen independently can again factor  $Z$ :  $Z_{tr} = \sum_s e^{-E_{tr}/kT} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-E_{tr}/kT} = \frac{L_x}{l_Q} \frac{L_y}{l_Q} \frac{L_z}{l_Q} = \frac{V}{v_Q}$ .

**7 Quantum Statistics 7.1 The Gibbs Factor** Gibbs factor =  $e^{-[E(s) - \mu N(s)]/kT}$

**7.2 Bosons and Fermions** Condition for previous  $Z$  expression: No particles in same state. This is not true for bosons. However, can be ignored if number of available single-particle states » number of particles:  $Z_1 \gg N$ , that is average distance between particles » average de Broglie w.l.:  $V/N \gg v_Q$  Condition depends on system's density, temperature and particle's mass.

**7.3 Degenerate Fermi Gass**

$D(n)dn = D(\epsilon)d\epsilon$  **7.4 Blackbody Radiation 7.6: Bose-Einstein Condensation**