Units and Values

Avogradro's number: $N_A = 6.023 \times 10^{23}$
Boltzmann's cosntant: $k = 1.381 \times 10^{-23} J/K$,
$R = 8.31 J/K$mol, $nR = Nk$.
Calorie: 1cal = 4.2J (amount of heat needed to raise the temperature of a gram of water by $1C$.)
Absolute zero: $0K = -273.15C$.

Definitions

Isotherm: constant temperature
Isobar: constant pressure
Isothermal compression: so slow that temperature does not rise
Adiabatic compression: so fast heat does not escape
fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible microstates are equally probable
thermodynamic limit: Let number of particles go to infinity

Important formulas

$$\Omega_{total}(N, n) = \Omega_A(N, n)\Omega_B(N, n)$$
$$N! \approx N^N e^{-N}\sqrt{2\pi N}$$
$$\ln(N!) \approx N \ln N - N$$
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} \quad \text{(isolated system)}$$
$$\text{Clausius} \quad \Delta S \geq \frac{dQ}{T} \rightarrow TdS = dU + pdV \quad \text{reversible}$$
$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$
$$C_V \rightarrow \text{constant} \quad \text{as} \quad T \rightarrow \infty$$
$$\Delta S = 0 \quad \rightarrow \quad \text{reversible}$$
$$\Delta S \geq 0 \quad \rightarrow \quad \text{irrreversible}$$

Important facts

- Macrostates with maximum multiplicity are the most likely and they correspond to the average values

Ideal Gas

Low density gas $PV = NkT$, ignore particle interactions. $\langle v^2 \rangle = 3kT/m$. Compression $W = NkT \ln V_i/V_f$. For indistinhuishable particles (we get $1/N!$)

$$\Omega(U, V, N) = f(N)V^N U^{3N/2} \approx \frac{V^N}{N!(3N/2)!}(2\pi mU/h^2)^{3N/2}$$
$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$
$$\Delta S = Nk \ln V_f/V_i \quad (U, N \text{ fixed})$$

Equipartition theorem

For each quadratic degree of freedom (kinetic v^2, spring k^2, rotational ω^2, etc.) contributes to $1/2kT$ to the average energy at equillibrium at temperature T. For N particles with f degrees of freedom $U = NfkT/2$. Safest to apply in changes of energy. Coutning f: one for each dimension, 2 from rotation (as one axis is symmetric), vibrateing counts twice (frozen out at room temperature) in a solid 3 vibrational directions $f+ = 6$. Equipartition theorem only works for kinetic energy in liquids. Use $f = 3$ for a monatmoic gas and $f = 5$ for a diatomic gas.

Derived by Boltzmannfactors $e^{-a\beta x^2}/Z$ and computing average of energy.

Heat and Work

$$\Delta U = Q + W \quad (1)$$

Assuming quasistatic compression $W = -P\delta V$. Use pressure from POV of gas, negative work means gas is doing work, positive work means the outside is doing work on the gas.

$$W = -\int_{V_i}^{V_f} P(V)dV \text{ quasistatic}$$

Heat Capacity

Heat capacity: amount of heat needed to raise temperature per degree temperature increase $C = Q/\Delta T$.
Specific heat capacity: Heat capacity per unit mass $c = C/m$.

$$C = (\Delta U - W)/\Delta T, C_V = \left(\frac{\partial U}{\partial T}\right)_V, C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)$$

At the phase transition you can put heat into system without increasing temperature, $C = \infty$. Latent heat $L = Q/m$ is the heat needed to accomplish phase transition per mass, assume constant pressure 1atm, and no other work.

Adiabatic compression

So fast no heat flows out, still quasistatic, $\Delta U = W$. $V^\gamma P = $ constant , $\gamma = (f + 2)/f$

Two state system

Multiplicity of the macrostate with N particles where $N_\uparrow$ point up

$$\Omega(N, n) = \frac{N!}{N_\uparrow!(N - N_\uparrow)!} = \frac{N!}{N_\uparrow!N_\downarrow!} \quad (2)$$

Einstein solid

$N/3$ atoms as harmonic oscillators which can oscillate in 3 dimensions with $q = (U_n - N\hbar\omega/2)/\hbar\omega$ units of energy

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \approx \frac{(q + N)!}{q!N!}N_\downarrow! \quad (3)$$

If a composite system: $q = q_A + q_B$ and $N = N_a + N_b$ and $\Omega = \Omega_A\Omega_B$.

$$\text{low } T \quad \Omega \approx \left(\frac{Ne}{q}\right)^q, \quad q << N$$
$$\text{high } T \quad \Omega \approx \left(\frac{qe}{N}\right)^N, \quad N << q$$
$$S = kN\left[\ln\left(\frac{q}{N} + 1\right)\right], \quad q = U/\hbar\omega$$

Van der Waals Equation

Low density gas $PV = NkT$, ignore particle interactions. $\langle v^2 \rangle = 3kT/m$. Compression $W = NkT \ln V_i/V_f$.

THERMODYNAMIC POTENTIALS

Enthalpy

In addition to talking about the energy of system we add the work needed to make room for it

$$H = U + PV \quad (4)$$

Energy needed to create the system out of nothing, and make room for it. $\Delta H = \Delta U + P\Delta V$. $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

Tricks

$$\sum_n^N \frac{N!}{n!(N - n)!}a^N b^{N-n} = (a + b)^N$$
$$\sum_n^N n\frac{N!}{n!(N - n)!}a^N b^{N-n} = a\frac{\partial}{\partial a}\sum_n^N \frac{N!}{n!(N - n)!}a^N b^{N-n}$$
$$Rp^R = p\frac{\partial}{\partial p}R^p$$

Taylor expansions

$$\ln 1 + x \approx x - x^2/2$$