1 Energy in Thermal Dynamics

Exchanged Quantity	Type of Equilibrium
energy	thermal
volume	mechanical
particles	diffusive

1.1 Ideal Gas

Ideal gas law

$$PV = nRT = NkT \tag{1}$$

$$N = nN_A, \qquad R = 8.31 J/mol \cdot K, \qquad N_A = 6.02 \cdot 10^{23} \qquad k = R/N_A = 1.381 \cdot 10^{-23} J/K \tag{2}$$

1.1.1 Microscopical Model

$$\bar{P} = \frac{\bar{F}_{\text{x, on piston}}}{A} = \frac{-\bar{F}_{\text{x, on particle}}}{A} = -\frac{m\left(\frac{\bar{\Delta v_x}}{\Delta t}\right)}{A} = \frac{mv_x^2}{V} \tag{3}$$

$$\Delta t = 2L/v_x, \qquad \Delta v_x = -2v_x \tag{4}$$

$$PV = Nm\bar{v}_x^2 \Rightarrow \overline{\frac{1}{2}mv_x^2} = \frac{1}{2}kT \Rightarrow \overline{K}_{trans} = 3 \cdot \frac{1}{2}kT \tag{5}$$

$$v_{rms} = \sqrt{\bar{v^2}} = \sqrt{\frac{3kT}{m}} \tag{6}$$

1.2 Equipartition Theorem

$$U_{thermal} = N \cdot f \cdot \frac{1}{2}kT \tag{7}$$

1.3 Heat and Work

Temperature: measure of the tendency of an object to spontaneously give up energy to its surroundings. **Heat**: any spontaneous flow of energy from one object to another, caused by a difference in temperatures. **Work**: any other transfer of energy in or out of the system.

$$\Delta U = Q + W \tag{8}$$

1.4 Compression Work

$$W = -P\Delta V \text{ (for quasistatic compression)} \tag{9}$$

With $P(V)$

$$W = -\int_{V_i}^{V_f} P(V)dV \tag{10}$$

1.4.1 Compression of Ideal Gas

$$W = NkT \ln\frac{V_i}{V_f} \Rightarrow Q = \Delta U - W = \Delta(1/2NfkT) - W = W = NkT \ln\frac{V_f}{V_i} \tag{11}$$

For adiabatic compression:

$$\Delta U = W \Rightarrow dU = \frac{1}{2}fnkdT = -PdV \Rightarrow \frac{f}{2}\frac{dT}{T} = -\frac{dV}{V} \tag{12}$$

$$V_f T_f^{f/2} = V_i T_i^{f/2} = \text{constant}, \qquad VT^{f/2} = \text{constant}, \qquad V^\gamma P = \text{constant} \tag{13}$$

$\gamma = (f+2)/f$ is the adiabatic exponent.

1.5 Heat Capacity

$$C = \frac{Q}{\Delta T} \text{ (heat capacity)}, \qquad c = \frac{C}{m} \text{ (specific heat capacity)} \tag{14}$$

$$C = \frac{Q}{\Delta T} = C = \frac{\Delta U - W}{\Delta T} \tag{15}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \qquad C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{16}$$

1.5.1 For Ideal Gas

$$C_V = \frac{\partial}{\partial T}\frac{NfkT}{2} = \frac{Nfk}{2}, \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\frac{NkT}{P} = \frac{Nk}{P} \Rightarrow C_P = C_V + Nk = C_V + nR \tag{17}$$

rule of Dulong And Petit: heat capacity of solid should go towards $3R$

1.6 Latent Heat

For phase transformation

$$L = \frac{Q}{m} \tag{18}$$

To accomplish the transformation.

1.7 Enthalpy

Total energy one has to come up with to create the system and put it into the environment

$$H = U + PV \tag{19}$$

$$\Delta H = \Delta U + P\Delta V = Q + W_{other} \text{ (constant P)} \tag{20}$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{21}$$

1.8 Rates of Processes

1.8.1 Heat Conduction

$$Q \propto \frac{A\Delta T\Delta t}{\Delta x} \Rightarrow \frac{Q}{\Delta t} = -k_t A\frac{dT}{dx} \tag{22}$$

Fourier heat conduction law

1.8.2 Conductivity of Idea Gas

$$\ell \approx \frac{1}{4\pi r^2}\frac{V}{N}, \qquad Q = -\frac{1}{2}C_V\ell\frac{dT}{dx}, \qquad k_t = \frac{1}{2}\frac{C_V}{V}\ell\bar{v} \tag{23}$$

$$\bar{v} \propto \sqrt{T} \tag{24}$$

1.8.3 Viscosity

$$F_x \propto \frac{A \cdot (u_{x,top} - u_{x,bottom})}{\Delta z} \Rightarrow \frac{|F_x|}{A} = \eta\frac{du_x}{dz} \tag{25}$$

1.8.4 Diffusion

$$J_x = -D\frac{dn}{dx} \tag{26}$$

J_x, flux has units number of particles per unit area per unit time.

2 The Second Law

2.1 Two-State System

$$\text{probability of n heads} = \frac{\Omega(n)}{\Omega(all)} \tag{27}$$

$$\Omega(N,n) = \frac{N!}{n!(N-n)!} = \binom{N}{n} \tag{28}$$

For paramagnet

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{29}$$

For Einstein Solid

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \tag{30}$$

N is oscillators, q is energy units.

2.2 Interacting Systems

$$N_A = N_B, \qquad q_{total} = q_A + q_B \tag{31}$$

Fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

2.3 Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}, \qquad \ln N! \approx N \ln N - N \tag{32}$$

2.4 Multiplicity of a Large Einstein Solid

$$\Omega(N,q) \approx \frac{(q+N)!}{q!N!} \tag{33}$$

$$\ln \Omega \approx N \ln \frac{q}{N} + N + \frac{N^2}{q} \tag{34}$$

(Remember to use $\ln(x+1) \approx x$.)

$$\Rightarrow \Omega(N,q) \approx e^{N\ln(q/N)} e^N = \left(\frac{eq}{N}\right)^N, \qquad q >> N \tag{35}$$

$$\text{width of peak} = \frac{q}{\sqrt{N}} \tag{36}$$

2.5 Ideal Gas

$$\Omega_1 \propto V \cdot V_p, \qquad 2mU = p_x^2 + p_y^2 + p_z^2, \qquad \Delta x \Delta p \approx h \tag{37}$$

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \cdot A_{hypersphere}, \qquad A_{hypersphere} = \frac{2\pi^{d/2}}{(d/2-1)!} r^{r-1} \tag{38}$$

$$\Omega(U,V,N) = f(N) V^N U^{3N/2} \tag{39}$$

2.5.1 Interacting Ideal Gas

$$\Omega_{total} = (f(N))^2 (V_A V_B)^2 (U_A U_B)^{3N/2} \tag{40}$$

$$\text{width of peak} = \frac{U_{total}}{\sqrt{3N/2}} \tag{41}$$

If can exchange volume:

$$\text{width of peak} = \frac{V_{total}}{\sqrt{N}} \tag{42}$$

2.6 Entropy

$$S = k \ln \Omega \tag{43}$$

2.7 Entropy of Ideal Gas

Monatomic ideal gas, Sackur-Tetrode eq:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{44}$$

For U, N fixed:

$$\Delta S = Nk \ln \frac{V_f}{V_i} \tag{45}$$

3 Interactions and Implications

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \tag{46}$$

at equilibrium.

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N,V} \tag{47}$$

3.1 Entropy and Heat

3.1.1 Predicting Heat capacity

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} \tag{48}$$

Algorithm:

- Use QM and some combinations to find an expression for Ω, in terms of U, V and N, and any other relevant variables
- Take to logarithm to find S
- Differentiate S with respect to U and the the reciprocal to find the temperature T as a function of U and other variables.

3.1.2 Measuring Entropies

For constant(or quatistatic) volume and no work

$$dS = \frac{dU}{T} = \frac{Q}{T} \tag{49}$$

More general

$$dS = \frac{C_V dT}{T}, \qquad \Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT, \qquad S - S(0) = \int_{T_i}^{0} \frac{C_V}{T} dT \tag{50}$$

Third law: $T \to 0 \Rightarrow S \to 0$

3.2 Paramagnetism

$$U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow), \qquad M = \mu(N_\uparrow - N_\downarrow) = -\frac{U}{B} \tag{51}$$

3.2.1 Analytic Solution

$$S/k \approx N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow) \tag{52}$$

$$\frac{1}{T} = \frac{k}{2\mu B} \ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right) \tag{53}$$

$$U = N\mu B \left(\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}}\right) = -N\mu B \tanh\frac{\mu B}{kT}, \qquad M = N\mu \tanh\frac{\mu B}{kT} \tag{54}$$

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk\frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)} \tag{55}$$

Bohr magnetron

$$\mu_B = \frac{eh}{4\pi m_e} = 9.274 \cdot 10^{-24} J/T = 5.788 \cdot 10^{-5} eV/T \tag{56}$$

For $\mu B/kT << 1$

$$M \approx \frac{N\mu^2 B}{kT} \Rightarrow M \propto 1/T \tag{57}$$

Curie's law.

3.3 Summery

Thermodynamic identity

$$dU = TdS - PdV + \mu dN \tag{58}$$

VNP :

Type of interaction	Exchange quantity	Governing variable	Constant	Formula
thermal	energy	temperature	V,N	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$
mechanical	volume	pressure	U,N	$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$
diffusive	particles	chemical potential	U,V	$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$

4 Engines and Refrigerators

4.1 Heat Engines

efficiency

$$e \equiv \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_h} \tag{59}$$

Q_h is heat from the hot reservoir with temperature T_h, and Q_c from the cold reservoir with temperature T_c.

$$Q_h = Q_c + W, \qquad e = 1 - \frac{Q_c}{Q_h} \tag{60}$$

From second law

$$S_c \geq S_h \Rightarrow \frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \Rightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h} \tag{61}$$

$$\Rightarrow e \leq 1 - \frac{T_c}{T_h} \tag{62}$$

4.2 Refrigerators

coefficient of preference:

$$COP \equiv \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W} \tag{63}$$

From first law $Q_h = Q_c + W$ we get

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1} \tag{64}$$

From second law (61) we get

$$COP \leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c} \tag{65}$$