

1 Energy in Thermal Dynamics

Exchanged Quantity	Type of Equilibrium
energy	thermal
volume	mechanical
particles	diffusive

1.1 Ideal Gas

Ideal gas law

$$PV = nRT = NkT \quad (1)$$

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

1.1.1 Microscopical Model

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

$$\Delta t = 2L/v_x, \quad \Delta v_x = -2v_x \quad (4)$$

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

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

1.2 Equipartition Theorem

$$U_{thermal} = N \cdot f \cdot \frac{1}{2}kT \quad (7)$$

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.

$$\Delta U = Q + W \quad (8)$$

1.4 Compression Work

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

With $P(V)$

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

1.4.1 Compression of Ideal Gas

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

For adiabatic compression:

$$\Delta U = W \Rightarrow dU = \frac{1}{2}fNkdT = -PdV \Rightarrow \frac{f}{2} \frac{dT}{T} = -\frac{dV}{V} \quad (12)$$

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

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

1.5 Heat Capacity

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

$$C = \frac{Q}{\Delta T} = C = \frac{\Delta U - W}{\Delta T} \quad (15)$$

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

1.5.1 For Ideal Gas

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

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

1.6 Latent Heat

For phase transformation

$$L = \frac{Q}{m} \quad (18)$$

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

$$H = U + PV \quad (19)$$

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

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

1.8 Rates of Processes

1.8.1 Heat Conduction

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

Fourier heat conduction law

1.8.2 Conductivity of Idea Gas

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

$$\bar{v} \propto \sqrt{T} \quad (24)$$

1.8.3 Viscosity

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

1.8.4 Diffusion

$$J_x = -D \frac{dn}{dx} \quad (26)$$

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

2 The Second Law

2.1 Two-State System

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

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

For paramagnet

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

For Einstein Solid

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

N is oscillators, q is energy units.

2.2 Interacting Systems

$$N_A = N_B, \quad q_{\text{total}} = q_A + q_B \quad (31)$$

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

2.3 Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}, \quad \ln N! \approx N \ln N - N \quad (32)$$

2.4 Multiplicity of a Large Einstein Solid

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

$$\ln \Omega \approx N \ln \frac{q}{N} + N + \frac{N^2}{q} \quad (34)$$

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

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

$$\text{width of peak} = \frac{q}{\sqrt{N}} \quad (36)$$

2.5 Ideal Gas

$$\Omega_1 \propto V \cdot V_p, \quad 2mU = p_x^2 + p_y^2 + p_z^2, \quad \Delta x \Delta p \approx h \quad (37)$$

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

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

2.5.1 Interacting Ideal Gas

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

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

If can exchange volume:

$$\text{width of peak} = \frac{V_{total}}{\sqrt{N}} \quad (42)$$

2.6 Entropy

$$S = k \ln \Omega \quad (43)$$

2.7 Entropy of Ideal Gas

Monatomic ideal gas, Sackur-Tetrode eq:

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

For U , N fixed:

$$\Delta S = Nk \ln \frac{V_f}{V_i} \quad (45)$$

3 Interactions and Implications

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad (46)$$

at equilibrium.

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

3.1 Entropy and Heat

3.1.1 Predicting Heat capacity

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

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 quastistic) volume and no work

$$dS = \frac{dU}{T} = \frac{Q}{T} \quad (49)$$

More general

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

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

3.2 Paramagnetism

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

3.2.1 Analytic Solution

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

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

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

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

Bohr magnetron

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

For $\mu B/kT \ll 1$

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

Curie's law.

3.3 Summery

Thermodynamic identity

$$dU = TdS - PdV + \mu dN \quad (58)$$

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

$$e \equiv \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_h} \quad (59)$$

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

$$Q_h = Q_c + W, \quad e = 1 - \frac{Q_c}{Q_h} \quad (60)$$

From second law

$$S_c \geq S_h \Rightarrow \frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \Rightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h} \quad (61)$$

$$\Rightarrow e \leq 1 - \frac{T_c}{T_h} \quad (62)$$

4.2 Refrigerators

coefficient of preference:

$$COP \equiv \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W} \quad (63)$$

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

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1} \quad (64)$$

From second law (61) we get

$$COP \leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c} \quad (65)$$

5 Free Energy and Chemical Thermodynamics

5.1 Free Energy as Available Work

Helmholtz Free Energy: Total energy needed to create the system, minus the heat you can get from the environment for free at temperature T . For constant T :

$$F = U - TS, \quad \Delta F = \Delta U - T\Delta S = Q + W - T\Delta S \quad (66)$$

For constant P and T , the work of a system is Gibbs Free Energy

$$G = H - TS = U - TS + PV, \quad \Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V \quad (67)$$

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5.2 Thermodynamic Identities

$$dU = TdS - PdV + \mu dN \quad (68)$$

$$dH = dU + PdV + VdP = TdS + VdP + \mu dN \quad (69)$$

$$dF = dU - TdS - SdT = -SdT - PdV + \mu dN \quad (70)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad (71)$$

$$dG = -SdT + VdP + \mu dN \quad (72)$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \quad (73)$$

5.3 Free Energy as a Force towards Equilibrium

$$dS_{total} = dS + dS_R, \quad dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (74)$$

$$dS_R = dU_T/T_R$$

$$dS_{total} = dS + \frac{1}{T_R}dU_R \quad (75)$$

$$dU_R = -dU$$

$$dS_{total} = dS - \frac{1}{T}dU = -\frac{1}{T}(dU - TdS) = -\frac{1}{T}dF \quad (76)$$

This is for constant T , V and N . For constant P

$$dS_{total} = -\frac{1}{T}dG \quad (77)$$

5.4 Extensive and Intensive Quantities

Double the amount of stuff: Quantities that doubles are extrinsic; those who do not are intensive. **Extensive:** V, N, S, U, H, F, G, mass. **Intensive:** T, P, μ , density. Extensive \times intensive = extensive. Extensive \times extensive = neither. Type \times same type = same type. Extensive + intensive is not allowed.

5.5 Gibbs Free Energy and Chemical Potential

Given constant T and P we have that

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P} \Rightarrow G = N\mu \text{ or } G = \sum_i N_i \mu_i \quad (78)$$

$$\Rightarrow \frac{\partial \mu}{\partial P} = \frac{\partial}{\partial P} \frac{G}{N} = \frac{V}{N} = \frac{kT}{P} \quad (79)$$

Integrating

$$\mu(T, P) = \mu^\circ(T, P) + kT \ln \frac{P}{P^\circ} \quad (80)$$

P° is the atmospheric pressure, and μ° is μ at this pressure and can be found in tables for for atmospheric pressures ($\mu = G/N$). For a mixture P is the partial pressure of that gas.

5.6 Phase Transformations of Pure Substances

Vapor pressure: Pressure at which a gas can coexist with its solid or liquid phase. **Triple point:** Point where all three phases can coexist. **Critical Point:** No longer a discontinuous change from liquid to gas. **Curie Temperature:** Temperature where magnetization disappears, so the phase boundary ends at a critical temperature.

5.7 Diamonds and Graphite

At a given temperature and pressure, the stable phase is always the one with the lower Gibbs free energy

To find the most stable state, use:

$$\left(\frac{\partial G}{\partial V} \right)_{T,N} = -P, \quad \left(\frac{\partial G}{\partial T} \right)_{P,N} = -S \quad (81)$$

Since graphite has more volume and entropy its Gibbs free energy increases more with pressure and decreases more with temperature. Thus raising the pressure makes diamonds more stable, and with higher temperature higher pressure is needed.

5.8 Clausius-Clapeyron Relation

$$G_l = G_g \quad (82)$$

at phase boundary. $dG_l = dG_g$ to remain at phase boundary. Thus

$$-S_l dT + V_l dP = -S_g dT + V_g dP \quad (83)$$

$$\Rightarrow \frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T\Delta V} \quad (84)$$

using the (total) latent heat $S_g - S_l = L/T$ and $V_g - V_l = \Delta V$. This is the Clausius-Clapeyron Relation.

5.9 The van der Waals Model

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \quad (85)$$

$$\text{total potential pressure} = -\frac{aN^2}{V} \Rightarrow P_{\text{due to p.e.}} = -\frac{d}{dV} \left(-\frac{aN^2}{V}\right) = -\frac{aN^2}{V^2} \quad (86)$$

attractive force: $NkT/(V - Nb)$:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \quad (87)$$

$$G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T) \quad (88)$$

$$0 = \int_{loop} dG = \int_{loop} \left(\frac{\partial G}{\partial P}\right)_T dP = \int_{loop} V dP \quad (89)$$

$$V_c = 3Nb, \quad P_c = \frac{1}{27} \frac{a}{b^2}, \quad kT_c = \frac{8}{27} \frac{a}{b} \quad (90)$$

5.10 Chemical Equilibrium

$$0 = dG = \sum_i \mu_i dN_i \quad (91)$$

Le Chatelier's Principle: When you disturb a system in equilibrium, it will respond in a way that partially offsets the disturbance.

5.11 Ionization of Hydrogen

$$H \leftrightarrow p + e \quad (92)$$

Saha equation:

$$\frac{P_p}{P_H} = \frac{kT}{P_e} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-I/kT} \quad (93)$$