

1 The Basic Structure of Thermodynamics

1.1 Problems and Postulates

1. Many DOFs \rightarrow few thermodynamic variables
2. Extensive variables: V, N, U
3. Conservation of energy (kinetic, potential, mass, light, ...)
 - (a) Consequence of time-reversal symmetry
4. **Postulate 1:** The “equilibrium” states of simple and homogeneous systems are fully characterized by U, V, N_j
 - (a) Examples
5. Definitions
 - (a) System and environment
 - (b) Walls - permeable and impermeable; adiabatic and diathermal
6. Work and heat - inexact differentials, path dependent
7. Internal energy $dU = \delta q + \delta W$
8. Mechanical measurement of energy, work $W = - \int P_{\text{ext}} dV$
9. Processes - Spontaneous, quasi-static, reversible
10. **Postulate 2:** A state function entropy S exists and is maximized at equilibrium
 - (a) The “fundamental” equation
11. **Postulate 3:** S is a nice, extensive, homogeneous function, monotonically increasing in U , $\partial S / \partial U \geq 0$
12. **Postulate 4:** Entropy vanishes at $T = 0$, third law of thermodynamics
13. Three overarching questions:
 - (a) Characterize thermodynamic equilibrium state of a system (gas, liquid, interface, ...)
 - (b) Determine new equilibrium state when a constraint is removed
 - (c) Determine (path dependent) effect on environment of moving between two equilibrium states.
 - (d) *Bonus problem:* Relate macroscopic to microscopic behavior
14. Impossible, reversible, quasi-static, and real processes

1.2 Interlude: Multivariate calculus

1. Partial derivatives

2. State functions and exact differentials: $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$

3. Fun with partial differentials

$$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1 \quad \left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial x}{\partial f}\right)_y^{-1} \quad \left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial t}\right)_y / \left(\frac{\partial x}{\partial t}\right)_y$$

4. Homogeneous functions of order n : $f(\lambda x, \lambda y) = \lambda^n f(x, y)$

(a) Thermodynamic state functions (extensive quantities) are homogeneous order 1

(b) First derivatives (intensive quantities) are homogeneous order 0

5. Euler relation: $= \left(\frac{\partial f}{\partial x}\right)_y x + \left(\frac{\partial f}{\partial y}\right)_x y$

1.3 Calculus of energy, entropy, and equilibrium

1. $U = U(S, V, N)$ state function (Table~1)

(a) Molar state function $u(s, v) = U(S/N, V/N, 1)/N$

2. Partial derivatives of U : intensive variables temperature, pressure, and chemical potential

3. Equations of state relate intensive variables

4. Euler relation

5. Entropy representation $S = S(U, V, N)$, $s = s(u, v)$

6. Thermal, mechanical, chemical equilibrium determined by equality of T , P , μ_i

7. Gibbs-Duhem relationship between intensive variables

$$(a) \quad SdT - VdP + \sum_i N_i d\mu_i = 0$$

1.4 Ideal and van der Waals gases

1. Ideal gas EOS $Pv = RT$, $u = cRT$

(a) Fundamental equation $s(u, v) = cR \ln(u/u_0) + R \ln(v/v_0) + s_0(u_0, v_0)$

2. Generalized ideal gas

(a) $Pv = RT$ and $u(T) = u_0 + \int_{T_0}^T c_v^*(T) dT$

(b) $\kappa_T = 1/P$, $\alpha = 1/T$, $c_p^* = c_v^* + R$

3. Isothermal process ($\Delta T = 0$)

(a) Ideal gas: $\Delta u = 0$, $\Delta s = R \ln(v/v_0)$, $q_{QS} = RT \ln(v/v_0) = -w_{QS}$

Table 1: Thermodynamic Potentials

$U = U(S, V, N)$	$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum \left(\frac{\partial U}{\partial N_i}\right)_{S,V} dN_i$ $dU = TdS - PdV + \sum \mu_i dN_i$ $U = TS - PV + \sum \mu N$
$S = S(U, V, N)$	$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \sum \left(\frac{\partial S}{\partial N_i}\right)_{U,V} dN_i$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum \frac{\mu_i}{T}dN_i$ $S = U/T + PV/T + \sum \mu_i N_i/T$
$H = H(S, P, N)$	$H = U + PV$ $dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \sum \left(\frac{\partial H}{\partial N_i}\right)_{S,P} dN_i$ $dH = TdS + VdP + \sum \mu_i dN_i$ $H = TS + \sum \mu_i N_i$
$F = F(T, V, N)$	$F = U - TS$ $dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \sum \left(\frac{\partial F}{\partial N_i}\right)_{T,V} dN_i$ $dF = -SdT - PdV + \sum \mu_i dN_i$ $F = PV + \sum \mu_i N_i$
$G = G(T, P, N)$	$G = U - TS + PV$ $dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \sum \left(\frac{\partial G}{\partial N_i}\right)_{T,P} dN_i$ $dG = -SdT + VdP + \sum \mu_i dN_i$ $G = \sum \mu_i N_i$

4. Adiabatic ($\Delta s = 0$) processes(a) Ideal gas adiabats ($\gamma = (c + 1)/c$): $Pv^\gamma = c$, $Tv^{\gamma-1} = c'$, $P^{(1-\gamma)/\gamma}T = c''$ (b) $w_{QS} = RT_0 [1 - (v/v_0)^{1-\gamma}] / (1 - \gamma)$, $q_{QS} = 0$

5. Free expansion: heat but no light!

6. van der Waals gas

(a) $P_{vdW} = RT/(v - b) - a/v^2$ and $u = cRT - a/v$ (b) Fundamental equation $s(u, v) = cR \ln((u + a/v)/(u_0 + a/v_0)) + R \ln((v - b)/(v_0 - b)) + s_0(u_0, v_0)$

(c) Simplest “cubic” EOS that gives qualitatively correct fluid properties

i. Coexistent of two phases

ii. Critical point (T_c, P_c, v_c) where two phases coalesce into one**1.5 Work and efficiency**

1. Maximum work theorem: maximum work is delivered by a process that overall produces zero entropy

(a) $dU_{\text{sys}} + \dot{d}q_{\text{rhs}} + \dot{d}w_{\text{rws}} = 0$, $dS_{\text{sys}} + dS_{\text{rhs}} = dS_{\text{sys}} + \dot{d}q_{\text{rhs}}/T_{\text{rhs}} = 0$

(b) Tells us what is possible, not how to achieve it!

2. Examples: expansion with a low T reservoir, separation, cooling water

3. Thermodynamic engines operate cyclically to convert heat to work or use work to move heat

4. Carnot efficiency and Carnot cycle, $\eta = 1 - T_c/T_h$ **1.6 Other thermodynamic potentials**

1. Energy minimum principle minimum at constant entropy

2. Legendre transforms

(a) $Y = Y(X) \rightarrow \psi(P) = Y(P) - PX(P)$ $P = \partial Y / \partial X$ (b) $P, \psi(P)$ give intercept and slope of tangents of Y 3. Enthalpy $H(S, P, N) = U + PV$ (a) Minimized at constant S , P , and N (b) Heat flow when only PV work done4. Helmholtz $A(T, V, N) = U - TS$ (a) Minimized at constant T , V , and N (b) Maximum useful work from a process at temperature T 5. Gibbs $G(T, P, N) = U + PV - TS$ (a) Minimized at constant T , P , and N

Table 2: Useful Maxwell Relationships

Enthalpy	Helmholtz	Gibbs
$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_S$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Table 3: Susceptibilities

Coefficient of thermal expansion	α	$\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$	$\frac{1}{v} \left(\frac{\partial^2 g}{\partial T \partial P}\right)_N$
Isothermal compressibility	κ_T	$-\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T$	$-\frac{1}{v} \left(\frac{\partial^2 g}{\partial P^2}\right)_{T,N}$
Constant pressure heat capacity	C_p	$T \left(\frac{\partial s}{\partial T}\right)_P$	$-T \left(\frac{\partial^2 g}{\partial T^2}\right)_{P,N}$
Constant volume heat capacity	C_v	$T \left(\frac{\partial s}{\partial T}\right)_v$	

(b) Most useful for chemical problems

(c) Gibbs-Helmholtz $\left(\frac{\partial(G/T)}{\partial T}\right)_{P,N} = -\frac{H}{T^2}$

6. Alles potential

(a) Gibbs-Duhem redux

7. Maxwell relations, see Table 2.

8. Three unique susceptibilities of a one-component material (Table 3)

(a) All thermodynamic properties can be described in terms of the susceptibilities

(b) Integrating susceptibilities

(c) Heat capacity and departure functions

9. Using thermodynamic relations

(a) Joule-Thompson effect

1.7 Stability and phase equilibria

1. Local stability condition

(a) (Free) energy minimized $dU = 0 \quad d^2U \geq 0$

(b) Entropy maximized $dS = 0 \quad d^2S \leq 0$

(c) Implies $c_p \geq c_v \geq 0, \kappa_T \geq \kappa_s \geq 0$

(d) Microscopic fluctuations and Le'Chatlier's principle

2. Global stability conditions

- (a) Common tangents and convex hull
- (b) Lever rule
- (c) Phase separation—two phases have lower free energy than one. Balance of energetic attractions and entropic “repulsion”
- (d) Critical points ($d^3u = 0$) attraction and repulsion exactly in balance
- (e) Stable, metastable (spinodal), and unstable regions
 - i. Extensive quantities discontinuous between phases (“latent” quantities)
 - ii. Intensive quantities equal between phases
 - iii. Susceptibilities discontinuous between phases

3. Gibbs-Duhem integrations

- 4. Equal area construction, $d\mu = v dP$ along an isotherm
- 5. $d\mu = -s dT$, chemical potential of each phase decreases with T
- 6. Phase diagrams—lines of equal chemical potential, $\mu(l) = \mu(v)$
- 7. Clausius equation
 - (a) Along coexistence line $dP/dT = \Delta s/\Delta v = \Delta h/T\Delta v$ in general
 - (b) Clausius-Clapeyron for ideal vapor $d \ln P/d(1/T) = -\Delta h/R$
- 8. Gibb’s phase rule and triple point
 - (a) $DOF = c - \pi - R + 2$

2 The Microscopic View

2.1 Micro-canonical ensemble

2.1.1 Energy is *quantized* at microscopic level

- 1. Consequence of quantum mechanics
- 2. electronic, vibrational, rotational, translational
- 3. Need machinery to average QM information over macroscopic systems
- 4. Equal *a priori* probabilities

2.1.2 Two-state model

- 1. Box of particles, each of which can have energy 0 or ϵ
- 2. Thermodynamic state defined by number of elements N , and number of quanta q , $U = q\epsilon$
- 3. Degeneracy of given N and q given by binomial distribution:

$$\Omega = \frac{N!}{q!(N-q)!}$$

4. Allow energy to flow between two such systems

- (a) Energy of a closed system is conserved (first law!)
- (b) Degeneracy of total system is always \geq degeneracy of the starting parts!
- (c) Boltzmann's tombstone, $S = k_B \ln \Omega$
- (d) Clausius: entropy of the universe seeks a maximum! Second Law...

5. Energy flow/thermal equilibrium between two large systems

- (a) Each subsystem has energy U_i and degeneracy $\Omega_i(U_i)$
- (b) Bring in thermal contact, $U = U_1 + U_2$, $\Omega = \Omega_1(U_1)\Omega_2(U_2)$
- (c) If systems are very large, one combination of U_1 , U_2 and Ω will be much more probably than all others
- (d) What value of U_1 and $U_2 = U - U_1$ maximizes Ω ?

$$\left(\frac{\partial \ln \Omega_1}{\partial U_1}\right)_N = \left(\frac{\partial \ln \Omega_2}{\partial U_2}\right)_N$$

$$\left(\frac{\partial S_1}{\partial U_1}\right)_N = \left(\frac{\partial S_2}{\partial U_2}\right)_N$$

1. Thermal equilibrium is determined by equal **temperature!**

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

- (a) When the temperatures of the two subsystems are equal, the entropy of the combined system is maximized!
- (b) (Same arguments lead to requirement that equal pressures (P_i) and equal chemical potentials (μ_i) maximize entropy when volumes or particles are exchanged)

2.1.3 Two-state model in limit of large N

- 1. Large N and Stirling's approximation
- 2. Fundamental thermodynamic equation of two-state system:

$$S(U) = -k_B (x \ln x + (1-x) \ln(1-x)), \text{ where } x = q/N = U/N\epsilon$$

3. Temperature is derivative of entropy wrt energy yields

$$U(T) = \frac{N\epsilon}{1 + e^{\epsilon/k_B T}}$$

- (a) $T \rightarrow 0, U \rightarrow 0, S \rightarrow 0$, minimum disorder
- (b) $T \rightarrow \infty, U \rightarrow N\epsilon/2, S \rightarrow k_B \ln 2$, maximum disorder

4. Differentiate again to get heat capacity

2.2 Canonical ensemble

2.2.1 Partition function

1. Where do fundamental equations come from?
2. Direct construction of $S(U)$ is generally intractable, so seek simpler approach
3. Imagine a system brought into thermal equilibrium with a much larger “reservoir” of constant T , such that the aggregate has a total energy U
4. Degeneracy of a given system microstate j with energy U_j is $\Omega_{res}(U - U_j)$

$$T = \frac{dU_{res}}{k_B d \ln \Omega_{res}}$$

$$\Omega_{res}(U - U_j) \propto e^{-U_j/k_B T}$$

5. Probability for system to be in a microstate with energy U_j given by Boltzmann distribution!

$$P(U_j) \propto e^{-U_j/k_B T} = e^{-U_j \beta}$$

6. Partition function “normalizes” distribution, $Q(T) = \sum_j e^{-U_j \beta}$
7. For system of identical (distinguishable) elements with energy states ϵ_i , can factor probability to show

$$P(\epsilon_i) \propto e^{-\epsilon_i/k_B T} = e^{-\epsilon_i \beta}, \quad \beta = 1/k_B T$$

2.2.2 Energy factoring

1. If system is large, how to determine its energy states U_j ? There would be many, many of them!
2. One simplification is if we can write energy as sum of energies of individual elements (atoms, molecules) of system:

$$U_j = \epsilon_j(1) + \epsilon_j(2) + \dots + \epsilon_j(N) \quad (1)$$

$$Q(N, V, T) = \sum_j e^{-U_j \beta} \quad (2)$$

$$= \sum_j e^{-(\epsilon_j(1) + \epsilon_j(2) + \dots + \epsilon_j(N))\beta} \quad (3)$$

3. If molecules/elements of system can be distinguished from each other (like atoms in a fixed lattice), expression can be factored:

$$Q(N, V, T) = \left(\sum_j e^{-\epsilon_j(1)\beta} \right) \dots \left(\sum_j e^{-\epsilon_j(N)\beta} \right) \quad (4)$$

$$= q(1) \dots q(N) \quad (5)$$

$$\text{Assuming all the elements are the same:} \quad (6)$$

$$= q^N \quad (7)$$

$$q = \sum_j e^{-\epsilon_j \beta} : \text{molecular partition function} \quad (8)$$

4. *If not* distinguishable (like molecules in a liquid or gas, or electrons in a solid), problem is difficult, because identical arrangements of energy amongst elements should only be counted once. Approximate solution, good almost all the time:}

$$Q(N, V, T) = q^N / N! \quad (9)$$

5. Sidebar: “Correct” factoring depends on whether individual elements are fermions or bosons, leads to funny things like superconductivity and superfluidity.

2.2.3 Two-state system again

1. Partition function, $q(T) = 1 + e^{-\epsilon\beta}$
2. State probabilities
3. Internal energy $U(T)$

$$U(T) = -N \left(\frac{\partial \ln(1 + e^{-\epsilon\beta})}{\partial \beta} \right) = \frac{N\epsilon e^{-\epsilon\beta}}{1 + e^{-\epsilon\beta}} \quad (10)$$

4. Heat capacity C_v
 - (a) Minimum when change in states with T is small
 - (b) Maximize when change in states with T is large
5. Helmholtz energy, $A = -\ln q / \beta$, decreasing function of T
6. Entropy
7. Distinguishable vs. indistinguishable particles
 - (a) Distinguishable (e.g., in a lattice): $Q(N, V, T) = q(V, T)^N$
 - (b) Indistinguishable (e.g., a gas): $Q(N, V, T) \approx q(V, T)^N / N!$
8. Thermodynamic functions in canonical ensemble

2.3 Ideal gases redux

2.3.1 Separability

$$Q_{ig}(N, V, T) = \frac{(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}})^N}{N!}$$

2.3.2 Particle-in-a-box (translational states of a gas)

1. Energy states $\epsilon_n = n^2 \epsilon_0$, $n = 1, 2, \dots$, ϵ_0 tiny for macroscopic V
2. $\Theta_{\text{trans}} = \epsilon_0 / k_B$ translational temperature

Table 4: Equations of the Canonical (NVT) Ensemble

$\beta = 1/k_B T$	Full Ensemble	Distinguishable particles (e.g. atoms in a lattice)	Indistinguishable particles (e.g. molecules in a fluid)
Single particle partition function		$q(V, T) = \sum_i e^{-\epsilon_i \beta}$	$q(V, T) = \sum_i e^{-\epsilon_i \beta}$
Full partition function	$Q(N, V, T) = \sum_j e^{-U_j \beta}$	$Q = q(V, T)^N$	$Q = q(V, T)^N / N!$
Log partition function	$\ln Q$	$N \ln q$	$N \ln q - \ln N!$ $\approx N(\ln Q - \ln N + 1)$
Helmholtz energy ($A = U - TS$)	$-\frac{\ln Q}{\beta}$	$-\frac{N \ln q}{\beta}$	$-\frac{N}{\beta} \left(\ln \frac{q}{N} + 1 \right)$
Internal energy (U)	$-\left(\frac{\partial \ln Q}{\partial \beta} \right)_{NV}$	$-N \left(\frac{\partial \ln q}{\partial \beta} \right)_V$	$-N \left(\frac{\partial \ln q}{\partial \beta} \right)_V$
Pressure (P)	$\frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial V} \right)_{N\beta}$	$\frac{N}{\beta} \left(\frac{\partial \ln q}{\partial V} \right)_\beta$	$\frac{N}{\beta} \left(\frac{\partial \ln q}{\partial V} \right)_\beta$
Entropy (S/k_B)	$\beta U + \ln Q$	$\beta U + N \ln q$	$\beta U + N (\ln(q/N) + 1)$
Chemical potential (μ)	$-\frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial N} \right)_{VT}$	$-\frac{\ln q}{\beta}$	$-\frac{\ln(q/N)}{\beta}$

NOTE! All energies are referenced to their values at 0 K. Enthalpy $H = U + PV$, Gibb's Energy $G = A + PV$.

3. $\Theta_{\text{trans}} \ll T \rightarrow$ many states contribute to $q_{\text{trans}} \rightarrow$ integral approximation

$$q_{\text{trans,1D}} = \int_0^\infty e^{-x^2 \beta \epsilon_0} dx = L/\Lambda$$

$$\Lambda = \left(\frac{h^2 \beta}{2\pi m} \right)^{1/2} \quad \text{thermal wavelength}$$

$$q_{\text{trans,3D}} = V/\Lambda^3$$

4. Internal energy
5. Heat capacity
6. Equation of state (!)
7. Entropy: Sackur-Tetrode equation

2.3.3 Rigid rotor (rotational states of a gas)

1. energy states and degeneracies
2. $\Theta_{\text{rot}} = \hbar^2/2Ik_B$
3. “High” T $q_{\text{rot}}(T) \approx \sigma \Theta_{\text{rot}}/T$

2.3.4 Harmonic oscillator (vibrational states of a gas)

1. $\Theta_{\text{vib}} = h\nu/k_B$

2.3.5 Electronic partition functions \rightarrow spin multiplicity

2.3.6 Solids

1. Equipartition
2. Law of Dulong and Petitt
3. Einstein crystal and heat capacity
4. Debye crystal

2.3.7 Other ensembles

1. Isothermal/isobaric
 - (a) $\Delta(T, P, N) = \sum_j e^{-U_j \beta} e^{-PV_j \beta}$
 - (b) $G(T, P, N) = -k_B T \ln \Delta(T, P, N)$
2. Grand canonical
 - (a) $\Xi(T, V, \mu) = \sum_j e^{-U_j \beta} e^{-PV_j \beta} e^{\mu N_j \beta}$
 - (b) $\Psi(T, V, \mu) = -k_B T \ln \Xi(T, V, \mu)$
 - (c) Langmuir isotherm example

Table 5: Statistical Thermodynamics of an Ideal Gas**Translational DOFs** 3-D particle in a box model

$$\theta_{\text{trans}} = \frac{\pi^2 \hbar^2}{2mL^2 k_B}, \Lambda = h \left(\frac{\beta}{2\pi m} \right)^{1/2}$$

For $T \gg \theta_{\text{trans}}$, $\Lambda \ll L$, $q_{\text{trans}} = V/\Lambda^3$ (essentially always true)

$$U_{\text{trans}} = \frac{3}{2}RT \quad C_{v,\text{trans}} = \frac{3}{2}R \quad S_{\text{trans}}^\circ = R \ln \left(\frac{e^{5/2} V^\circ}{N^\circ \Lambda^3} \right) = R \ln \left(\frac{e^{5/2} k_B T}{P^\circ \Lambda^3} \right)$$

Rotational DOFs Rigid rotor model

Linear molecule $\theta_{\text{rot}} = hcB/k_B$

$$q_{\text{rot}} = \frac{1}{\sigma} \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\theta_{\text{rot}}/T} \approx \frac{1}{\sigma} \frac{T}{\theta_{\text{rot}}}, \quad T \gg \theta_{\text{rot}} \quad \sigma = \begin{cases} 1, & \text{unsymmetric} \\ 2, & \text{symmetric} \end{cases}$$

$$U_{\text{rot}} = RT \quad C_{v,\text{rot}} = R \quad S_{\text{rot}}^\circ = R(1 - \ln(\sigma \theta_{\text{rot}}/T))$$

Non-linear molecule $\theta_{\text{rot},\alpha} = hcB_\alpha/k_B$

$$q_{\text{rot}} \approx \frac{1}{\sigma} \left(\frac{\pi T^3}{\theta_{\text{rot},\alpha} \theta_{\text{rot},\beta} \theta_{\text{rot},\gamma}} \right)^{1/2}, \quad T \gg \theta_{\text{rot},\alpha,\beta,\gamma} \quad \sigma = \text{rotational symmetry number}$$

$$U_{\text{rot}} = \frac{3}{2}RT \quad C_{v,\text{rot}} = \frac{3}{2}R \quad S_{\text{rot}}^\circ = \frac{R}{2} \left(3 - \ln \frac{\sigma \theta_{\text{rot},\alpha} \theta_{\text{rot},\beta} \theta_{\text{rot},\gamma}}{\pi T^3} \right)$$

Vibrational DOFs Harmonic oscillator model

Single harmonic mode $\theta_{\text{vib}} = h\nu/k_B$

$$q_{\text{vib}} = \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} \approx \frac{T}{\theta_{\text{vib}}}, \quad T \gg \theta_{\text{vib}}$$

$$U_{\text{vib}} = \frac{R \theta_{\text{vib}}}{e^{\theta_{\text{vib}}/T} - 1} \quad C_{v,\text{vib}} = R \left(\frac{\theta_{\text{vib}}}{T} \frac{e^{\theta_{\text{vib}}/2T}}{e^{\theta_{\text{vib}}/T} - 1} \right)^2 \quad S_{\text{vib},i}^\circ = R \left(\frac{\theta_{\text{vib}}/T}{e^{\theta_{\text{vib}}/T} - 1} - \ln(1 - e^{-\theta_{\text{vib}}/T}) \right)$$

Multiple harmonic modes $\theta_{\text{vib},i} = h\nu_i/k_B$

$$q_{\text{vib}} = \prod_i \frac{1}{1 - e^{-\theta_{\text{vib},i}/T}}$$

$$U_{\text{vib}} = R \sum_i \frac{\theta_{\text{vib},i}}{e^{\theta_{\text{vib},i}/T} - 1} \quad C_{v,\text{vib}} = R \sum_i \left(\frac{\theta_{\text{vib},i}}{T} \frac{e^{\theta_{\text{vib},i}/2T}}{e^{\theta_{\text{vib},i}/T} - 1} \right)^2 \quad S_{\text{vib},i}^\circ = R \left(\frac{\theta_{\text{vib},i}/T}{e^{\theta_{\text{vib},i}/T} - 1} - \ln(1 - e^{-\theta_{\text{vib},i}/T}) \right)$$

Electronic DOFs q_{elec} = spin multiplicity

Table 6: Contributions of Molecular Degrees of Freedom to Gas Thermodynamics

DOF	Characteristic energy	Characteristic temperature	#states at ≈ 300 K	Internal energy
Translational	$\epsilon_{\text{trans}} = \frac{h^2}{2mL^2} \approx 10^{-21} \text{ cm}^{-1}$	$\theta_{\text{trans}} \approx 10^{-21} \text{ K}$	$\approx 10^{30}$	$U = \frac{3}{2}RT$
Rotational	$\epsilon_{\text{rot}} \approx 1 \text{ cm}^{-1}$	$\theta_{\text{rot}} \approx 1 \text{ K}$	$\approx 100s$	$\approx \# \text{DOF} \cdot RT$
Vibrational	$\epsilon_{\text{vib}} \approx 1000 \text{ cm}^{-1}$	$\theta_{\text{vib}} \approx 1000 \text{ K}$	≈ 1	non-classical, $0 \rightarrow RT$
Electronic	$\epsilon_{\text{elec}} \approx 10000 \text{ cm}^{-1}$	$\theta_{\text{elec}} \approx 10000 \text{ K}$	≈ 1	0

$$Q = (q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}})^N / N!$$

$$U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}}, \dots$$

3 Thermodynamics of Stuff

3.1 Theory of non-ideal fluids

3.1.1 Non-ideality

1. Real molecules interact through vdW interactions
 - (a) dipole-dipole, dipole-induced dipole, induced dipole-induced dipole (London dispersion)
 - (b) scale with dipole moments ($\vec{\mu}$ and polarizability volumes (α) of molecules
 - (c) $U(r) \approx -c/r^6$
2. Particle-in-a-box model breaks down, have to work harder but can still get at same ideas
3. Configurational integral $Q_{\text{config}} = \int \dots \int e^{-U(r)\beta} dr_1 \dots dr_n$

3.1.2 van der Waals gas

1. Hard sphere + $1/r^6$ potential + mean-field approximation ($g(r) = 1$)
2. $Q_{\text{config}} = ((V - Nb) \exp(-(\phi/2)\beta))^N \rightarrow \text{vdW EOS}$
3. See Hill, *J. Chem. Ed.* **1948**, 25, 347, <http://dx.doi.org/10.1021/ed025p347>
4. Free energy has two competing contributions
5. $f_{\text{vdW}} = -k_B T \ln\{(v - b)(k_B T)^{3/2}\} - a/v - k_B T$
6. $P_{\text{vdW}} = RT/(v - b) - a/v^2$

3.1.3 Radial distribution functions, $g(r)$, for gases, liquids, solids

3.1.4 Virial expansion

1. Configurational integral can be expanded in powers of $1/v$ times “virial” coefficients $B_j(T)$
2. $f(T, P) = f_{\text{ig}}(T, P) - RT\{B_2(T)/v + B_3(T)/v^2 + \dots\}$
3. $Z = 1 + B_2(T)/v + B_3(T)/v^2 + \dots$
4. “Second” virial coefficient $B_2(T)$ limiting low density “departure” of volume from that of an ideal gas, $v_{\text{res}}(T, v) = v - v_{\text{ig}} = (RT/P)(Z - 1)$

$$B_2(T) = \lim_{v \rightarrow \infty} v_{\text{res}},$$

- Virial coefficients integrate “clusters” of intermolecular interactions, 2-body, 3-body, ...

5. $B_2(T) = -2\pi N_A \int_0^\infty \{e^{-u(r)/k_B T} - 1\} r^2 dr$
6. $B_2^{\text{vdW}}(T) = b - a/RT$
7. Lennard-Jones potential

3.1.5 Modern approach is to use numerical methods

1. “forcefield” to represent intra- and intermolecular properties
2. molecular dynamics or Monte Carlo to sample interactions
3. Fluid property challenge at AIChE

3.2 Engineering representations of fluids

3.2.1 How to represent properties of real fluids?

1. Mechanical equations of state (empirical)
2. Thermodynamic tabulations (JANAF, steam tables)
3. Theoretical models (virial expansion)
4. Computer simulations (molecular interactions)

3.2.2 Thermodynamic integrations

1. Integrate susceptibilities
2. Integrate PvT relationship plus $C_p^{\text{ig}}(T)$

3.2.3 Compressibility

1. Fluids deviate from ideality because they have finite size and interact over distances, origin of two-parameter EOS
2. Compressibility $Z(T, P) = P/P^{ig} = Pv/RT$ measures deviation from ideality
3. Critical compressibility $Z_c \approx 0.27$ for all “normal” fluids
4. Reduced variable $T_R = T/T_c$, $P_R = P/P_c$, $v_R = v/v_c$
5. “Law” of corresponding states—all “normal” fluids have the same PvT behavior in reduced variables
6. Allows fluids to be described on generalized compressibility chart

3.2.4 Cubic mechanical equations of state

1. van der Waals, $Z_c = 0.375$
2. Redlich-Kwong, $Z_c = 0.333$
3. Peng-Robinson, $Z_c = 0.307$
4. Empirically parameterized, all obey law of corresponding states, none perfect

3.2.5 Departure functions measure thermodynamic potential difference between real state and hypothetical “ideal gas” state

1. $\Delta_{\text{whatever}} = \Delta_{\text{ideal}} + \Delta_{\text{departure}}$
2. From generalized compressibility or accurate EOS integration
3. Entropy departure $s(T, P) - s^{ig}(T, P) = R \ln Z(T, P) + \int_{\infty}^{v(T, P)} \left[\left(\frac{\partial P}{\partial T} \right)_v - \frac{R}{v} \right] dv$
4. Enthalpy departure $h(T, P) - h^{ig}(T, P) = RT(Z - 1) + \int_{\infty}^{v(T, P)} \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$

3.2.6 Fugacity measures departure of free energy ideality

1. Define $\mu(T, P) = \mu^\circ(T) + RT \ln f(T, P)/f^\circ(T)$

$$\lim_{P \rightarrow 0} \mu = -\infty \quad \lim_{P \rightarrow 0} f = P^{ig} = 0$$

$$\ln f/P = \frac{RT}{P} \int_0^P (Z - 1) dP$$

2. $\mu^\alpha = \mu^\beta$ implies $f^\alpha = f^\beta$.
3. Fugacity coefficient $\gamma(T, P) = f(T, P)/P$

$$\ln \gamma = \int_0^P \frac{Z - 1}{P} dP$$

3.3 Single-phase mixtures

3.3.1 Ideal gas mixtures

1. Statistical mechanical approach
2. Properties of ideal mixture

$$\Delta u_{\text{mix}} = \Delta v_{\text{mix}} = 0 \quad \Delta s_{\text{mix}} = -k_B \sum_i y_i \ln y_i$$

3. Partial pressure $P_i = y_i P$
4. Chemical potential $\mu_i(y_i, T) = \mu_i^\circ(T) + k_B T \ln(y_i P / P^\circ)$
5. Work of separation and Gibbs paradox

3.3.2 Non-ideal gas mixtures

1. Inconvenient that $\lim_{y_i \rightarrow 0} \mu_i(y_i, T, P) = -\infty$
2. Construct *fugacity* to obey same equilibrium conditions as chemical potential but to tend to $y_i P$ in infinite dilution

$$\bar{f}_i(y_i, T, P) = P^\circ \exp[(\mu_i(y_i, T, P) - \mu_i^\circ(T))/k_B T]$$

3. Chemical potential $\mu_i(y_i, T, P) = \mu_i^\circ(T) + k_B T \ln(\bar{f}_i / P^\circ)$
4. Fugacity coefficient $\phi_i(y_i, T, P) = \bar{f}_i(y_i, T, P) / (y_i P)$
5. Fugacity can be computed from a mixture-explicit EOS

$$RT \ln(\bar{f}_i / y_i P) = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP = \frac{1}{RT} \left(\frac{\partial(F - F^{\text{ig}})}{\partial N_i} \right)_{T, V, N_{j \neq i}} - \ln Z$$

6. Virial mixture equation, vdW equation, ...
7. Lorentz-Berthelot mixing

$$b = \sum_i b_i \quad a = \sum_i \sum_j y_i y_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j}$$

8. Lewis (ideal) fugacity rule $\bar{f}_i \approx y_i f_i$ generalization of ideal gas

3.3.3 Ideal liquid mixtures

1. Lattice model with random distribution of molecules

$$\Delta u_{\text{mix}} = \Delta v_{\text{mix}} = 0 \quad \Delta s_{\text{mix}} = -k_B \sum_i x_i \ln x_i$$

$$\mu_i(x_i, T) = \mu_i^\circ(T) + k_B T \ln(x_i)$$

2. True for liquids of comparable molecular dimensions and interactions

3.3.4 Partial molar quantities

1. For any extensive quantity or susceptibility, J :

$$\bar{J}_i = \left(\frac{\partial J}{\partial N_i} \right)_{N_{j \neq i}} \quad J = \sum_i \bar{J}_i N_i \quad j = \sum \bar{J}_i x_i$$

$$\Delta j_{\text{mix}} = \sum_i \bar{J}_i x_i - \sum_i j_i x_i$$

2. Gibbs-Duhem says partial molar properties are not independent: $\sum_i N_i d\bar{J}_i = 0$

3.3.5 Non-ideal liquid mixtures

1. Bragg-Williams/mean field approximation
2. Differential exchange parameter χ_{AB}

$$\chi_{12} = \frac{z}{k_B T} \left(u_{12} - \frac{u_{11} + u_{22}}{2} \right)$$

3. Hildebrand regular solution and excess mixing quantities

$$\Delta g_{\text{xs}}/k_B T = \chi_{12} x_1 (1 - x_2)$$

$$\mu_1(T, x_1) = \mu_1^{\text{ideal}}(T, x_1) + k_B T \chi_{12} (1 - x_1)^2$$

4. Activity and activity coefficient
 - (a) Solvent convention
 - (b) Solute convention
5. Liquid-liquid phase diagrams
 - (a) Phase separation, critical point
6. Freezing point depression/boiling point elevation

3.3.6 Ionic mixtures

1. Debye-Huckel

3.4 Gas-liquid equilibria

3.4.1 Ideal-ideal liquid-vapor mixtures

1. Equal chemical potentials in each phase
2. Equilibrium cycle (relate to single component phase equilibrium): start from single component l-v equilibrium, compress each component to desired pressure, then mix.
3. Gas compression important, liquid compression (Poynting correction) less so.

4. Ideal vapor-liquid equilibrium \rightarrow Raoult's Law:

$$\mu_i^{\text{gas}} = \mu_i^{\text{liq}} \rightarrow y_i P = x_i P_i^*$$

5. Pressure-composition diagram
6. Temperature-composition diagram

3.4.2 Non-ideal liquid/ideal vapor

1. Regular solution

$$\chi_{12} \begin{cases} > 0 & \text{positive deviation from Raoult's Law,} \\ = 0 & \text{Raoult's Law,} \\ < 0 & \text{negative deviation from Raoult's Law} \end{cases}$$

2. Temperature-composition diagrams
 - (a) Liquid-vapor
 - (b) Eutectics, ...
3. Henry's Law (dilute) limit
4. Gibbs-Duhem consequences

4 Thermodynamics of Change

4.1 Chemical thermodynamics and equilibria

1. Chemical reactions
2. Thermodynamic potential differences
 - (a) Standard states
 - (b) Reaction entropy $\Delta S^\circ(T) = S_B^\circ(T) - S_A^\circ(T)$
 - (c) Reaction energy $\Delta U^\circ(T) = U_B^\circ(T) - U_A^\circ(T) + \Delta E(0)$
 - (d) Gibbs-Helmholtz
3. Equilibrium-closed system
 - (a) Equilibrium constants and algebraic solutions
 - (b) Free energy minimization
 - (c) Parallel reactions
4. Equilibrium-open system
 - (a) Reaction phase diagrams
5. Partition functions and K_{eq}
6. Non-ideal activities
7. Electrochemical reactions

Table 7: Equilibrium and Rate Constants**Equilibrium Constants** $a A + b B \rightleftharpoons c C + d D$

$$K_{eq}(T) = e^{\Delta S^\circ(T,V)/k_B} e^{-\Delta H^\circ(T,V)/k_B T}$$

$$K_c(T) = \left(\frac{1}{c^\circ}\right)^{\nu_c + \nu_d - \nu_a - \nu_b} \frac{(q_c/V)^{\nu_c} (q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a} (q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}$$

$$K_p(T) = \left(\frac{k_B T}{P^\circ}\right)^{\nu_c + \nu_d - \nu_a - \nu_b} \frac{(q_c/V)^{\nu_c} (q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a} (q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}$$

Unimolecular Reaction $[A] \rightleftharpoons [A]^\ddagger \rightarrow C$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{\bar{q}_\ddagger(T)/V}{q_A(T)/V} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + k_B T \quad A = e^1 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

Bimolecular Reaction $A + B \rightleftharpoons [AB]^\ddagger \rightarrow C$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{q_\ddagger(T)/V}{(q_A(T)/V)(q_B(T)/V)} \left(\frac{1}{c^\circ}\right)^{-1} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + 2k_B T \quad A = e^2 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

Table 8: Physical units

N_{Av} :	6.02214×10^{23}	mol^{-1}		
1 amu:	1.6605×10^{-27}	kg		
k_{B} :	1.38065×10^{-23}	J K^{-1}	8.61734×10^{-5}	eV K^{-1}
R :	8.314472	$\text{J K}^{-1} \text{mol}^{-1}$	8.2057×10^{-2}	$\text{l atm mol}^{-1} \text{K}^{-1}$
σ_{SB} :	5.6704×10^{-8}	$\text{J s}^{-1} \text{m}^{-2} \text{K}^{-4}$		
c :	2.99792458×10^8	m s^{-1}		
h :	6.62607×10^{-34}	J s	4.13566×10^{-15}	eV s
\hbar :	1.05457×10^{-34}	J s	6.58212×10^{-16}	eV s
hc :	1239.8	eV nm		
e :	1.60218×10^{-19}	C		
m_e :	$9.10938215 \times 10^{-31}$	kg	0.5109989	MeV c^{-2}
ϵ_0 :	8.85419×10^{-12}	$\text{C}^2 \text{J}^{-1} \text{m}^{-1}$	5.52635×10^{-3}	$e^2 \text{\AA}^{-1} \text{eV}^{-1}$
$e^2/4\pi\epsilon_0$:	2.30708×10^{-28}	J m	14.39964	eV \AA
a_0 :	0.529177×10^{-10}	m	0.529177	\AA
E_{H} :	1	Ha	27.212	eV

4.2 Non-equilibrium thermodynamics