

2.S: Summary

References

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Summary

• **Extensive and intensive variables:** The equilibrium state of a thermodynamic system is characterized by specifying a number of *state variables* which can be either *extensive* (scaling linearly with system size), or *intensive* (scaling as the zeroth power of system size). Extensive quantities include: energy E , entropy S , particle number N , magnetization \mathbf{M} . Intensive quantities include temperature T , pressure p , number density n , magnetic field \mathbf{H} . The ratio of two extensive quantities is intensive, $n = N/V$. In the *thermodynamic limit*, all extensive state variables tend to infinity (in whatever units are appropriate), while their various ratios are all finite. A full description of the state of any thermodynamic system must involve at least one extensive variable (but may or may not include intensive variables).

• **Work:** The internal energy of a thermodynamic system can change as a result of a *generalized displacement* dX_i , as a result of work W done by the system. We write the differential form of W as

$$\delta W = - \sum_i y_i dX_i - \sum_a \mu_a dN_a, \quad (2.S.1)$$

where $-y_i$ is the *generalized force* conjugate to the generalized displacement X_i , and μ_a is the *chemical potential* of species a , which is conjugate to the number of particles of that species, N_a . Think of chemical work as the work required to assemble particles out of infinitely remote constituents. The slash through the differential symbol indicates that δW is an *inexact differential*, there is no function $W(T, p, V, \dots)$.

• **Heat:** Aside from work done by or on the system, there is another way of changing the system's internal energy, which is by transferring *heat*, Q . Heat is a form of energy contained in the random microscopic motions of the constituent particles. Like δW , the differential δQ is also inexact, and there is no heat function $Q(T, p, V, \dots)$. Transfer of heat under conditions of constant volume or pressure and constant particle number results in a change of the thermodynamic state via a change in temperature: $dT = \delta Q/C$, where C is the *heat capacity* of the system at fixed volume/pressure and particle number.

• **First Law:** The First Law of Thermodynamics is a statement of energy conservation which accounts for both types of energies: $\Delta E = Q - W$, or in differential form $dE = \delta Q - \delta W$.

• **Single component systems:** A single component system is completely specified by three state variables, which can be taken to be E , V , and N , and writing $\delta W = p dV - \mu dN$, we have

$$\delta Q = dE + p dV - \mu dN. \quad (2.S.2)$$

If, for example, we want to use variables (T, V, N) , we write

$$dE = \left(\frac{\partial E}{\partial T} \right)_{V,N} dT + \left(\frac{\partial E}{\partial V} \right)_{T,N} dV + \left(\frac{\partial E}{\partial N} \right)_{T,V} dN. \quad (2.S.3)$$

Proceeding in this way, one can derive expressions like

$$C_{V,N} = \left(\frac{\partial Q}{\partial T} \right)_{V,N} = \left(\frac{\partial E}{\partial T} \right)_{V,N}, \quad C_{p,N} = \left(\frac{\partial Q}{\partial T} \right)_{p,N} = \left(\frac{\partial E}{\partial T} \right)_{p,N} + p \left(\frac{\partial V}{\partial T} \right)_{p,N}. \quad (2.S.4)$$

- *Equations of state:* An equation of state is a relation among state variables. Examples include the familiar ideal gas law, $pV = Nk_B T$, and the van der Waals equation of state, $(p + \frac{aN^2}{V^2})(V - Nb) = Nk_B T$.
- *Ideal gases:* For ideal gases, one has $pV = Nk_B T$ and $E = \frac{1}{2} f N k_B T$, where f is the number of kinetic degrees of freedom ($f = 3$ for monatomic, $f = 5$ for diatomic, and $f = 6$ for polyatomic gases, assuming only translational and rotational freedoms are excited).
- *Special thermodynamic processes:* Remember adiabatic ($\partial Q = 0$), isothermal ($dT = 0$), isobaric ($dp = 0$), and isochoric ($dV = 0$). A *quasistatic* process is one which follows a continuous path in a space of state variables infinitely slowly, so that the system is in equilibrium at any instant. A *reversible* process is necessarily quasistatic, and moreover is nondissipative (no friction), so that its thermodynamic path may be followed in reverse.

• *Heat engines and the Second Law:* A heat engine takes a thermodynamic system through a repeated cycle of equilibrium states $A \rightarrow B \rightarrow C \rightarrow \dots \rightarrow A$, the net result of which is to convert heat into mechanical work, or *vice versa*. A perfect engine, which would extract heat Q from a large thermal reservoir¹, such as the ocean, and convert it into work $W = Q$ each cycle, is not possible, according to the Second Law of Thermodynamics. Real engines extract heat Q_2 from an upper reservoir at temperature T_2 , dump heat Q_1 into a lower reservoir at temperature T_1 , and transform the difference into useful mechanical work $W = Q_2 - Q_1$. A refrigerator is simply an engine operating in reverse: work is done in order to extract heat Q_1 from the lower reservoir, and $Q_2 = W + Q_1$ is dumped into the upper reservoir in each cycle. The *efficiency* of the engine cycle is defined to be $\eta = 1 - \frac{Q_1}{Q_2}$. The engine efficiency is bounded from above by the efficiency of a reversible cycle operating between those two reservoirs, such as the Carnot cycle (two adiabats and two isotherms). Thus, $\eta \leq \eta_C = 1 - \frac{T_1}{T_2}$.

• *Entropy:* The Second Law guarantees that an engine operating between two reservoirs must satisfy $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0$, with the equality holding for reversible cycles. Here $Q_1 = -Q_1$ is the (negative) heat transferred to the engine from reservoir #1. Since an arbitrary curve in the p - V plane (at fixed N) can be composed of a combination of Carnot cycles, one concludes $\oint \frac{\partial Q}{T} \leq 0$, again with equality holding for reversible cycles. Clausius, in 1865, realized that one could thereby define a new state function, the *entropy*, S , with $dS = \frac{\partial Q}{T}$. Thus, $\partial Q \leq T dS$, with equality holding for reversible processes. The entropy is extensive, with units $[S] = J/K$.

• *Gibbs-Duhem relation:* For reversible processes, we now have

$$dE = T dS + \sum_i y_i dX_i + \sum_a \mu_a dN_a, \quad (2.S.5)$$

which says $E = E(S, \{X_i\}, \{N_a\})$, which is to say E is a function of all the extensive variables. It therefore must be homogeneous of degree one, $\lambda E = E(\lambda S, \{\lambda X_i\}, \{\lambda N_a\})$, and from Euler's theorem it then follows that

$$E = TS + \sum_i y_i X_i + \sum_a \mu_a N_a$$

$$0 = S dT + \sum_i X_i dy_i + \sum_a N_a d\mu_a .$$

This means that there is one equation of state which can be written as a function of all the 'proper' intensive variables.

- **Thermodynamic potentials:** Under equilibrium conditions, one can make Legendre transforms to an appropriate or convenient system of thermodynamic variables. Some common examples:

$E(S, V, N) = E$	$dE = T dS - p dV + \mu dN$
$F(T, V, N) = E - TS$	$dF = -S dT - p dV + \mu dN$
$H(S, p, N) = E + pV$	$dH = T dS + V dp + \mu dN$
$G(T, p, N) = E - TS + pV$	$dG = -S dT + V dp + \mu dN$
$\Omega(T, V, \mu) = E - TS - \mu N$	$d\Omega = -S dT - p dV - N d\mu$

Under general nonequilibrium conditions, the Second Law says that each of the equalities on the right is replaced by an inequality, $dG \leq -S dT + V dp + \mu dN$. Thus, under conditions of constant temperature, pressure, and particle number, the Gibbs free energy G will achieve its minimum possible value via spontaneous processes. Note that Gibbs-Duhem says that $G = \mu N$ and $\Omega = -pV$.

- **Maxwell relations:** Since the various thermodynamic potentials are state variables, we have that the mixed second derivatives can each be expressed in two ways. This leads to relations of the form

$$\frac{\partial^2 G}{\partial T \partial p} = - \left(\frac{\partial S}{\partial p} \right)_{T, N} = \left(\frac{\partial V}{\partial T} \right)_{p, N} . \quad (2.S.6)$$

- **Thermodynamic stability:** Suppose T , p , and N are fixed. Then

$$\Delta G = \frac{1}{2} \left[\frac{\partial^2 E}{\partial S^2} (\Delta S)^2 + \frac{\partial^2 E}{\partial S \partial V} \Delta S \Delta V + \frac{\partial^2 E}{\partial V^2} (\Delta V)^2 \right] + \dots , \quad (2.S.7)$$

and since in equilibrium G is at a minimum, $\Delta G > 0$ requires that the corresponding Hessian matrix of second derivatives be positive definite:

$$\frac{\partial^2 E}{\partial S^2} = \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0$$

$$\frac{\partial^2 E}{\partial V^2} = - \left(\frac{\partial p}{\partial V} \right)_S = \frac{1}{V \kappa_S} > 0$$

$$\frac{\partial^2 E}{\partial S^2} \cdot \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 = \frac{T}{V \kappa_S C_V} - \left(\frac{\partial T}{\partial V} \right)_S^2 > 0 .$$

- **Response coefficients:** In addition to heat capacities $C_V = T \left(\frac{\partial S}{\partial T} \right)_V$ and $C_p = T \left(\frac{\partial S}{\partial T} \right)_p$, one defines the isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$ and the adiabatic compressibility $\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$, as well as the thermal expansion coefficient $\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$. Invoking the Maxwell relations, one derives certain identities, such as

$$C_p - C_V = \frac{VT \alpha_p^2}{\kappa_T} , \quad \kappa_T - \kappa_S = \frac{VT \alpha_p^2}{C_p} . \quad (2.S.8)$$

- **Entropy of mixing:** The entropy of any substance obeying the ideal gas law is given by the expression $S(T, V, N) = N k_B \ln(V/N) + N \phi(T)$. If different ideal gases at the same p and T were separated via physical barriers, and the barriers were then removed, the change in entropy would be $\Delta S = -N k_B \sum_a x_a \ln x_a$, where $x_a = N_a/N$ with $N = \sum_a N_a$ being the total number of particles over all species. This is called the *entropy of mixing*.

- **Weak solutions and osmotic pressure:** If one species is much more plentiful than the others, we give it a particle label $a = 0$ and call it the *solvent*. The Gibbs free energy of a weak solution is then

$$G(T, p, N_0, \{N_a\}) = N_0 g_0(T, p) + \sum_a N_a \left\{ k_B T \ln \left(\frac{N_a}{e N_0} \right) + \psi_a(T, p) \right\} + \frac{1}{2 N_0} \sum_{a,b} A_{ab}(T, p) N_a N_b. \quad (2.S.9)$$

Assuming $x_a = N_a/N_0 \ll 1$ for $a > 0$, we have $\mu_0 = g_0 - x k_B T$ and $\mu_a = k_B T \ln x_a + \psi_a$. If $x > 0$ on the right side of a semipermeable membrane and $x = 0$ on the left, then assuming the membrane is permeable to the solvent, we must have $\mu_0(T, p) = g_0(T, p) - x k_B T$. This leads to a pressure difference, π , called the *osmotic pressure*, given by $\pi = p_R - p_L = x k_B T \ln \left(\frac{\mu_0(T, p)}{\mu_0(T, p) - x k_B T} \right)$. Since a Maxwell relation guarantees $\left(\frac{\partial \mu_0}{\partial p} \right)_{T, N} = \left(\frac{\partial V_0}{\partial N} \right)_{T, p}$, we have the equation of state $\pi v = x R T$, where v is the molar volume of the solvent.

• **Binary solutions:** In a mixture of A and B species, let $x = N_B/(N_A + N_B)$. The Gibbs free energy per particle is

$$g(T, p, x) = (1-x) \mu_A^0(T, p) + x \mu_B^0(T, p) + k_B T [x \ln x + (1-x) \ln(1-x)] + \lambda_{AB} x(1-x). \quad (2.S.10)$$

If $\lambda_{AB} > 0$, the components repel, and the mixture becomes unstable. There is a local instability, corresponding to *spinodal decomposition*, when $g''(x) = 0$. This occurs at a temperature $k_B T^* = 2 \lambda_{AB} x(1-x)$. But for a given x , an instability toward phase separation survives to even higher temperature, and is described by the Maxwell construction. The coexistence boundary is obtained from $[g(x_2) - g(x_1)]/(x_2 - x_1) = g'(x_1) = g'(x_2)$, and from the symmetry under $x \leftrightarrow 1-x$, one finds $k_B T_{coex} = \lambda_{AB} (1-2x)/\ln(x^{-1} - 1)$, where *nucleation* of the minority phase sets in.

• **Miscible fluids and liquid-vapor coexistence:** If $\lambda_{AB} < 0$, there is no instability toward phase separation, and the fluids are said to be *completely miscible*. Example: benzene C_6H_6 and toluene $C_6H_5CH_3$. At higher temperatures, near the liquid gas transition, there is an instability toward phase separation. In the vapor phase, $\lambda_{AB}^V \approx 0$, while for the liquid $\lambda_{AB}^L < 0$. The free energy curves $g_L(T, p, x)$ and $g_V(T, p, x)$ are then both convex as a function of x , but choosing the minimum $g(x) = \min(g_L(x), g_V(x))$, one is forced toward a Maxwell construction, hence phase coexistence. In the case of 'ideal liquids' with different boiling points, we can even take $\lambda_{AB}^L \approx 0$. By successively boiling and then separating and condensing the resulting vapor, the mixture may be *distilled* (see Fig. [FIG3]). When $\lambda_{AB}^L \neq 0$, the mixture may be *azeotropic* in which case the extremum of the boiling point occurs at an intermediate concentration (see Fig. [FIG4]).

• **Thermochemistry:** A chemical reaction among σ species may be represented

$$\zeta_1 A_1 + \zeta_2 A_2 + \cdots + \zeta_\sigma A_\sigma = 0, \quad (2.S.11)$$

where A_a is a chemical formula, and ζ_a is a *stoichiometric coefficient*. If $\zeta_a > 0$, then A_a is a *product*, while for $\zeta_a < 0$, A_a is a *reactant*. Chemical equilibrium requires $\sum_{a=1}^\sigma \zeta_a \mu_a = 0$. For a mixture of ideal gases, one has the *law of mass action*,

$$\kappa(T, p) \equiv \prod_{a=1}^{\sigma} x_a^{\zeta_a} = \prod_{a=1}^{\sigma} \left(\frac{k_B T \xi_a(T)}{p \lambda_a^3} \right)^{\zeta_a}, \quad (2.S.12)$$

where $\xi_a(T)$ is the internal coordinate partition function for molecular species a . $\kappa(T, p)$ is the *equilibrium constant* of the reaction. When κ is large, products are favored over reactants. When κ is small, reactants are favored over products. One may further show

$$\left(\frac{\partial \ln \kappa}{\partial T} \right)_p = \frac{\Delta h}{k_B T^2}, \quad (2.S.13)$$

where Δh is the enthalpy of the reaction. When $\Delta h < 0$, the reaction is *exothermic*. At finite pressure, this means that heat is transferred to the environment: $Q = \Delta E + p \Delta V = \Delta H < 0$, where $H = E + pV$. When $\Delta h > 0$, the reaction is *endothermic*, and requires heat be transferred from the environment.

• *Clapeyron relation*: Across a *coexistence curve* $p(T)$ separating two phases, the chemical potential μ is continuous. This says $dg_1 = -s_1 dT + v_1 dp = -s_2 dT + v_2 dp = dg_2$, where g , s , and v are the Gibbs free energy, entropy, and volume per mole, respectively. Then

$$\left(\frac{\partial p}{\partial T} \right)_{\text{coex}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T \Delta v}, \quad (2.S.14)$$

where $\ell = T \Delta s = T(s_2 - s_1)$ is the *molar latent heat of transition* which must be supplied in order to change from phase #1 to phase #2, even without changing T or p .

• *Gibbs phase rule*: For a system with σ species, Gibbs-Duhem says $\mu_\sigma = \mu_\sigma(T, p, \mu_1, \dots, \mu_{\sigma-1})$, so a maximum of $\sigma + 1$ intensive quantities may be specified. If a system with σ species has equilibrium among φ phases, then there are $\sigma(\varphi - 1)$ independent equilibrium conditions $\mu_a^{(j)} = \mu_a^{(j')}$, where a labels species and j labels phases, among the $2 + \varphi(\sigma - 1)$ intensive variables, and so φ -phase equilibrium can exist over a space of dimension $d = 2 + \sigma - \varphi$. Since this cannot be negative, we have $\varphi \leq 2 + \sigma$. Thus, for a single species, we can at most have three phase coexistence, which would then occur on a set of dimension zero, as is the case for the triple point of water, for example.

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1. A thermal reservoir, or *heat bath*, is any very large object with a fixed temperature. Because it is so large, the change in temperature $\Delta T = Q/C$ which results from a heat transfer Q is negligible, since the heat capacity C is an extensive quantity.↵

Endnotes

1. For a system of N molecules which can freely rotate, we must then specify $3N$ additional orientational variables – the Euler angles – and their $3N$ conjugate momenta. The dimension of phase space is then $12N$.↵
2. Hence, 1 guacamole = 6.0221415×10^{23} guacas.↵
3. One calorie (cal) is the amount of heat needed to raise 1 g of H_2O from $T_0 = 14.5^\circ C$ to $T_1 = 15.5^\circ C$ at a pressure of $p_0 = 1$ atm. One British Thermal Unit (BTU) is the amount of heat needed to raise 1 lb. of H_2O from $T_0 = 63^\circ F$ to $T_1 = 64^\circ F$ at a pressure of $p_0 = 1$ atm.↵

4. We use the symbol \nolimits^{d} in the differential $\nolimits^{\text{d}}W$ to indicate that this is not an exact differential. More on this in section 4 below.↵
5. As we shall see further below, thermomechanical equilibrium in fact leads to constant p/T , and thermochemical equilibrium to constant μ/T . If there is thermal equilibrium, then T is already constant, and so thermomechanical and thermochemical equilibria then guarantee the constancy of p and μ .↵
6. In most metals, the difference between C_V and C_p is negligible.↵
7. See the description in E. Fermi, *Thermodynamics*, pp. 22-23.↵
8. Carnot died during cholera epidemic of 1832. His is one of the 72 names engraved on the Eiffel Tower.↵
9. See F. L. Curzon and B. Ahlborn, *Am. J. Phys.* **43**, 22 (1975). I am grateful to Professor Asle Sudbø for correcting a typo in one expression and providing a simplified form of another.↵
10. We neglect any interfacial contributions to the entropy change, which will be small compared with the bulk entropy change in the thermodynamic limit of large system size.↵
11. Note $V/N = v/N_A$.↵
12. Some exotic phase transitions in quantum matter, which do not quite fit the usual classification schemes, have recently been proposed.↵
13. The melting curve has a negative slope at relatively low pressures, where the solid has the so-called Ih hexagonal crystal structure. At pressures above about 2500 atmospheres, the crystal structure changes, and the slope of the melting curve becomes positive.↵
14. For a recent discussion, see R. Rosenberg, *Physics Today* **58**, 50 (2005).↵
15. For example, they could be of the van der Waals form, due to virtual dipole fluctuations, with an attractive $1/r^6$ tail.↵
16. We assume $\tilde{c}_{\text{ns}}^{\text{sr}}(T)$ and $\tilde{c}_{\text{ns}}^{\text{sl}}(T)$ have no appreciable temperature dependence, and we regard them both as constants.↵
17. Set $j = 1$ and let j' range over the $\varphi - 1$ values $2, \dots, \varphi$.↵
18. The same can be said for multicomponent systems: the phase diagram in the (T, x) plane at constant p looks different than the phase diagram in the (T, μ) plane at constant p .↵
19. 'Semipermeable' in this context means permeable to the solvent but not the solute(s).↵
20. We shall discuss latent heat again in §12.2 below.↵
21. See table [latentheats], and recall $M = 18 \text{ g}$ is the molar mass of H_2O .↵
22. It is more customary to write $\Delta T^* = T_{\text{pure solvent}}^* - T_{\text{solution}}^*$ in the case of the freezing point depression, in which case ΔT^* is positive.↵
23. An emulsion is a mixture of two or more immiscible liquids.↵
24. We assume the boiling temperatures are not exactly equal!↵
25. Antoine Lavoisier, the "father of modern chemistry", made pioneering contributions in both chemistry and biology. In particular, he is often credited as the progenitor of stoichiometry. An aristocrat by birth, Lavoisier was an administrator of the *Ferme générale*, an organization in pre-revolutionary France which collected taxes on behalf of the king. At the age of 28, Lavoisier married Marie-Anne Pierette Paulze, the 13-year-old daughter of one of his business partners. She would later join her husband in his research, and she played a role in his disproof of the phlogiston theory of combustion. The phlogiston theory was superseded by Lavoisier's work, where, based on contemporary experiments by Joseph Priestley, he correctly identified the pivotal role played by oxygen in both chemical and biological processes (respiration). Despite his fame as a scientist, Lavoisier succumbed to the Reign of Terror. His association with the *Ferme générale*, which collected taxes from the poor and the downtrodden, was a significant liability in revolutionary France (think Mitt Romney vis-a-vis Bain Capital). Furthermore – and let this be a lesson to all of us – Lavoisier had unwisely ridiculed a worthless pseudoscientific pamphlet, ostensibly on the physics of fire, and its author, Jean-Paul Marat. Marat was a journalist with scientific pretensions, but apparently little in the way of scientific talent or acumen. Lavoisier effectively blackballed Marat's candidacy to the French Academy of Sciences, and the time came when Marat sought revenge. Marat was instrumental in getting Lavoisier and other members of the *Ferme générale* arrested on charges of counterrevolutionary activities, and on May 8, 1794, after a trial lasting less than a day, Lavoisier was guillotined. Along with Fourier and Carnot, Lavoisier's name is one of the 72 engraved on the Eiffel Tower. Source: www.vigyanprasar.gov.in/scientists/ALLLavoisier.htm.↵
26. Note that $g(p)$ may be a negative number, if the line $y = px$ lies everywhere below $f(x)$.↵

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