2 Thermodynamics : 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 $\boldsymbol{M}$, *etc.* Intensive quantities include temperature T, pressure p, number density n, magnetic field $\boldsymbol{H}$, *etc.* The ratio of two extensive quantities is intensive, *e.g.* $n = N/V$. 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

$$đW = -\sum_i y_i \, dX_i - \sum_a \mu_a \, dN_a \quad ,$$

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 $đW$ is an *inexact differential*, *i.e.* there is no function $W(T, p, V, \ldots)$.

• *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 $đW$, the differential $đQ$ is also inexact, and there is no heat function $Q(T, p, V, \ldots)$. Transfer of heat under conditions of constant volume or pressure and constant particle number results in a change of the the thermodynamic state via a change in temperature: $dT = đQ/C$, 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 $dE = đQ - đW$.

• *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 $đW = p \, dV - \mu \, dN$, we have

$$đQ = dE + p \, dV - \mu \, dN \quad .$$

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

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

Proceeding in this way, one can derive expressions like

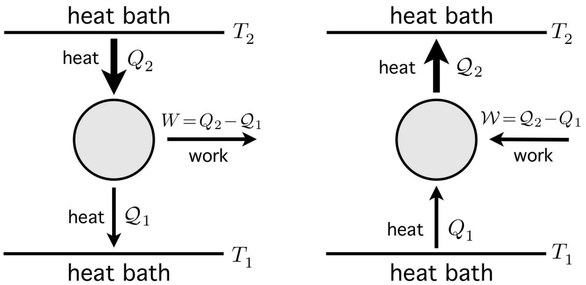
$$C_{V,N} = \left(\frac{đQ}{dT}\right)_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} \quad , \quad C_{p,N} = \left(\frac{đQ}{dT}\right)_{p,N} = \left(\frac{\partial E}{\partial T}\right)_{p,N} + p \left(\frac{\partial V}{\partial T}\right)_{p,N} \quad .$$

• *Equations of state*: An equation of state is a relation among state variables. Examples include the familiar ideal gas law, $pV = Nk_{\rm B}T$, and the van der Waals equation of state, $\big(p + \frac{aN^2}{V^2}\big)(V - Nb) = Nk_{\rm B}T$.

• *Ideal gases*: For ideal gases, one has $pV = Nk_{\rm B}T$ and $E = \frac{1}{2}fNk_{\rm B}T$, 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 ($\text{đ}Q = 0$), isothermal ($dT = 0$), isobaric ($dp = 0$), and isochoric ($dV = 0$). A *quasistatic* process is one which follows a continuous path is 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 (*i.e.* 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 $\mathsf{A} \to \mathsf{B} \to \mathsf{C} \to \cdots \to \mathsf{A}$, 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 reservoir[1], 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 $\mathcal{Q}_1$ into a lower reservoir at temperature T_1, and transform the difference into useful mechanical work $W = Q_2 - \mathcal{Q}_1$. A refrigerator is simply an engine operating in reverse: work is done in order to extract heat Q_1 from the lower reservoir, and $\mathcal{Q}_2 = W + Q_1$ is dumped into the upper reservoir in each cycle. The *efficiency* of the engine cycle is defined to be $\eta = 1 - \frac{\mathcal{Q}_1}{Q_2}$. 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, $\eta \le \eta_{\rm C} = 1 - \frac{T_1}{T_2}$.



(a) engine (b) refrigerator

Figure 1: An engine (left) extracts heat Q_2 from a reservoir at temperature T_2 and deposits a smaller amount of heat $\mathcal{Q}_1$ into a reservoir at a lower temperature T_1, during each cycle. The difference $W = Q_2 - \mathcal{Q}_1$ is transformed into mechanical work. A refrigerator (right) performs the inverse process, drawing heat Q_1 from a low temperature reservoir and depositing heat $\mathcal{Q}_2 = Q_1 + \mathcal{W}$ into a high temperature reservoir, where $\mathcal{W}$ is the work done per cycle.

• *Entropy*: The Second Law guarantees that an engine operating between two reservoirs must satisfy $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \le 0$, with the equality holding for reversible cycles. Here $Q_1 = -\mathcal{Q}_1$ 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

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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.

concludes $\oint \frac{\text{đ}Q}{T} \leq 0$, again with equality holding for reversible cycles. Clausius, in 1865, realized that one could thereby define a new state function, the *entropy*, S, with $dS = \frac{\text{đ}Q}{T}$. Thus, $\text{đ}Q \leq T\,dS$, with equality holding for reversible processes. The entropy is extensive, with units $[S] = \mathrm{J/K}$.

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

$$dE = T\,dS + \sum_i y_i\,dX_i + \sum_a \mu_a\,dN_a \quad ,$$

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

$$\begin{aligned} E &= TS + \sum_i y_i\,X_i + \sum_a \mu_a\,N_a \\ 0 &= S\,dT + \sum_i X_i\,dy_i + \sum_a N_a\,d\mu_a \quad . \end{aligned}$$

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:

$$\begin{aligned} E(S,V,N) &= E & dE &= T\,dS - p\,dV + \mu\,dN \\ F(T,V,N) &= E - TS & dF &= -S\,dT - p\,dV + \mu\,dN \\ \mathsf{H}(S,p,N) &= E + pV & d\mathsf{H} &= T\,dS + V\,dp + \mu\,dN \\ G(T,p,N) &= E - TS + pV & dG &= -S\,dT + V\,dp + \mu\,dN \\ \mathit{\Omega}(T,V,\mu) &= E - TS - \mu N & d\mathit{\Omega} &= -S\,dT - p\,dV - N\,d\mu \quad . \end{aligned}$$

Under general nonequilibrium conditions, the Second Law says that each of the equalities on the right is replaced by an inequality, *i.e.* $dG \leq -S\,dT + V\,dp + \mu\,dN$. 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 $\mathit{\Omega} = -pV$.

• *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

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

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

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

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

$$\begin{aligned}
\frac{\partial^2 E}{\partial S^2} &= \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \\
\frac{\partial^2 E}{\partial V^2} &= -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V \kappa_S} > 0 \\
\frac{\partial^2 E}{\partial S^2} \cdot \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S\,\partial V}\right)^2 &= \frac{T}{V \kappa_S\, C_V} - \left(\frac{\partial T}{\partial V}\right)_S^2 > 0 \quad .
\end{aligned}$$

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

$$C_p - C_V = \frac{VT\alpha_p^2}{\kappa_T} \qquad , \qquad \kappa_T - \kappa_S = \frac{VT\alpha_p^2}{C_p} \quad .$$

• *Entropy of mixing*: The entropy of any substance obeying the ideal gas law is given by the expression $S(T,V,N) = N k_{\rm B} \ln(V/N) + N\phi(T)$. 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 $\Delta S = -N k_{\rm B} \sum_a x_a \ln x_a$, 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

$$G\big(T,p,N_0,\{N_a\}\big) = N_0\, g_0(T,p) + \sum_a N_a \left\{ k_{\rm B} T \ln\!\left(\frac{N_a}{eN_0}\right) + \psi_a(T,p) \right\} + \frac{1}{2N_0} \sum_{a,b} A_{ab}(T,p)\, N_a\, N_b \quad .$$

Assuming $x_a = N_a/N_0 \ll 1$ for $a > 0$, we have $\mu_0 = g_0 - x k_{\rm B} T$ and $\mu_a = k_{\rm B} T \ln x_a + \psi_a$. 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 $\mu_0 = g_0(T, p_{\rm L}) = g_0(T, p_{\rm R}) - x k_{\rm B} T$. This leads to a pressure difference, π, called the *osmotic pressure*, given by $\pi = p_{\rm R} - p_{\rm L} = x k_{\rm B} T / \big(\frac{\partial \mu_0}{\partial p}\big)_{T,N}$. Since a Maxwell relation guarantees $\big(\frac{\partial \mu_0}{\partial p}\big)_{T,N} = \big(\frac{\partial V_0}{\partial N}\big)_{T,p}$, we have the equation of state $\pi v = xRT$, where v is the molar volume of the solvent.

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

$$g(T,p,x) = (1-x)\, \mu^0_{\sf A}(T,p) + x\, \mu^0_{\sf B}(T,p) + k_{\rm B} T \Big[x \ln x + (1-x)\ln(1-x) \Big] + \lambda_{\sf AB}\, x(1-x) \quad .$$

If $\lambda_{\mathsf{AB}} > 0$, the A and B 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 $k_{\rm B}T^* = 2\lambda_{\mathsf{AB}}\, x(1-x)$. 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 $\big[g(x_2) - g(x_1)\big]/(x_2 - x_1) = g'(x_1) = g'(x_2)$, and from the symmetry under $x \leftrightarrow 1 - x$, one finds $k_{\rm B}T_{\rm coex} = \lambda_{\mathsf{AB}}(1-2x)/\ln\!\big(x^{-1} - 1\big)$, where *nucleation* of the minority phase sets in.

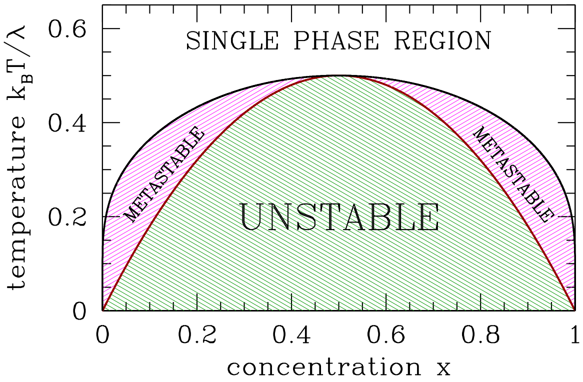

Figure 2: Phase diagram for the binary system. The black curve is the coexistence curve, and the dark red curve is the spinodal. A-rich material is to the left and B-rich to the right.

• *Miscible fluids and liquid-vapor coexistence*: If $\lambda_{\mathsf{AB}} < 0$, there is no instability toward phase separation, and the A and B 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, $\lambda^{\mathsf{V}}_{\mathsf{AB}} \approx 0$, while for the liquid $\lambda^{\mathsf{L}}_{\mathsf{AB}} < 0$. The free energy curves $g_{\mathsf{L}}(T,p,x)$ and $g_{\mathsf{V}}(T,p,x)$ are then both convex as a function of x, but choosing the minimum $g(x) = \min\!\big(g_{\mathsf{L}}(x), g_{\mathsf{V}}(x)\big)$, one is forced toward a Maxwell construction, hence phase coexistence. In the case of 'ideal liquids' with different boiling points, we can even take $\lambda^{\mathsf{L}}_{\mathsf{AB}} \approx 0$. By successively boiling and then separating and condensing the resulting vapor, the mixture may be *distilled* (see Fig. 3). When $\lambda^{\mathsf{L}}_{\mathsf{AB}} \neq 0$, the mixture may be *azeotropic* in which case the extremum of the boiling point occurs at an intermediate concentration (see Fig. 4).

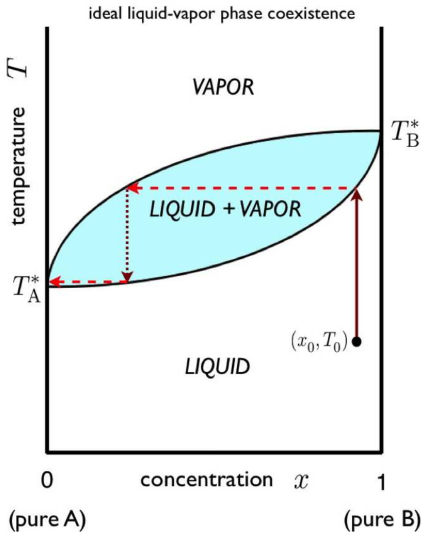

Figure 3: Phase diagram and distillation sequence for an ideal mixture.

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

$$\zeta_1\,\mathsf{A}_1 + \zeta_2\,\mathsf{A}_2 + \cdots + \zeta_\sigma\,\mathsf{A}_\sigma = 0 \quad ,$$

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*,

$$\kappa(T,p) \equiv \prod_{a=1}^{\sigma} x_a^{\zeta_a} = \prod_{a=1}^{\sigma} \left(\frac{k_{\rm B}T\,\xi_a(T)}{p\lambda_a^3}\right)^{\zeta_a} \quad ,$$

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

$$\left(\frac{\partial \ln \kappa}{\partial T}\right)_{\!p} = \frac{\Delta\mathsf{h}}{k_{\rm B} T^2} \quad ,$$

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

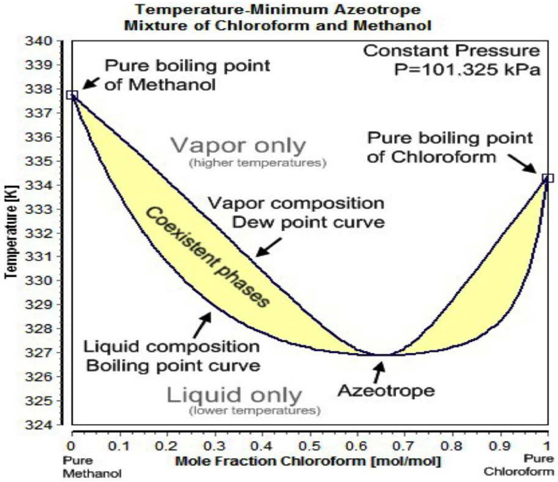

Figure 4: Phase diagram for the positive azeotrope chloroform plus methanol.

• *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

$$\left(\frac{\partial p}{\partial t}\right)_{\rm coex} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\,\Delta v} \quad ,$$

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 $\mu_\sigma = \mu_\sigma(T, p, \mu_1, \ldots, \mu_{\sigma-1})$, 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.