

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 M , etc. Intensive quantities include temperature T , pressure p , number density n , magnetic field 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

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

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 dW is an *inexact differential*, i.e. 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 dW , the differential dQ 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 the thermodynamic state via a change in temperature: $dT = dQ/C$, 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 $dE = dQ - dW$.

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

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

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

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

- *Equations of state:* An equation of state is a relation among state variables. Examples include the familiar ideal gas law, $pV = Nk_B T$, 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 $E = \frac{1}{2}fNk_B T$, 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 ($dQ = 0$), 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 (*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 $A \rightarrow B \rightarrow C \rightarrow \dots \rightarrow A$, 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, $\eta \leq \eta_C = 1 - \frac{T_1}{T_2}$.

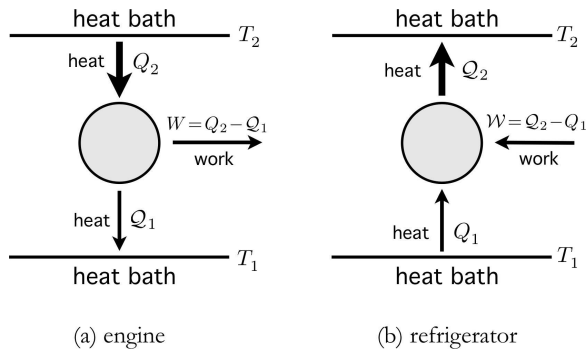


Figure 1: An engine (left) extracts heat Q_2 from a reservoir at temperature T_2 and deposits a smaller amount of heat Q_1 into a reservoir at a lower temperature T_1 , during each cycle. The difference $W = Q_2 - Q_1$ is transformed into mechanical work. A refrigerator (right) performs the inverse process,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

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- *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

¹A 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 $\oint \frac{dQ}{T} \leq 0$, again with equality holding for reversible cycles. Clausius, in 1865, realized that one could thereby define a new state function, the *entropy*, S , with $dS = \frac{dQ}{T}$. Thus, $dQ \leq T dS$, with equality holding for reversible processes. The entropy is extensive, with units $[S] = \text{J/K}$.

- *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 $E = E(S, \{X_i\}, \{N_a\})$, which is to say E is a function of all the extensive variables. It therefore must be homogeneous of degree one, *i.e.* $\lambda E = E(\lambda S, \{\lambda X_i\}, \{\lambda N_a\})$, 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:

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

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 $\Omega = -pV$.

- *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

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

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

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

• *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

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

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

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

Assuming $x_a = N_a/N_0 \ll 1$ for $a > 0$, we have $\mu_0 = g_0 - xk_B T$ 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 $\mu_0 = g_0(T, p_L) = g_0(T, p_R) - xk_B T$. This leads to a pressure difference, π , called the *osmotic pressure*, given by $\pi = p_R - p_L = xk_B T / \left(\frac{\partial \mu_0}{\partial p} \right)_{T, N}$. 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 $\pi v = xRT$, 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

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

If $\lambda_{AB} > 0$, 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 $k_B T^* = 2\lambda_{AB} x(1-x)$. 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 $k_B T_{\text{coex}} = \lambda_{AB}(1-2x)/\ln(x^{-1}-1)$, where *nucleation* of the minority phase sets in.

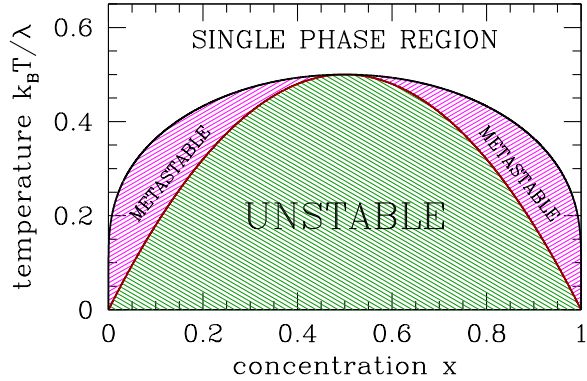


Figure 2: Phase diagram for the binary system. The black curve is the coexistence curve, and the dark red curve is the spinodal. A-rich material is to the left and B-rich to the right.

- *Miscible fluids and liquid-vapor coexistence*: If $\lambda_{AB} < 0$, 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, $\lambda_{AB}^V \approx 0$, 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. 3). 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. 4).

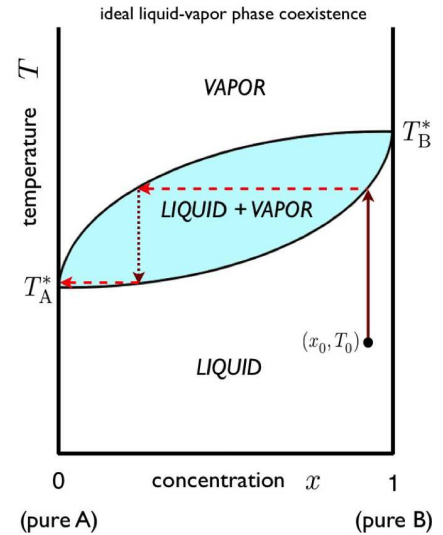
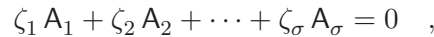


Figure 3: Phase diagram and distillation sequence for an ideal mixture.

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



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*,

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

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

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

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

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

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.

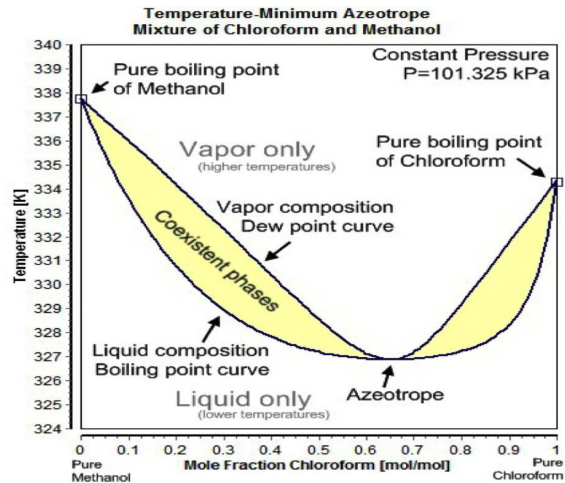


Figure 4: Phase diagram for the positive azeotrope chloroform plus methanol.