CHEM 2301: Introduction to Physical Chemistry I

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Contents

Chapter 1

Gases and Equations of State

1.1 Ideal Gases

The molecules in an ideal gas have

- no attractive intermolecular interactions
- effectively zero volume relative to the container

Their behaviour is described by the ideal gas law:

$$\boxed{PV = nRT} \tag{1.1}$$

where P is pressure, V is volume, T is temperature in Kelvin, n is the number of gas molecules, and R is the gas constant.

This is valid in the limits of high T, low P, and large V.

This relation is called an equation of state, which is a mathematical relationship between the quantities that describe a chemical system.

The value of R is dependent on the units of P and V:

- $R = 8.314$ J K^{-1} mol^{-1} for P in Pa, V in m^3.
- R=0.08206 L atm K^{-1} mol^{-1} for P in atm, V in L.

Note that 1 Pa = 1 N m^{-2} = 1 J m^{-3} and 1 L = 10^{-3} m^3

Pressures can also be given in Torr (mm of Hg from a barometer), with 760 Torr = 1 atm.

Writing the ideal gas law in terms of the intensive variables (independent of the quantity of matter):

$$P\bar{V} = RT$$

where $\bar{V} = V/n$ is the molar volume.

The molar volume of an ideal gas at 1 atm and 0°C (273 K) is 22.4 L/mol (independent of composition).

This allows the molar mass to be determined by weighing a set volume of an ideal gas.

In experiments, one intensive variable is typically held constant:

- constant T for a heat/ice bath – isothermal process

- constant P for a flask left open to the air – isobaric process

- constant V for a sealed reaction vessel – isochoric process

The ideal gas law was formulated by combining known behaviour for each of these paths.
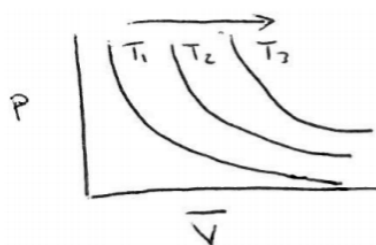
$$P = (RT)\frac{1}{\bar{V}} \text{ or } P\bar{V} = \text{constant}$$

Inverse relationship, P increases as V decreases and vice versa. This is Boyle's law.
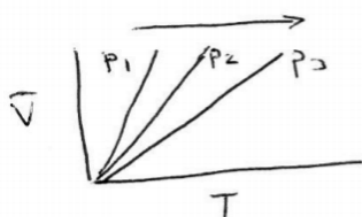
$$\bar{V} = \left(\frac{R}{P}\right)T$$

Volume increases with T, so the gas expands when heated. The extent of expansion is lower at higher P. This is Charles' law.
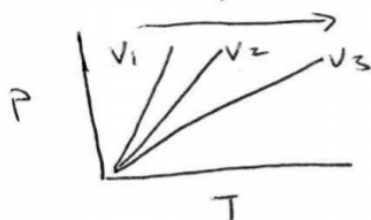
$$P = \left(\frac{R}{\bar{V}}\right)T$$

Pressure increases with T as the gas is heated and the extent of increase is lower for larger volume. This is Gay-Lussac's law.

For a mixture of gases, the ideal gas law applies to the total n and P – concentrations of the individual components are given by their partial pressures:

$$P_i = \frac{n_i}{n}P \text{ or } P_i = x_i P$$

where $x_i = n_i/n$ is the mole fraction of gas i. The total number of moles is $n = \sum_i n_i$ and the total pressure is the sum of the partial pressures, $P = \sum_i P_i$

1.2 Introduction of Partial Derivatives

Recall that, for a function f that involves a product of two variables x and y,

$$f = xy$$

to take the derivative, use product rule:

$$\frac{d}{dx}(f) = \frac{df}{dx} = \frac{dx}{dx}y + x\frac{dy}{dx} = y + x\frac{dy}{dx}$$

However, for partial derivative, $\frac{\partial f}{\partial x}$ or $\frac{\partial f}{\partial y}$, assume the other variable is a constant. This is like taking a level path around a hill, instead of any other path, where your elevation is changing.

$$\frac{\partial f}{\partial x} = \frac{\partial x}{\partial x}y = y$$

$$\frac{\partial f}{\partial y} = x\frac{\partial y}{\partial y} = x$$

1.3 Real Gases

The ideal gas law predicts that $\bar{V}, P \to 0$ as $T \to 0$, which is not physically reasonable. This is a consequence of the assumptions of non-interacting, infinitely-small gas molecules.

To modify the ideal gas law, we need to account for the size of the molecules, which decreases the available volume, so

$$P = \frac{RT}{\bar{V} - b}$$

where b is the molar volume of the compound in the condensed (solid or liquid) phase reached at low temperature. This can be treated as a molecule-specific constant, since solids and liquids are very much less compressible than gases. Rearranging gives

$$\bar{V} = \frac{RT}{P} + b$$

and prevents the unphysical ideal-gas result that $\bar{V} \to 0$ as $T \to 0$ or $P \to \infty$.

Additionally, there are attractive, intermolecular interactions between real gas molecules called van der Waals interactions, due to London dispersion, dipole-dipole interactions, hydrogen-bonding, etc.

These can be represented by a Lennard-Jones 6-12 potential, which described the potential energy curve between two molecules.
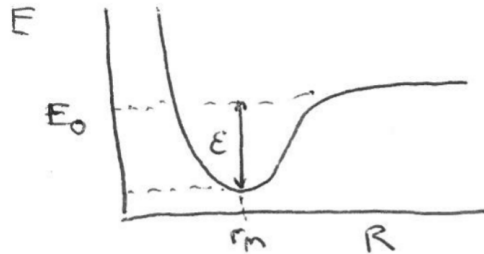
$$E = \varepsilon \left[\left(\frac{r_m}{R} \right)^{12} - 2 \left(\frac{r_m}{R} \right)^{6} \right]$$

The strength of the specific intermolecular interaction determines the well depth or binding energy (ε) and the optimum (or minimum-energy) intermolecular separation (r_m).

Attractive intermolecular interactions cause a reduction in the gas pressure. Because the interactions are pairwise, the pressure lowering is proportional to the square of the gas concentration ($1/\bar{V}^2$)

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{1.2}$$

a is a positive, molecule-specific constant that describes the intermolecular interaction strength. It roughly corresponds to the vapourization energy of the liquid or the boiling point.

The relation is called the van der Waals equation of state and is sometimes rewritten as:

$$\left(P + \frac{a}{\bar{V}^2} \right) \left(\bar{V} - b \right) = RT \tag{1.3}$$

To determine if a particular gas is behaving ideally, consider the ratio $Z = \frac{P\bar{V}}{RT}$, called the compression factor.

$$Z = 1 \quad \text{ideal gas behaviour}$$
$$Z < 1 \quad P < P_{\text{ideal}} \text{ attraction dominates}$$
$$Z > 1 \quad P > P_{\text{ideal}} \text{ repulsion dominates}$$

Plots of $Z(P)$ reveal these different regimes.
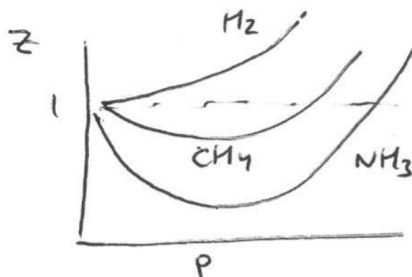
As $P \to 0$ the gas is more ideal and $Z \to 1$.

At low to moderate P, attraction dominates, $Z < 1$.

At high P, repulsion dominates, $Z > 1$.

The stronger the intermolecular interactions, the greater the attractive dip and the deviation from ideal behaviour.

To describe these curves using the vdW equation of state

$$Z = \frac{P\bar{V}}{RT} = \left(\frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}\right)\frac{\bar{V}}{RT} = \frac{1}{1-b/\bar{V}} - \frac{a}{RT\bar{V}}$$

At low pressure, $b/\bar{V} << 1$ so $\frac{1}{1-b/\bar{V}} \approx 1 + b/\bar{V}$ (from the Taylor expansion). Using this in the expansion for Z,

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}}$$

and substituting for $\bar{V}$,

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{P}{RT}$$

The initial slope of $Z(P)$ is given by

$$\frac{\partial Z}{\partial P}\bigg|_{P=0} = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$$

This, when T is low, the attractive $-\frac{a}{RT}$ term dominates and $Z < 1$. When T is high, the repulsive b term dominates and $Z > 1$. At some intermediate temperature, called the Boyle temperature, the initial slope is zero and the gas behaves nearly ideally over a large pressure range

$$\left(b - \frac{a}{RT_B}\right) = 0 \ \Rightarrow \ T_B = \frac{a}{bR}$$

so the effects of molecular size and intermolecular interactions roughly compensate.

1.4   Phase Diagrams and Isotherms
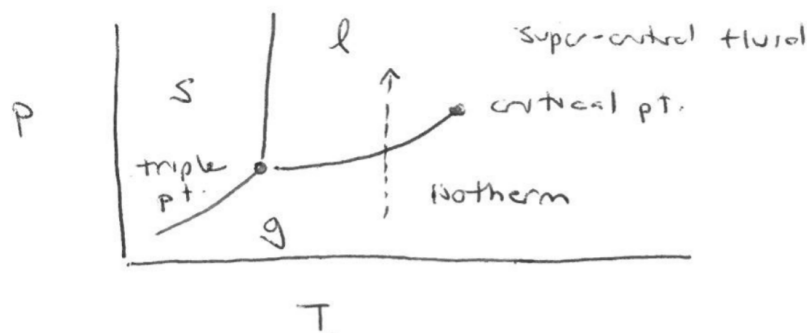
Phase diagram for a single-component system. The lines separate the distinct phase regions.

For $T_{\text{triple}} < T < T_c$, a gas can condense if P is increased. A $g \rightleftharpoons \ell$ equilibrium occurs at the points on the curve between the two phases.

For $T \geq T_c$, there are no longer distinct gas and liquid phases, but a single phase, called a supercritical fluid.

The change that a gas undergoes at fixed T is depicted by plots of P vs. $\bar{V}$, called isotherms. These can be generated for gas in a sealed vessel compressed by a piston.
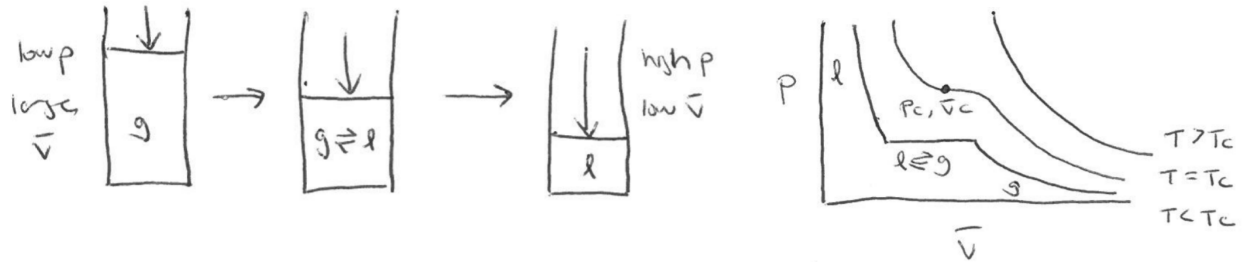
For $T < T_c$, there are 3 regimes in the isotherm. At low P, the system is all gaseous and $P \propto 1/\bar{V}$, as for an ideal gas. When the pressure reaches the co-existence line on the phase diagram, it remains constant as the liquid condenses. When all the liquid has condensed, the pressure increases sharply with further decreases in volume due to the high compressibility.

As $T \to T_c$, the volume range spanned by the plateau decreases and at T_c there is only an inflection point.

For $T > T_c$, there is only a single phase and the isotherm resembles that of an ideal gas.

The vdW equation of state gives improved isotherms relative to the ideal gas law, but will break down for $\bar{V} < b$ and at very low T, where it gives unphysical, negative pressures.
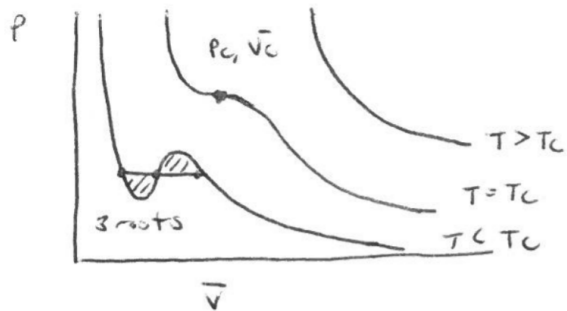
The vdW equation of state captures the inflection point, but for $T < T_c$ gives 3 roots for $\bar{V}$ because of its cubic form.

Rearranging the vdW equation to show its cubic form:

$$
\begin{aligned}
\left(P + \frac{a}{\bar{V}}\right)\left(\bar{V} - b\right) &= RT \\
\left(P\bar{V}^2 + a\right)\left(\bar{V} - b\right) &= RT\bar{V}^2 \\
P\bar{V}^3 - RT\bar{V}^2 - bP\bar{V}^2 + a\bar{V} - ab &= 0 \\
\bar{V}^3 - \left(\frac{RT}{P} + b\right)\bar{V}^2 + \left(\frac{a}{P}\right)\bar{V} - \frac{ab}{P} &= 0
\end{aligned}
$$

There are 3 roots for $\bar{V}$ given a set P,T. To approximate the horizontal part of the isotherm, we use the Maxwell construction, in which the oscillating part of the isotherm is divided into two regions of equal area.

The vdW equation of state can also be used to predict the position of the critical point, where all 3 roots are equal:

$$\left(\bar{V} - \bar{V}_c\right)^3 = 0$$

$$\bar{V}^3 - 3\bar{V}_c\bar{V}^2 + 3\bar{V}_c^2\bar{V} - \bar{V}_c^3 = 0$$

Equating the coefficients with the equation above

$$\frac{RT_c}{P_c} + b = 3\bar{V}_c \qquad \Rightarrow \qquad T_c = \frac{P_c}{R}\left(3\bar{V}_c - b\right)$$

$$\frac{a}{P_c} = 3\bar{V}_c^2 \qquad \Rightarrow \qquad P_c = \frac{a}{3\bar{V}_c^2}$$

$$\frac{ab}{P_c} = \bar{V}_c^3 \qquad \Rightarrow \qquad P_c = \frac{ab}{\bar{V}_c^3}$$

Solving for $\bar{V}_c$, P_c, and T_c in terms of a and b,

$$\frac{a}{3\bar{V}_c^2} = \frac{ab}{\bar{V}_c^3} \qquad \Rightarrow \qquad \bar{V}_c = 3b$$

$$P_c = \frac{a}{3(3b)^2} \qquad \Rightarrow \qquad P_c = \frac{a}{27b^2}$$

$$T_c = \frac{a}{27b^2 R}(9b - b) \qquad \Rightarrow \qquad T_c = \frac{8a}{27Rb}$$

In practise, it is more common for experimental measurements of T_c and P_c to be used to determine a and b parameters for a particular gas.

Solving for a and b in terms of T_c and P_c,

$$\frac{RT_c}{P_c} + b = 3(3b) \qquad \Rightarrow \qquad b = \frac{RT_c}{8P_c}$$

$$a = 27P_c\left(\frac{RT}{8P_c}\right)^2 \qquad \Rightarrow \qquad a = \frac{27}{64}\frac{(RT_c)^2}{P_c}$$

1.5   Kinetic Theory of Gases

A gas is composted of a very large number of atoms of molecules moving in all directions at a distribution of speeds and obeying the classical equations of motion. The molecules collide with each other and with the container elastically, meaning that the total kinetic energy is conserved.
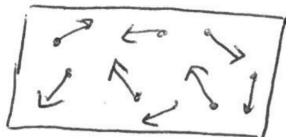
The pressure of the gas is due to the force (per unit area) exerted on the container from impacts and rebounds of the gas molecules. The force is the average momentum, times the collision rate.

$$P = \frac{1}{3}Nmc^2/V$$

N is the number of molecules, m is the mass, c is the average velocity, and the factor of $1/3$ is present because the velocity is evenly distributed in the x, y, and z directions.

Also, the kinetic energy for translational motion of one mole of gas is

$$U_{\text{trans}} = \frac{1}{2}N_A mc^2$$

Substituting the result for pressure,

$$U_{\text{trans}} = \frac{3}{2}\frac{N_A}{N}PV = \frac{3}{2}\frac{PV}{n}$$

where n is the moles of gas. Using the ideal gas law, the total translational kinetic energy is

$$U_{\text{trans}} = \frac{3}{2}RT$$

which is evenly distributed as $\frac{1}{2}RT$ from each of the x, y, z directions (or degrees of freedom). This is called the equipartition law.

Similarly, the kinetic energy from rotation of a mole of molecules is $\frac{1}{2}RT$ for each direction of rotation (2D for linear molecules, 3D for non-linear).

$$\begin{aligned} U_{\text{rot}} &= RT \quad \text{(linear molecules)} \\ U_{\text{rot}} &= \frac{3}{2}RT \quad \text{(non-linear molecules)} \end{aligned}$$

This is the average kinetic energy for one mole. The kinetic energy of each atom or molecule follows a probability distribution, called the Maxwell-Boltzmann distribution.
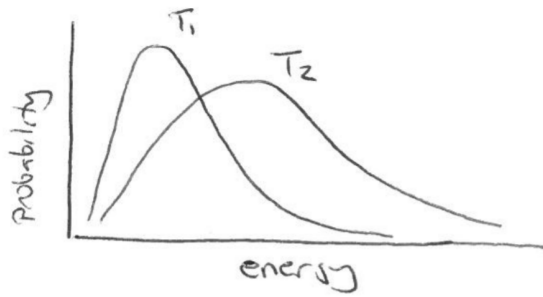
$$f(E) = 2\pi \left(\frac{1}{RT}\right)^{3/2} E^{1/2} e^{-E/RT}$$

Higher temperatures shift the average kinetic energy to higher values and broaden the distribution.

Chapter 2

The Laws of Thermodynamics

2.1 The Zeroth Law of Thermodynamics

When two systems are brought into thermal contact, they will reach equilibrium, sharing a common temperature.
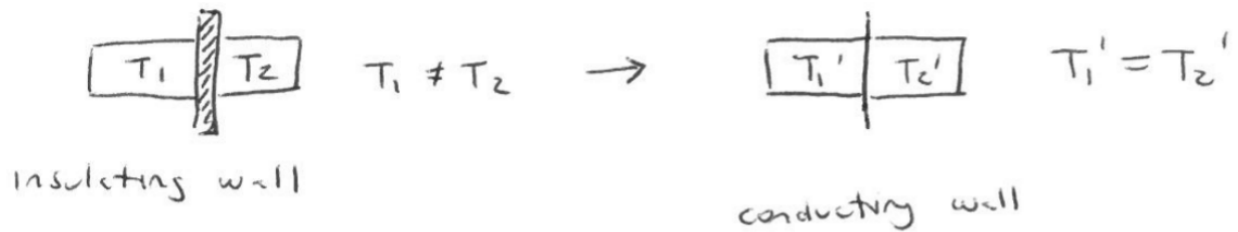
Two systems that are in thermal equilibrium with a third system must be in thermal equilibrium with each other.

This makes sense in terms of kinetic theory since gases at different temperatures will transfer energy via elastic collisions. The hotter (faster) molecules will lose energy on average and the colder (slower) molecules will gain energy on average, until a new, intermediate distribution is reached.
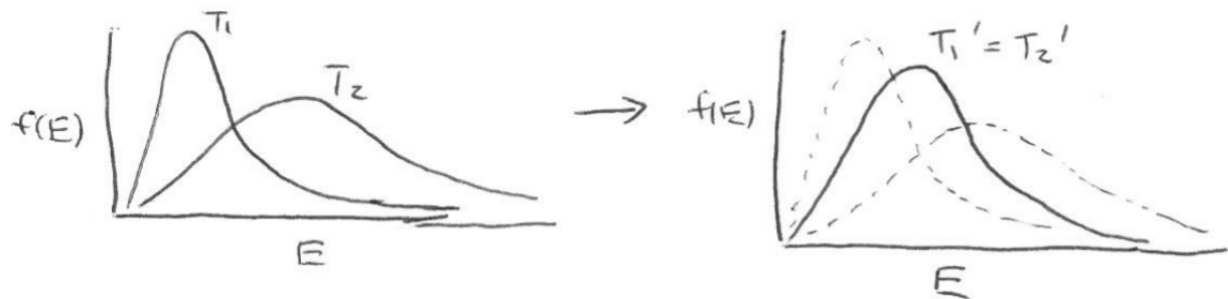
The final T will depend on the initial temperatures and heat capacities of the two systems.

The heat capacity is the amount of energy required to raise the temperature of a system by 1 K.

For a system with constant volume, the heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

which is the partial derivative of U with respect to T at constant V.

For an ideal gas, C_V can be obtained from kinetic theory

$$
\begin{aligned}
C_V &= \frac{3}{2}R \quad \text{monoatomic gas} \\
C_V &= \frac{5}{2}R \quad \text{diatomic (or other linear) gas molecules} \\
C_V &= 3R \quad \text{non-linear gas molecules}
\end{aligned}
$$

C_V can be higher than this estimate, particularly at high T or for heavy elements, due to vibrational motion, which is neglected here.

2.2   Thermodynamic Definitions
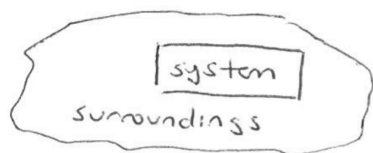
System and surroundings – the system is the particular thing of interest, while the surroundings is everything else and is separated from the system by a boundary. The surroundings can be viewed as a reservoir of energy, some of which can be exchanged with the system via heat and work.

A system is isolated if no matter or energy can cross the boundary.

A system is closed if energy can cross the boundary, but not matter. This means the system is in thermal contact with the surroundings.

A system is open if both matter and energy can cross the boundary.

The state of a system is determined by its chemical and physical properties and is specified by the composition and two other independent variables – two of T, P, and V.

Change of state – the system undergoes a change in P, T, V from an initial (i) to final (f) state, as a new equilibrium is reached.

Path – exactly how the initial state is changed to the final state.

Path function – quantities that depend on the particular path of a change of state (heat and work).

State function – quantities that depend only on the state of the system and not on the path (energy, enthalpy, entropy, free energy).

Reversible path – the state is changed infinitely slowly so that the system remains in a quasi-equilibrium with the surroundings. Real processes are not reversible, but this is a convenient path to consider in calculations.

Irreversible path – the state is changed quickly, with large, finite changes in P, T, or V. Real processes are irreversible.

Internal energy (U) – the total energy of all molecules in the system. It is a sum of kinetic (translation, rotational, and vibrational) and potential (intermolecular and intramolecular) energies.

Heat (q) – a mode of energy transfer resulting from a temperature imbalance between the system and surroundings. From the zeroth law, heat will be transferred until thermal equilibrium is reached. The head transferred is proportional to the temperature gradient and depends on the heat capacity.

$$q = \int_i^f CdT \qquad (2.1)$$

By convention, heat is positive when it is transferred to the system from the surroundings, to raise the system's internal energy.

Work (w) – a mode of energy transfer resulting from a change in the volume of the system, subject to an external pressure from the surroundings. Work is force times distance, and force is pressure times area, so

$$w = - \int_i^f P_{\text{ext}}dV \qquad (2.2)$$

By convention, work is positive when work is done on the system, so that its volume decreases, raising the system's internal energy. Note that the work is given in terms of the applied, external pressure, not the system pressure.

2.3   The First Law of Thermodynamics

For a change of state, heat and work are transferred between the system and surroundings, so that the change in the system's internal energy is

$$\boxed{\Delta U = q + w} \tag{2.3}$$

ΔU is a state function, so for a cyclic process with the same initial and final states, $\Delta U = 0$, and the heat and work offset. Heat transferred to the system is offset by work done by the system. Heat transferred to the surroundings is offset by work done by the surroundings.

The total energy of the system and surroundings is conserved for any change of state, which is another statement of the first law.

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$

Since U is independent of path, a practical approach to problems is to use the path where calculation of q and w is easy.

2.4   Work over Different Paths

Irreversible, constant P_{ext} – to evaluate the integral, we need $P_{\text{ext}}(V)$; for constant P_{ext}, this gives

$$w = -P_{\text{ext}} \int_i^f dV = -P_{\text{ext}}\Delta V$$

an example is expansion against a piston with constant applied weight.
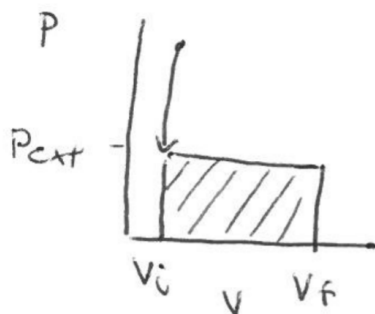
For an irreversible process, there is a sharp change in P_{ext} as the weight on the piston is removed. The work done is the area under the curve.

Reversible paths – P_{ext} equals the gas pressure since the system remains in quasi-equilibrium with the surroundings.

- Isochoric change (constant V): $\Delta V = 0$ so $w = 0$
- Isobaric change (constant P): $w = -P \int_i^f dV = -P\Delta V$

- Isothermal change (constant T): $w = -\int_i^f P(V)dV$ and we need to obtain $P(V)$ from an equation of state.

For an ideal gas, $P = nRT/V$ so the integral is

$$w = -nRT \int_i^f \frac{dV}{V} = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

For a vdW gas, use

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

in the integrand.
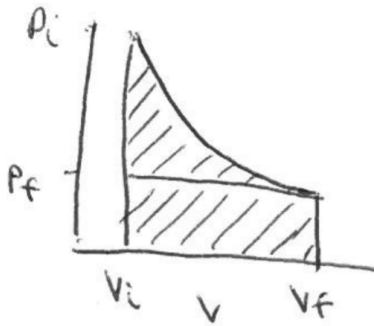
For a reversible process, the gas pressure changes gradually, as $1/V$. The area under the curve can be viewed as an infinite number of irreversible steps.

The reversible path provides the maximum area or maximum work.

2.5 Heat over Different Paths

The heat capacity is frequently treated as a constant as it only changes significantly over large temperature ranges, or near zero Kelvin. However, the particular heat capacity still depends on the path.

- Isochoric path (constant V) – use C_V:

$$q = C_V \int_i^f dT = C_V \Delta T$$

- Isobaric path (constant P) – use C_P:

$$q = C_P \int_i^f dT = C_P \Delta T$$

At constant V, no work is done and all energy transferred to the system serves to raise T. At constant P, some of the energy transferred must must be used to do the work

needed to maintain the pressure, so more energy is required to raise T by the same amount and $C_P > C_V$.

For an ideal gas, we will show later that

$$\boxed{\bar{C}_P = \bar{C}_V + R \ \text{ or } \ C_P = C_V + nR} \tag{2.4}$$

For a liquid or solid, the volume change is negligible, so $C_P \approx C_V$.

- Isothermal path (constant T) – $\Delta T = 0$ but that does not mean that $q = 0$ as heat will be transferred to or from the system to maintain the constant temperature. Here, q must be obtained from the first law:

$$q = \Delta U - w$$

For the case of an ideal gas, $\Delta U = 0$ when $\Delta T = 0$ (only kinetic energy as there are no intermolecular interactions), so $q = -w$.

2.6   Energy and Enthalpy

Returning to the first law, $\Delta U = q + w$, and ΔU is determined by evaluating q and w over a particular path.

For an isochoric path (constant V), $q = C_V \Delta T$ and $\Delta V = 0$ so $w = 0$.

$$\boxed{\Delta U = C_V \Delta T \quad \text{isochoric path, or ideal gas any path}} \tag{2.5}$$

This also holds for an ideal gas for any process, since ΔU depends only on changes in T.

ΔU can thus be measured from the heat of reaction performed under constant V (bomb calorimeter). However, in chemistry, it is much more common to carry out reactions at constant P (open vessel on the bench top).

For an isobaric path (constant P), $q = C_P \Delta T$ and $w = -P\Delta V$.

$$\Delta U = C_P \Delta T - P\Delta V \quad \text{isobaric path}$$

Rearranging gives $C_P \Delta T = \Delta U + P\Delta V$.

The RHS is a combination of state functions (U, P, V), so the LHS must also be a state function. We define a new state function, the Enthalpy, H:

$$\Delta H = \Delta U + \Delta(PV)$$

Thus,

$$\boxed{\Delta H = C_P \Delta T \quad \text{isobaric path, or ideal gas any path}} \tag{2.6}$$

and ΔH can be measured from the heat of reaction performed under constant P.

For an ideal gas with constant n, the relation between ΔH and ΔU can be simplified to

$$\Delta H = \Delta U + nR\Delta T$$

2.7 Adiabatic Processes

For a thermally-insulating boundary, no heat is transferred from the surroundings, so $q = 0$ and $\Delta U = w$.

For adiabatic expansion, $\Delta V > 0$, so the internal energy and T decrease.

For adiabatic compression, $\Delta V < 0$, so the internal energy and T increase.

The temperature change will depend on the work and heat capacity. Looking at the relation between the differentials (infinitesimally small changes in U and w),

$$dU = C_V dT = -P_{\text{ext}} dV$$

For constant external pressure, we can integrate to obtain

$$\Delta U = C_V \Delta T = -P_{\text{ext}} \Delta V$$

$$T_f = T_i - \frac{P_{\text{ext}}}{C_V}(V_f - V_i)$$

The final pressure will equilibrate to the external pressure, so for an ideal gas,

$$T_f = T_i - \frac{P_{\text{ext}}}{n\bar{C}_V}\left(\frac{nRT_f}{P_{\text{ext}}} - \frac{nRT_i}{P_i}\right)$$

$$T_f\left(1 + \frac{R}{\bar{C}_V}\right) = T_i\left(1 + \frac{R}{\bar{C}_V}\frac{P_{\text{ext}}}{P_i}\right)$$

For a reversible adiabatic process involving an ideal gas, $P_{\text{ext}} = P = nRT/V$. Returning to

the differentials:

$$
\begin{aligned}
C_V \, dT &= -P_{\text{ext}} \, dV \\
C_V \, dT &= -\frac{nRT}{V} \, dV \\
C_V \int_i^f \frac{dT}{T} &= -nR \int_i^f \frac{dV}{V} \\
\ln\left(\frac{T_f}{T_i}\right) &= -\frac{nR}{C_V} \ln\left(\frac{V_f}{V_i}\right) \\
\ln\left(\frac{T_f}{T_i}\right) &= \frac{R}{\bar{C}_V} \ln\left(\frac{V_i}{V_f}\right) \\
T_f &= T_i \left(\frac{V_i}{V_f}\right)^{R/\bar{C}_V}
\end{aligned}
$$

Once T_f is determined, the total energy change is $\Delta U = C_V \Delta T$.

The ideal gas relation can be used repeatedly to obtain:

$$
T_f = T_i \left(\frac{P_f}{P_i}\right)^{R/\bar{C}_P} \quad \text{and} \quad P_f = P_i \left(\frac{V_i}{V_f}\right)^{1 + R/\bar{C}_V}
$$

The pressure is now proportional to $1/V^{(1+R/\bar{C}_V)}$ rather than the usual $1/V$, so the pressure drop is greater for adiabatic expansion than for isothermal expansion This occurs because no heat is transferred from the surroundings, so the lower system T causes a lower final P.

Conversely, the volume is now proportional to $1/P^{(1-R/\bar{C}_V)}$ rather than the usual $1/P$, so the volume change is greater for isothermal expansion than for adiabatic expansion.
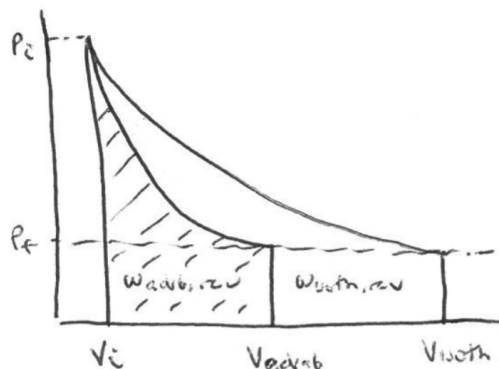
For the same pressure change, we will have

$$
w_{\text{adiab,rev}} < w_{\text{isoth,rev}}
$$

The isothermal process generates more work than the adiabatic since the heat transferred from the surroundings in the isothermal case drives further expansion.

2.8 Thermochemistry

Chemical processes are described by whether heat is required or released, which is given by the sign of the enthalpy change.
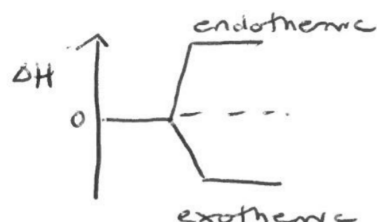
Exothermic:
- $\Delta H < 0$
- heat given off to surroundings
- final state more stable

Endothermic:
- $\Delta H > 0$
- heat absorbed from surroundings
- final state less stable

There are no "absolute" enthalpy values – we always report changes in enthalpy for various processes, typically per mole of reactants or products.

Physical changes:
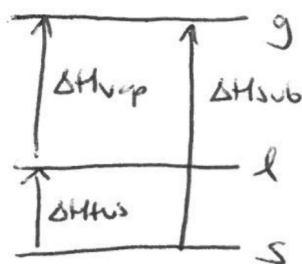
ΔH_{vap} – heat of vapourization $(\ell \to g)$

ΔH_{fus} – heat of fusion $(s \to \ell)$

ΔH_{sub} – heat of sublimation $(s \to g)$

ΔH_{sol} – heat of solvation $(s \to \text{solution})$

Chemical changes:

- Ionization enthalpy – enthalpy for removal of an electron.

$$\text{EX.} \qquad \text{Na}_{(g)} \longrightarrow \text{Na}^+_{(g)} + e^-$$
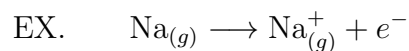
- Bond dissociation enthalpy – enthalpy to break a chemical bond.

$$\text{EX.} \qquad \text{C}_2\text{H}_{6(g)} \longrightarrow 2\text{CH}_{3(g)}$$
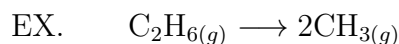
- Atomization enthalpy – enthalpy to break a substance into isolated atoms.

$$\text{EX.} \qquad \text{C}_2\text{H}_{6(g)} \longrightarrow 2\text{C}_{(g)} + 6\text{H}_{(g)}$$
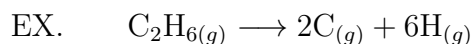
However these involve unstable, reactive species like H, C, CH_3. Instead, we typically tabulate either:

- Enthalpy/heat of combustion – enthalpy change for reaction of one mole of a compound with $O_{2(g)}$, yielding complete conversion to $CO_{2(g)}$ and $H_2O_{(\ell)}$.

$$\text{EX.} \qquad C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(\ell)} \qquad \Delta H^\circ_{\text{comb}}[C_2H_{6(g)}]$$
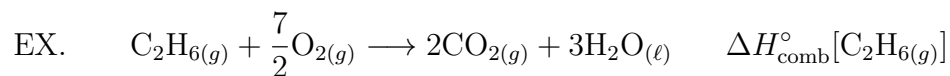
- Enthalpy/heat of formation (ΔH°_f) – enthalpy change for formation of one mole of a compound from the elements in their standard states.

$$\text{EX.} \qquad 2C_{(s,\text{graphite})} + 3H_{2(g)} \longrightarrow C_2H_{6(g)} \qquad \Delta H^\circ_f[C_2H_{6(g)}]$$

$$\text{EX.} \qquad H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)} \qquad \Delta H^\circ_f[H_2O_{(\ell)}]$$

The standard state $(^\circ)$ of a substance is its most stable state at $P = 1$ atm. Standard enthalpies are typically reported at 298 K. The enthalpy of formation of an element in its standard state is zero since reactants/products are identical.

$$\text{EX.} \qquad \Delta H^\circ_f[O_{2(g)}] = 0$$

Because enthalpy is a state function, ΔH for any reaction is a sum of enthalpy changes for a set of component steps – this is Hess's law.

EX. Combustion of methane:

$$
\begin{array}{rcll}
C_{(s,\text{graphite})} + O_{2(g)} & \longrightarrow & CO_{2(g)} & \Delta H^\circ_f[CO_{2(g)}] \\
2H_{2(g)} + O_{2(g)} & \longrightarrow & H_2O_{(\ell)} & 2\Delta H^\circ_f[H_2O_{(\ell)}] \\
CH_{4(g)} & \longrightarrow & C_{(s,\text{graphite})} + H_{2(g)} & -\Delta H^\circ_f[CH_{4(g)}] \\
\hline
CH_{4(g)} + 2O_{2(g)} & \longrightarrow & CO_{2(g)} + 2H_2O_{(\ell)} & \Delta H^\circ_{\text{comb}}[CH_{4(g)}]
\end{array}
$$
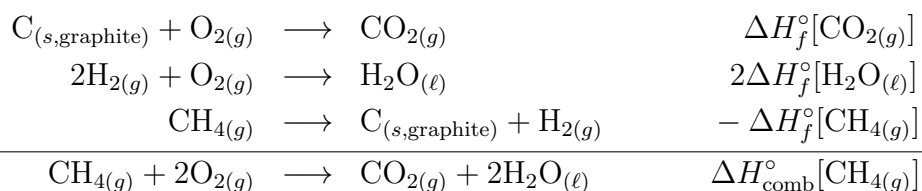
Thus,

$$\Delta H^\circ_{\text{comb}}[CH_{4(g)}] = \Delta H^\circ_f[CO_{2(g)}] + 2\Delta H^\circ_f[H_2O_{(\ell)}] - \Delta H^\circ_f[CH_{4(g)}]$$

by summing the individual steps.

In general, the enthalpy change for a process is

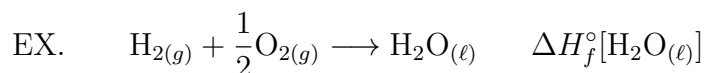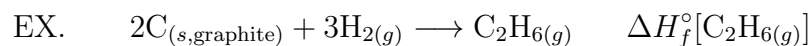$$\boxed{\Delta H = \sum_{\text{products}} \nu_i \Delta H^\circ_f[i] - \sum_{\text{reactants}} \nu_i \Delta H^\circ_f[i]} \qquad (2.7)$$

where the ν_i are the stoichiometric coefficients in the balanced chemical equation.

$$\text{EX.} \qquad a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$
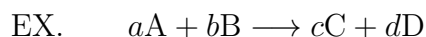
$$\Delta H = c\Delta H^\circ_f[C] + d\Delta H^\circ_f[D] - a\Delta H^\circ_f[A] - b\Delta H^\circ_f[B]$$
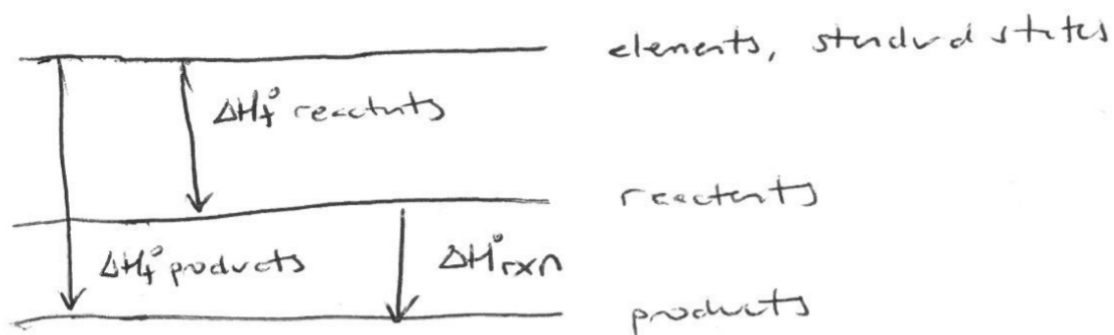
Enthalpy measurements typically use bomb calorimeters, which are sealed vessels to prevent escape of gas. This is an isochoric process, so the heat of reactions is described by $\Delta U = C_V \Delta T$ rather than ΔH. Assuming ideal gases,

$$\Delta H = \Delta U + \Delta n R T$$

where Δn is the change in the number of moles of gas in the balanced reaction. More generally,

$$\Delta H = \Delta U + \Delta(PV)$$

and we will consider how to evaluate the $\Delta(PV)$ term for non-ideal gases later as these depend on the intermolecular interactions.

To predict ΔH for temperatures other than the standard 298 K, we need to consider how the enthalpies of the reactants and products vary with temperature.

From the kinetic model, the internal energy, and consequently the enthalpy, will increase with T due to the higher kinetic energy. However, the enthalpies of the reactants/products may increase at different rates, depending on their constant-pressure heat capacities:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$
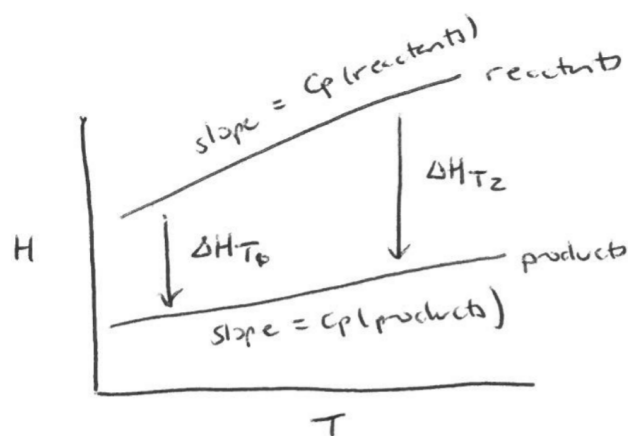
For a single species,

$$H^\circ_{T_2} = H^\circ_{T_1} + \int_{T_1}^{T_2} C_P dT$$

and ΔH for the reaction is

$$\Delta H^\circ = H^\circ(\text{products}) - H^\circ(\text{reactants})$$

For ΔH at a non-standard temperature T, rather than the standard temperature T_0,

$$\Delta H_T^\circ = \Delta H_{T_0}^\circ + \int_{T_0}^{T} C_P(\text{products})dT - \int_{T_0}^{T} C_P(\text{reactants})dT$$

$$\Delta H_T^\circ = \Delta H_{T_0}^\circ + \int_{T_0}^{T} \Delta C_P dT$$

where $\Delta C_P = C_P(\text{products}) - C_P(\text{reactants})$. This result is called Kirchoff's law. In general, we need an expression for $\Delta C_P(T)$ to integrate, but if the temperature range is small, the individual C_P's can be considered constant and

$$\Delta H_T^\circ = \Delta H_{T_0}^\circ + \Delta C_P(T - T_0) = \Delta H_{T_0}^\circ + \Delta C_P \Delta T$$

2.9   Entropy

So far, we have predicted final states of various processes, but not whether they occur spontaneously or whether they require an input of energy.

Spontaneous processes are characterized by energy becoming more dispersed and matter becoming more disordered.

For example, when two blocks of metal at different temperatures are brought into thermal contact, heat will flow from the hot block to the cold one (according to the zeroth law). The kinetic energy of the molecules will become more dispersed between the blocks.

high T, high KE   low T, low KE   intermediate T, KE
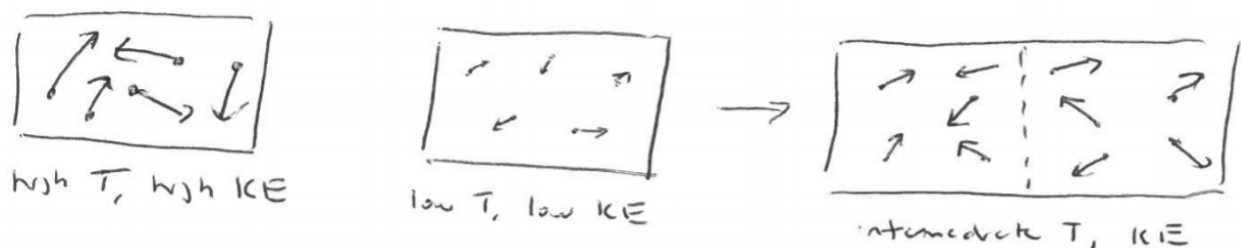
It is not spontaneous for the hot block to get hotter and the cold block to get colder, which would result in a more concentrated distribution of kinetic energy.

To quantify the extent of randomization of energy, we propose a new state function, the entropy, S. It is related to the amount of heat transferred by the differential equation

$$dS = \frac{dq_{\text{rev}}}{T} \quad \text{or} \quad \Delta S = \int_{i}^{f} \frac{dq_{\text{rev}}}{T}$$

Since q depends on the path, we need to pick a specific path to ensure that S is a state function. The reversible path is chosen for convenience.

At very low temperature, the system is highly ordered so introducing heat will cause relatively more randomness

very low T
ordered lattice
of molecules
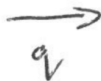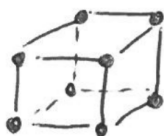
higher T
molecules rotate and
vibrate in lattice

and this results in a greater increase in disorder compared to a gas at high temperature that is already very disordered – adding more heat does not cause as large a change in entropy. This, in the definition of S, we divide by T since adding heat will result in a greater increase in disorder at lower temperatures.

2.10 The Second Law of Thermodynamics

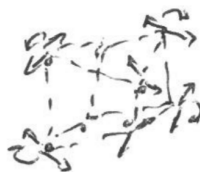The overall entropy of the universe (system + surroundings) must increase for a process to be spontaneous.

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Recall that the entropy of the system is

$$\Delta S_{\text{sys}} = \int_i^f \frac{dq_{\text{sys,rev}}}{T}$$

For a reversible process, $q_{\text{surr}} = -q_{\text{sys,rev}}$ so

$$\Delta S_{\text{surr}} = \int_i^f \frac{dq_{\text{surr}}}{T} = -\int_i^f \frac{dq_{\text{sys,rev}}}{T} = -\Delta S_{\text{sys}}$$

so $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ for a reversible process and neither the forward or reverse process is spontaneous. This makes sense since, for a reversible process, the system and surroundings are in quasi-equilibrium.

For irreversible processes, $q_{\text{surr}} = -q_{\text{sys,irrev}} \neq -q_{\text{sys,rev}}$ and $\Delta S_{\text{surr}} \neq -\Delta S_{\text{sys}}$. Thus, the difference between the reversible and irreversible processes is the entropy change of the surroundings.

2.11 Entropy Changes for Different Processes

- Adiabatic process: no heat is transferred, so $dq_{\text{rev}} = 0$ and $\Delta S = 0$

- Isochoric process: $dV = 0$ so $dU = C_V dT = dq_{\text{rev}}$

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} = \int_i^f \frac{C_V dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right)$$

- Isothermal process: T is constant, so $\Delta S = \frac{q_{\text{rev}}}{T}$

  For a phase change (i.e. $\ell \rightleftharpoons g$), the process is both isothermal and isobaric, but C_P is not constant since it is different for each phase.

$$\Delta H = q_{\text{rev}}|_P \quad \text{so} \quad \Delta S = \frac{\Delta H}{T} \quad \text{(phase change)}$$

- Ideal gas, any process: the energy is $dU = C_V dT$ and from the first law, $dU = dq_{\text{rev}} - PdV$. Equating these and rearranging,

$$dq_{\text{rev}} = C_V dT + PdV$$

  using the ideal gas law,

$$dq_{\text{rev}} = C_V dT + nRT\frac{dV}{V}$$

$$\frac{dq_{\text{rev}}}{T} = C_V \frac{dT}{T} + nR\frac{dV}{V}$$

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} = C_V \int_i^f \frac{dT}{T} + nR \int_i^f \frac{dV}{V}$$

$$\Delta S = C_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) \quad \text{ideal gas}$$

2.12   Absolute Entropy and the Third Law

The third law defines an absolute entropy scale. The entropy of a perfectly-ordered crystal is zero at 0 K. This means that all substances have a positive entropy at finite temperatures, where they show thermal motion and are disordered.

The absolute entropy at any temperature can be obtained by integrating the entropy expression from 0 to T

$$S(T) = \int_0^T \frac{dq_{\text{rev}}}{T}$$

The integration is typically performed along the isobaric path for convenience and requires the heat capacities of each phase, along with the heats of fusion and vapourization

$$S(T) = \int_0^{T_m} \frac{C_{P,(s)} dT}{T} + \frac{\Delta H_{\text{fus}}}{T_m} + \int_{T_m}^{T_b} \frac{C_{P,(\ell)} dT}{T} + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_b}^{T} \frac{C_{P,(g)} dT}{T}$$

The standard entropy, $S°$, indicates the absolute entropy of a compound in its standard state. The standard entropy of reaction can be obtained in an analogous way as for the enthalpy,

$$\Delta S = \sum_{\text{products}} \nu_i S°[i] - \sum_{\text{reactants}} \nu_i S°[i]$$

where the ν_i are the stoichiometric coefficients in the balanced chemical equation.

The entropy for each component in the reaction will have a temperature dependence given by

$$S_i°(T_2) = S_i°(T_1) + \int_{T_1}^{T_2} \frac{C_{P,i}(T)}{T} dT$$

The temperature dependence of the standard reaction entropy is

$$\Delta S°(T_2) = \Delta S°(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_P}{T} dT$$

where $\Delta C_P = \sum_i \nu_i C_{P,i}$. This result is completely analogous to Kirchoff's law for the temperature dependence of the reaction enthalpy. If ΔC_P is independent of temperature, it can be factored out of the integral and this result simplifies to

$$\Delta S°(T_2) = \Delta S°(T_1) + \Delta C_P \ln\left(\frac{T_2}{T_1}\right)$$

2.13 Free Energy and Spontaneity

The second law states that the overall entropy, $\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$, must increase for a process to be spontaneous, but we would prefer a spontaneity criterion based only on properties of the system. This can be done for two paths: (1) constant V, T and (2) constant P, T.

From the second law,

$$dS_{\text{sys}} + dS_{\text{surr}} = dS_{\text{sys}} + \frac{dq_{\text{surr}}}{T_{\text{surr}}} \geq 0$$

For an isothermal path, $T = T_{\text{sys}} = T_{\text{surr}}$ and $dq_{\text{surr}} = -dq_{\text{sys}}$, so

$$dS_{\text{sys}} - \frac{dq_{\text{sys}}}{T} \geq 0$$

The first term is for a reversible path (by the definition of the system entropy), but the second is for any isothermal path, and these two terms will differ for irreversible paths.

For constant volume, $dq_{\text{sys}} = dU$, so $dS_{\text{sys}} - dU/T \geq 0$ and rearranging gives

$$dU - TdS \leq 0$$

For constant pressure, $dq_{\text{sys}} = dH$, so $dS_{\text{sys}} - dH/T \geq 0$ and rearranging gives

$$dH - TdS \leq 0$$

We define two new state functions:

- The Helmholtz energy: $\Delta A = \Delta U - T\Delta S$ (constant V)

- The Gibbs energy: $\Delta G = \Delta H - T\Delta S$ (constant P)

For a process to be spontaneous, either

$$\Delta A \leq 0 \quad (\text{constant } V, T) \quad \text{or} \quad \Delta G \leq 0 \quad (\text{constant } P, T)$$

Since most chemical processes are carried out under constant P, rather than constant V, we usually focus on ΔG and not ΔA.

Gibbs energy changes for a reaction can be obtained from the corresponding free energies of formation (analogous to standard entropies and formation enthalpies)

$$\Delta G^{\circ} = \sum_{\text{products}} \nu_i \Delta G_f^{\circ}[i] - \sum_{\text{reactants}} \nu_i \Delta G_f^{\circ}[i]$$

ΔG° can also be obtained directly from the standard enthalpies (ΔH°) and entropies (ΔS°) of reaction. Analogous statements can be made for the standard Helmholtz energy, ΔA°.

Note that $\Delta G = 0$ corresponds to the reversible process, where the system is in equilibrium.

$\Delta G < 0$ for spontaneity and all systems react to decrease their Gibbs energy. $\Delta H < 0$ and $\Delta S > 0$ both lower ΔG and are favourable for reaction.

The conditions for spontaneity can be summarized as:

ΔH	ΔS	ΔG	
$-$	$+$	$-$	spontaneous at all T
$-$	$-$	$\pm$	spontaneous at low T
$+$	$+$	$\pm$	spontaneous at high T
$+$	$-$	$+$	not spontaneous at any T

EX. Combustion of graphite

$$C_{(s,\text{graphite})} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H < 0, \Delta S > 0 \rightarrow \text{spontaneous}$$

EX. Melting of ice

$$H_2O_{(s)} \longrightarrow H_2O_{(\ell)} \qquad \Delta H > 0, \Delta S > 0 \rightarrow \text{high } T$$
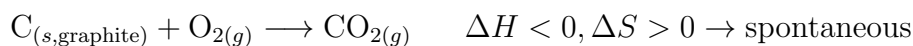
EX. Formation of ammonia (Haber process)

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \longrightarrow NH_{3(g)} \qquad \Delta H < 0, \Delta S < 0 \rightarrow \text{low } T$$
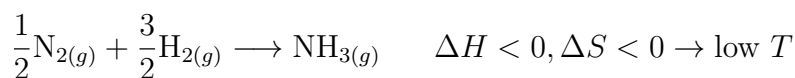
Note that ΔG does not have any connection to the reaction rate. A spontaneous reaction can be slow (rusting of iron) or fast (burning of acetylene), but will eventually proceed given a long enough time span, while a non-spontaneous reaction will never proceed.

2.14 Maximum Work

The Helmholtz energy has another physical interpretation beyond spontaneity – it can give us the maximum work that can be done by the system. Recall the definition of the entropy:

$$dS = \frac{dq_{\text{rev}}}{T} \quad \text{or integrating at constant } T, \quad T\Delta S = q_{\text{rev}}$$

From the first law, $\Delta U = q + w$ so

$$\Delta U = T\Delta S + w_{\text{rev}}$$

$$w_{\text{rev}} = \Delta U - T\Delta S = \Delta A$$

and the maximum work occurs for the reversible path, so $w_{\text{max}} = \Delta A$. This is the origin of the term "free" energy. ΔA is the part of the internal energy change (ΔU) not involved in random thermal motion of the atoms or molecules ($T\Delta S$) and is consequently free to do work.

An analogous interpretation exits for ΔG, which is the maximum additional non-expansion work. Recall that PV work is done by the system (for a constant P, T process) to expand the volume against the external pressure. The non-expansion work is any further work that can be done by the system, such as electrical work. Partitioning the total reversible work into these contributions,

$$w_{\text{rev}} = -P\Delta V + w_{\text{add,max}}$$

where again the maximum additional work will be obtained for the reversible path.

From the definitions of the Gibbs energy and enthalpy,

$$dG = dH - TdS = dU + PdV - TdS$$

and at constant P, T

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

Substituting from the first law, $\Delta U = q_{\text{rev}} + w_{\text{rev}}$ and $T\Delta S = q_{\text{rev}}$,

$$\Delta G = q_{\text{rev}} + w_{\text{rev}} + P\Delta V - q_{\text{rev}}$$

$$w_{\text{rev}} = -P\Delta V + \Delta G$$

Comparing with the above result, $w_{\text{add,max}} = \Delta G$ and ΔG is the maximum additional non-expansion work that can be done by the system. This is particularly useful in assessing the maximum electrical work that can be produced by fuel cells and electrochemical cells (batteries).

Chapter 3

Maxwell Relations

3.1 Total Derivatives

For a function of two variables, $f(x, y)$, the slope in the x-direction is $(\frac{\partial f}{\partial x})_y$, indicating the partial derivative of f with respect to x, with y held constant. Similarly, the slope in the y-direction is $(\frac{\partial f}{\partial y})_x$. The total change in f when both x and y are changed to $x + dx$ and $y + dy$ is a sum of the changes in each direction. This gives the total derivative:

$$\boxed{df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy} \tag{3.1}$$
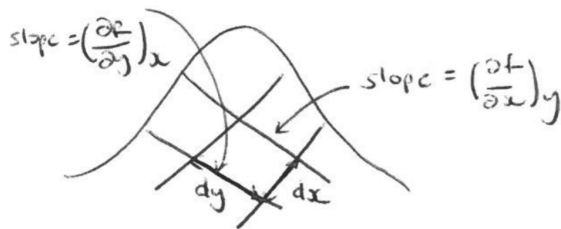
A simple analogy is to consider a hill, where you have a grid of streets.

When working with partial derivatives, two useful simplifications are:

$$\left(\frac{\partial x}{\partial x}\right)_y = 1 \qquad \text{since this is the change in a variable with respect to itself}$$

$$\left(\frac{\partial y}{\partial x}\right)_y = 0 \qquad \text{there is no change in } y \text{ since it is held constant}$$

If we have

$$df = \left(\frac{\partial y}{\partial z}\right)_x dx$$

31

for some function f, we can divide through by dx to get

$$\frac{df}{dx} = \left(\frac{\partial y}{\partial z}\right)_x$$

Alternatively, we could integrate both sides to find $f(x)$

$$f = \int df = \int \left(\frac{\partial y}{\partial z}\right)_x dx$$

Next, we will demonstrate two useful properties of partial derivatives. First, starting from the total derivative for $x(y, z)$:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Dividing through by dx:

$$1 = \left(\frac{\partial x}{\partial y}\right)_z \frac{dy}{dx} + \left(\frac{\partial x}{\partial z}\right)_y \frac{dz}{dx}$$

Let z be held constant, to give:

$$1 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_z$$

but the last partial is zero and

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \qquad \text{or} \qquad \left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z^{-1}$$

which is called the inverse property.

Returning to our total derivative for $x(y, z)$:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

if we differentiate with respect to z with constant x,

$$0 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y$$

and re-arranging,

$$\left(\frac{\partial x}{\partial z}\right)_y = -\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x$$

which is called the permutation relation.

3.2   Maxwell Relations and the Fundamental Equations of Thermodynamics

Combining the first and second laws, $dU = dq_{\text{rev}} + dw_{\text{rev}}$ and $dq_{\text{rev}} = TdS$, along with the reversible work, $dw_{\text{rev}} = -PdV$ gives

$$\boxed{dU = TdS - PdV} \tag{3.2}$$

This is valid for all paths since it is composed entirely of state functions. This is often called the fundamental equation of thermodynamics. It can be used along with the definitions of dH, dA, and dG to give three analogous fundamental equations.

The definition of enthalpy is $H = U + PV$, so $dH = dU + PdV + VdP$. Substituting the above expression for dU gives

$$\boxed{dH = TdS + VdP} \tag{3.3}$$

The definition of the Helmholtz energy is $A = U - TS$, so $dA = dU - TdS + SdT$. Substituting for dU gives

$$\boxed{dA = -PdV - SdT} \tag{3.4}$$

The definition of the Gibbs energy is $G = H - TS$, so $dG = dH - TdS - SdT$. Substituting for dH gives

$$\boxed{dG = VdP - SdT} \tag{3.5}$$

These 4 equations can be used to generate 4 relations between the entropy and the independent variables, P, V, T, called the Maxwell relations.

1. Write $U = U(S, V)$ and take the total derivative

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Comparing with the above result and equating coefficients,

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \text{and} \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Also, since U is a state function, the order of derivatives commute, so

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

and substituting gives

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \tag{3.6}$$

2. Write $H = H(S, P)$ and take the total derivative

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Comparing with the above result and equating coefficients,

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \text{and} \qquad \left(\frac{\partial H}{\partial P}\right)_S = V$$

Applying the state function condition that the derivatives commute,

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right]_P$$

and substituting gives

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P} \qquad (3.7)$$

3. Write $A = A(V, T)$ and take the total derivative

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

Comparing with the above result and equating coefficients,

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad \text{and} \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

Applying the state function condition that the derivatives commute,

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right]_V = \left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right]_T$$

and substituting gives

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T} \qquad (3.8)$$

4. Write $G = G(P, T)$ and take the total derivative

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

Comparing with the above result and equating coefficients,

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \text{and} \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Applying the state function condition that the derivatives commute,

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T$$

and substituting gives

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \qquad (3.9)$$

3.3   Total Derivatives of U and H

We would like to have expressions that allow determination of ΔU and ΔH for any path in terms of P, V, T and other easy-to-measure quantities.

For $U = U(T, V)$, the total derivative is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

but the first term here is C_V so

$$\boxed{dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV} \qquad (3.10)$$

To evaluate U for non-ideal gases along anything but the isochoric path, we need an expression for $\left(\frac{\partial U}{\partial V}\right)_T$.

Similarly, for $H = H(T, P)$, the total derivative is

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

but the first term here is C_P so

$$\boxed{dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP} \qquad (3.11)$$

and we need an expression for $\left(\frac{\partial H}{\partial P}\right)_T$.

$\left(\frac{\partial U}{\partial V}\right)_T$ is the change in energy of a gas with respect to volume at constant T and is related to the strength of the intermolecular interactions.

From the fundamental equation

$$dU = TdS - PdV$$

take the derivative with respect to V at constant T

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Substituting the Maxwell relation gives

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \tag{3.12}$$

This can be evaluated given any equation of state for the gas.

For an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right) - \frac{nRT}{V} = 0$$

which is expected since there are no intermolecular interactions.

For a vdW gas,

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \qquad \text{and} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V} - b}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{\bar{V} - b} - \left(\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}\right) = \frac{a}{\bar{V}^2}$$

$\left(\frac{\partial H}{\partial P}\right)_T$ is also related to the intermolecular interactions. From the fundamental equation

$$dH = TdS + VdP$$

take the derivative with respect to P at constant T

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Substituting the Maxwell relation gives

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V} \tag{3.13}$$

which can again be evaluated for a given equation of state.

For an ideal gas,

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\frac{\partial}{\partial T}\left(\frac{nRT}{P}\right) - \frac{nRT}{P} = 0$$

again since there are no intermolecular interactions. However, this partial cannot be evaluated directly for a vdW gas, given the cubic form of the equation of state.

3.4 Relation between C_P and C_V

The ideal-gas result $\bar{C}_P = \bar{C}_V + R$ can be derived using total derivatives

$$dU = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

and for a constant-pressure process

$$dU = q + w = C_P dT - P dV$$

Equating these expressions,

$$C_P dT = C_V dT + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] dV$$

Dividing by dT, and recalling the P is constant,

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$$

so the difference between C_P and C_V is related to the work per unit increase in T and the energy required to overcome intermolecular interactions and pull the molecules apart.

For an ideal gas, there are no intermolecular interactions, so

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

also,

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}$$

and substituting these results gives

$$C_P = C_V + nR$$

so the relation for the molar heat capacities is $\bar{C}_P = \bar{C}_V + R$.

3.5 Thermal Expansion and Compressibility

In addition to using an equation of state, we would also like to have expressions for $\left(\frac{\partial U}{\partial V} \right)_T$ and $\left(\frac{\partial H}{\partial P} \right)_T$ in terms of two easily measured materials properties, α and κ.

The coefficient of thermal expansion, α, is

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{3.14}$$

and describes the change in volume of a material with temperature.

The coefficient of compressibility, κ, is

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{3.15}$$

and describes the change in volume of a material with pressure.

Thus,

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(V\alpha\right) + V = V\left(1 - \alpha T\right)$$

For the partial involving U, we need to write $\left(\frac{\partial P}{\partial T}\right)_V$ in terms of α and κ. Using the permutation relation:

$$\left(\frac{\partial x}{\partial z}\right)_y = -\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x$$

with $x = P$, $y = V$, $z = T$, this means

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = \frac{\alpha}{\kappa}$$

and substituting gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa} - P$$

3.6   Joule-Thompson Cooling

The Joule-Thompson coefficient,

$$\mu_{\text{JT}} = \left(\frac{\partial T}{\partial P}\right)_H$$

is useful in refrigeration, were expansion of a gas is used for cooling. It describes the change in temperature of a material with pressure for adiabatic processes, where work is done to push a stream of gas through a small valve into a region of lower pressure, causing expansion.

The particular experimental set-up is such that the net work is $w = P_f V_f - P_i V_i$. Also, since the process is adiabatic, $q = 0$ and $\Delta U = w$, so

$$\Delta H = \Delta U + \Delta(PV) = w - w = 0$$

and the enthalpy is constant.

To evaluate μ_{JT}, multiply by C_P,

$$C_P \mu_{\mathrm{JT}} = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\partial H}{\partial P}\right)_T$$

Recall that $\left(\frac{\partial H}{\partial P}\right)_T$ is related to the intermolecular interaction strength and is zero for ideal gases.

For real gases, Joule-Thompson expansion usually, but not always, decreases the temperature. To show this, recall

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V$$

and consider the compressibility for a vdW gas in the low-pressure limit:

$$Z = \frac{P\bar{V}}{RT} \approx 1 + \left(b - \frac{a}{RT}\right)\frac{P}{RT}$$

rearranging,

$$\bar{V} = \frac{RT}{P} + b - \frac{a}{RT}$$

and differentiating,

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2}$$

For one mole of gas,

$$C_P \mu_{\mathrm{JT}} = T\left(\frac{\partial \bar{V}}{\partial T}\right)_P - \bar{V}$$

and substituting,

$$\begin{aligned}
C_P \mu_{\mathrm{JT}} &= T\left(\frac{R}{P} + \frac{a}{RT^2}\right) - \left(\frac{RT}{P} + b - \frac{a}{RT}\right) \\
&= \frac{2a}{RT} - b \\
\mu_{\mathrm{JT}} &= \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)
\end{aligned}$$

$\mu_{\text{JT}} > 0$ when the attractive "a" term dominates. As the gas expands, it has to overcome intermolecular attraction, which increases its potential energy, lowering the kinetic energy of the gas.

$\mu_{\text{JT}} < 0$ when the repulsive "b" term dominates. As the gas expands, it experiences less non-bonded repulsion, lowering its potential energy, and increasing its kinetic energy.
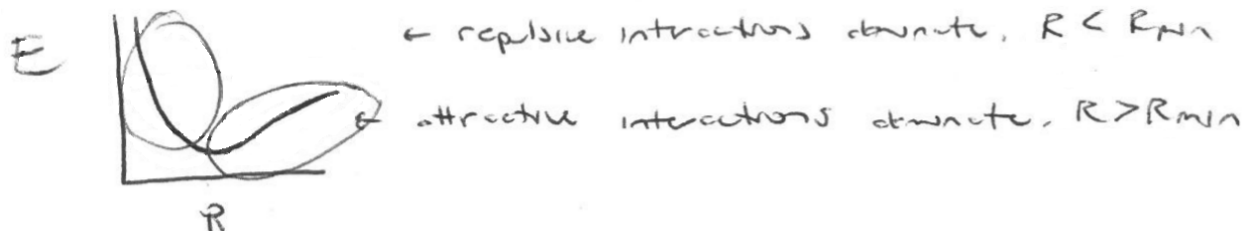
Gases can only be used in refrigeration if $\mu_{\text{JT}} > 0$ (i.e. T decreases on expansion). In practise, T must be below an inversion temperature, T_{inv}, analogous to the Boyle temperature, T_B,

$$\frac{2a}{RT_{\text{inv}}} - b = 0 \qquad \Rightarrow \qquad T_{\text{inv}} = \frac{2a}{bR} = 2T_B$$

to give a positive JT coefficient. At room temperature, only 3 gases with very weak intermolecular interactions (H_2, He, and Ne) have $\mu_{\text{JT}} < 0$.

3.7 Recap – Calculation of ΔU, ΔH, and ΔS

In practical calculations to obtain ΔU and ΔH for non-ideal gases, start from the pair of equations

$$\begin{aligned}
dU &= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\
dH &= C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP
\end{aligned}$$

where the first terms on the RHS are for the ideal gas, and the second terms are correction terms to account for the intermolecular interactions.

The two partials in the correction terms may be evaluated using

$$\begin{aligned}
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P \\
\left(\frac{\partial H}{\partial P}\right)_T &= -T\left(\frac{\partial V}{\partial T}\right)_P + V
\end{aligned}$$

given some equation of state.

To evaluate $\left(\frac{\partial P}{\partial T}\right)_V$, we need $P = P(V, T)$, which is easily expressed for the vdW equation of state and gives

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$$

However, to evaluate $\left(\frac{\partial V}{\partial T}\right)_P$, we need $V = V(P, T)$, which cannot be written directly for the vdW equation given its cubic form. Alternatively, we can obtain ΔH from ΔU as

$$\Delta H = \Delta U + \Delta(PV)$$

where $\Delta(PV) = P_f V_f - P_i V_i$ may be evaluated using the equation of state. We can also use the approximation

$$\bar{V} \approx \frac{RT}{P} + \left(b - \frac{a}{RT}\right)$$

obtained from the expansion of the compressibility factor, Z, in the low-pressure limit.

To obtain ΔS for isothermal processes, use the last two Maxwell relations, depending on which quantity (V or P) is known for the initial and final states.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \Rightarrow \qquad dS = \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \Rightarrow \qquad dS = -\left(\frac{\partial V}{\partial T}\right)_P dP$$

As above, we need to evaluate either $\left(\frac{\partial P}{\partial T}\right)_V$ or $\left(\frac{\partial V}{\partial T}\right)_P$ using an equation of state.

ΔU, ΔH, or ΔS may then be obtained from the expressions for dU, dH, or dS by integrating the differential equation from the initial to final state.

EX. for the vdW gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$$

and substituting this into the expression for dU,

$$dU = C_V dT + \frac{an^2}{V^2} dV$$

$$\Delta U = C_V \Delta T + an^2 \int_i^f \frac{1}{V^2} dV$$

In some cases, an equation of state is not known, but instead we have access to experimental measurements of

$$\text{thermal expansion,} \quad \alpha \;=\; \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{compressibility,} \quad \kappa \;=\; -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

These definitions can be manipulated to give

$$\left(\frac{\partial V}{\partial T}\right)_P \;=\; \alpha V$$

$$\left(\frac{\partial P}{\partial T}\right)_V \;=\; \frac{\alpha}{\kappa}$$

which can be used in the Maxwell relations to evaluate ΔS, or in the correction terms for ΔU and ΔH.

Lastly, κ can be used to obtain volumes given pressures, or vice versa, for isothermal processes:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$-\kappa dP = \frac{1}{V}dV$$

and integrating,

$$\ln\left(\frac{V_f}{V_i}\right) = -\kappa \Delta P$$

$$V_f = V_i e^{-\kappa \Delta P}$$

Chapter 4

Chemical and Phase Equilibria

4.1   The Chemical Potential

We have not yet explicitly considered changes in system composition that occur during reactions. The chemical potential, μ, is defined as the change in Gibbs energy with respect to the amount of a particular substance

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

where n_i is the number of moles of substance i. For a pure substance, μ is the Gibbs energy per mole, $\bar{G}$. For systems with varying composition, the Gibbs energy definition is expanded to include dependence on μ and n.

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

4.2   Mixing of Gases

In the derivation of the Maxwell relations, we found

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

At constant T, $dG = VdP$, so integrating gives

$$\Delta G = \int_{P_i}^{P_f} V(P,T)dP \qquad \text{(isothermal)}$$

For solids and liquids, the compressibility is negligible, so $\Delta G = V\Delta P$, but for a gas, an equation of state is needed to integrate $V(P,T)$.

For an ideal gas,

$$\Delta G = nRT \int_i^f \frac{dP}{P} = nRT \ln\left(\frac{P_f}{P_i}\right)$$

Taking $P_i = P°$, which is the standard state of 1 atm,

$$G(P) = G° + nRT \ln P$$

Then, the chemical potential is

$$\mu = \mu° + RT \ln P$$

and for a gas mixture, the chemical potentials will depend on the partial pressures of the components

$$\mu_i = \mu_i° + RT \ln P_i$$

The partial pressure is determined from the mole fraction, $P_i = x_i P$, so the chemical potential for gas i in the mixture is

$$\mu_{i,\text{mix}} = \mu_i° + RT \ln P + RT \ln x_i = \mu_{i,\text{pure}} + RT \ln x_i$$

Since $x_i < 1$, the last term is negative and the chemical potential for an ideal gas in a mixture is always less than for a pure ideal gas, $\mu_{i,\text{mix}} < \mu_{i,\text{pure}}$, under the same total pressure.

The Gibbs energy of mixing is

$$\begin{aligned}
\Delta G_{\text{mix}} &= \sum_i n_i \mu_{i,\text{mix}} - \sum_i n_i \mu_{i,\text{pure}} \\
&= RT \sum_i n_i \ln x_i
\end{aligned}$$

but $n_i = x_i n$, so

$$\Delta G_{\text{mix}} = nRT \sum_i x_i \ln x_i$$

and $\Delta G_{\text{mix}} < 0$. For an ideal gas, there are no intermolecular interactions, so $\Delta H_{\text{mix}} = 0$ and mixing is driven entirely by an increase in entropy. However, for real gases, the difference in intermolecular interactions can be either favourable or unfavourable.

4.3   Gibbs Energy and Chemical Equilibria

For a general chemical reaction,

$$\Delta G = \sum_i \nu_i \mu_i$$

where the ν_i's are the signed stoichiometric coefficients in the balanced chemical equation (+ for products, − for reactants).

If all reactants and products are ideal gases, then

$$\Delta G = \sum_i \nu_i \left(\mu_i^\circ + RT \ln P_i \right)$$

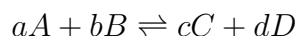and $\Delta G^\circ = \sum_i \nu_i \mu_i^\circ$, so collecting all the terms at standard state,

$$\Delta G = \Delta G^\circ + \sum_i \nu_i RT \ln P_i$$

Combining the ln terms, the sum can be converted to a product

$$\Delta G = \Delta G^\circ + RT \ln \left(\prod_i P_i^{\nu_i} \right)$$

where the $\prod$ notation indicates a product (analogous to $\sum$ for a sum).

For the example reaction

$$aA + bB \rightleftharpoons cC + dD$$

this means

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

The argument of the ln term is defined as the pressure-based reaction quotient, $Q_P = \prod_i P_i^{\nu_i}$, such that

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q_P} \tag{4.1}$$

The difference in ΔG relative to the standard state is determined by the composition of the reaction mixture.

If the system is composed of mostly reactants, $Q_P << 1$ so $\ln Q_P$ will be negative and lower ΔG. If the system is composed of mostly products, $\ln Q_P$ will be positive and raise ΔG.

When equilibrium is reached, $\Delta G = 0$ so

$$\Delta G^\circ = -RT \ln \left(\prod_i P_{i,\mathrm{eq}}^{\nu_i} \right)$$

This particular reaction quotient involving the equilibrium partial pressures is defined as the pressure-based equilibrium constant, $K_P = \prod_i P_{i,\mathrm{eq}}^{\nu_i}$

$$\boxed{\Delta G^\circ = -RT \ln K_P} \tag{4.2}$$

This result means that ΔG° can be determined from the equilibrium composition of the system.

Also, the value of K_P can be determined as a function of T given the thermodynamic functions $\Delta H^\circ(T)$ and $\Delta S^\circ(T)$ since

$$-RT \ln K_P = \Delta H^\circ - T\Delta S^\circ = \Delta G^\circ$$

$$\ln K_P = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

and both ΔH° and ΔS° can be evaluated at a range of temperatures from heat capacity data.

The dependence of K_P on T can also be determined starting from $\ln K_P = -\Delta G^\circ/RT$,

$$\begin{aligned}
\frac{\partial}{\partial T} \ln K_P &= \frac{\partial}{\partial T}\left(-\frac{\Delta G^\circ}{RT}\right) \\
&= \frac{\partial}{\partial T}\left(-\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right) \\
&= \frac{\partial}{\partial T}\left(-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}\right) \\
&= \frac{\Delta H^\circ}{RT^2}
\end{aligned}$$

Integrating from T_0 to T,

$$\boxed{\ln K_P = \ln K_{P,0} - \frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \tag{4.3}$$

If the reaction is exothermic, $\Delta H^\circ < 0$ and K_P decreases with increasing T, favouring the reactants. If the reaction is endothermic, $\Delta H^\circ > 0$ and K_P increases with T, favouring the products. This is one aspect of Le Châtelier's Principle.

For heterogeneous equilibria, with one or more liquids or solids, K_P involves only the gases. Recall that $\Delta G = \sum_i \nu_i \mu_i$ and $\mu_i = \mu_i^\circ + RT \ln P_i$, but for liquids and solids, μ is insensitive to pressure and $\mu_i = \mu_i^\circ$.

Equilibrium constants are often reported using concentration or mole fraction instead of pressures. The concentration is $c_i = n_i/V$ and for an ideal gas, $P_i = c_i RT$, so

$$K_P = K_c(RT)^{\Delta\nu}$$

where $\Delta\nu = \sum_i \nu_i$ is the difference in stoichiometric coefficients. For the mole fraction, $P_i = x_i P$, so

$$K_P = K_x P^{\Delta\nu}$$

For heterogeneous equilibria, consider only gases in evaluation of $\Delta\nu$.

## 4.4   Phase Changes of Pure Substances

The chemical potential allows us to derive the shape of the phase diagram for a pure substance. For a single-component substance, $\mu = \bar{G}$ and

$$d\mu = -\bar{S}dT + \bar{V}dP$$

and comparing this with the total derivative for $\mu(T, P)$ gives

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -\bar{S} \qquad \text{and} \qquad \left(\frac{\partial \mu}{\partial P}\right)_T = -\bar{V}$$

Because S is always positive, $\left(\frac{\partial \mu}{\partial T}\right)_P$ is always negative. Also, $\bar{S}_{\text{gas}} \gg \bar{S}_{\text{liq}} > \bar{S}_{\text{solid}}$ and, assuming the entropy varies slowly with T, we can sketch the following:
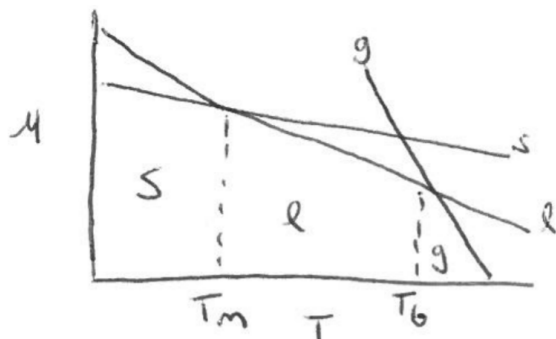
At a given T, the most-stable state has the lowest μ.

$T < T_m$, μ_s is lowest, solid most stable

$T_m < T < T_b$, μ_ℓ is lowest, liquid most stable.

$T > T_b$, μ_g is lowest, gas most stable.

At T_m, $\mu_s = \mu_\ell$ and the solid and liquid phases are in equilibrium.

At T_b, $\mu_\ell = \mu_g$ and the liquid and gas phases are in equilibrium.

To obtain the phase diagram, we need to derive an equation relating T and P for the three phase equilibria. For equilibrium between phases α and β, $\mu_\alpha = \mu_\beta$, so

$$
\begin{aligned}
-\bar{S}_\alpha dT + \bar{V}_\alpha dP &= -\bar{S}_\beta dT + \bar{V}_\beta dP \\
(\bar{V}_\alpha - \bar{V}_\beta)dP &= (\bar{S}_\alpha - \bar{S}_\beta)dT \\
\frac{dP}{dT} &= \frac{\Delta S}{\Delta V}
\end{aligned}
$$

which is one form of the Clapeyron equation. Also, for phase equilibrium, $\Delta S = \Delta H/T$ so

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

which is the other form of the Clapeyron equation. This is applicable to heats and volumes of fusion, vapourization, and sublimation.

For fusion, integrating gives

$$\int_{P_0}^{P} dP = \int_{T_0}^{T} \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \frac{dT}{T}$$

and ΔH and ΔV are constants, so

$$\boxed{P = P_0 + \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln\left(\frac{T}{T_0}\right) \qquad \text{(fusion)}} \tag{4.4}$$

The slope of the $s \rightleftharpoons \ell$ co-existence line is very steep since ΔV is quite small, although it can be either positive (most materials) or negative (ice is less dense than water).

For the $\ell \rightleftharpoons g$ and $s \rightleftharpoons g$ equilibria, the molar volume of a gas is much greater than for a solid or liquid, so $\Delta \bar{V} \approx \bar{V}_{\text{gas}} = RT/P$ (ideal gas).

$$\int_{P_0}^{P} \frac{dP}{P} = \int_{T_0}^{T} \frac{\Delta H_{\text{fus}}}{RT^2} dT$$

and integrating gives

$$\boxed{\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad \text{(vapourization or sublimation)}} \tag{4.5}$$
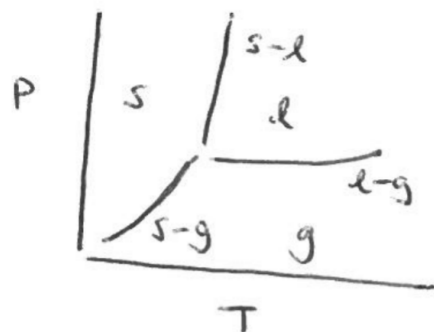
ΔH_{vap} and ΔH_{sub} are always positive, so P increases with T.

$\Delta H_{\text{sub}} > \Delta H_{\text{vap}}$ so the slope of the solid-gas line is slightly larger than the liquid-gas line.

4.5   Colligative Properties

These are properties that depend on the concentration of a solute, but not on its identity. The T and P conditions for phase equilibria are colligative properties and are affected by solutes in the liquid phase. We will consider 4 properties: vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

For an ideal solution, the solute is not volatile and does not contribute to the vapour pressure. As solute is added, the vapour pressure is

$$P = P^{\circ} x_{\text{solvent}} = P^{\circ}(1 - x_{\text{solute}})$$

where $P°$ is the vapour pressure of the pure liquid. The solute lowers the vapour pressure and this is Raoult's law.

The chemical potential of the solvent also decreases due to the solute (entropy of mixing). For a pure liquid in equilibrium with its vapour,
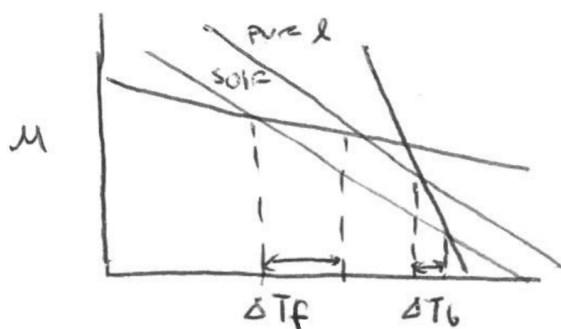
$$\mu_\ell° = \mu_g° + RT \ln P°$$

but for a solution this is

$$\mu_\ell = \mu_g° + RT \ln[P°(1 - x_{\text{solute}})]$$

Subtracting gives

$$\mu_\ell - \mu_\ell° = RT \ln[P°(1 - x_{\text{solute}})]$$

Since $\ln(1 - x) < 0$, the chemical potential of the solution is lower than for the pure liquid.

The shift in μ_ℓ explains the boiling point increase and freezing point decrease.

To obtain the boiling point elevation, we have $\mu_\ell = \mu_g°$ for this equilibrium. Then,

$$\Delta G_{\text{vap}} = \mu_g° - \mu_\ell° = \mu_\ell - \mu_\ell° = RT \ln(1 - x_{\text{solute}})$$

Substituting for ΔG,

$$\ln(1 - x_{\text{solute}}) = \frac{\Delta H_{\text{vap}}}{RT} - \frac{\Delta S_{\text{vap}}}{R}$$

and rearranging,

$$\frac{\Delta S_{\text{vap}}}{R} = \frac{\Delta H_{\text{vap}}}{RT} - \ln(1 - x_{\text{solute}})$$

As $\Delta S_{\text{vap}}/R$ is constant, we can equate the results for the pure liquid ($x = 0$) and the solution,

$$\frac{\Delta H_{\text{vap}}}{RT_0} - \ln(1) = \frac{\Delta H_{\text{vap}}}{RT} - \ln(1 - x)$$

and solving,

$$\boxed{\ln(1 - x) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \tag{4.6}$$

This can also be rearranged to give

$$\frac{1}{T} - \frac{1}{T_0} = \frac{R \ln(1 - x)}{\Delta H_{\text{vap}}}$$

If the solute is dilute, $x \ll 1$, so $\ln(1 - x) \approx -x$. Also, the temperature change will be small, so

$$\frac{1}{T} - \frac{1}{T_0} = \frac{T_0 - T}{T_0 T} \approx -\frac{T - T_0}{T_0^2}$$

and substituting gives the dilute-solute approximation

$$\Delta T_b = \frac{RT_0^2}{\Delta H_{\text{vap}}} x_{\text{solute}}$$

Similarly, to obtain the freezing point depression, we have $\mu_\ell = \mu_s^\circ$ for this equilibrium. Then,

$$\Delta G_{\text{fus}} = \mu_\ell^\circ - \mu_s^\circ = \mu_\ell^\circ - \mu_\ell = -RT \ln(1 - x_{\text{solute}})$$

Substituting for ΔG,

$$\ln(1 - x_{\text{solute}}) = -\frac{\Delta H_{\text{fus}}}{RT} + \frac{\Delta S_{\text{fus}}}{R}$$

and rearranging,

$$\frac{\Delta S_{\text{fus}}}{R} = \frac{\Delta H_{\text{fus}}}{RT} + \ln(1 - x_{\text{solute}})$$

As $\Delta S_{\text{fus}}/R$ is constant, we can equate the results for the pure liquid ($x = 0$) and the solution,

$$\frac{\Delta H_{\text{fus}}}{RT_0} + \ln(1) = \frac{\Delta H_{\text{fus}}}{RT} + \ln(1 - x)$$

and solving,

$$\boxed{\ln(1 - x) = -\frac{\Delta H_{\text{fus}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \tag{4.7}$$

This can also be rearranged to give

$$\frac{1}{T} - \frac{1}{T_0} = -\frac{R \ln(1 - x)}{\Delta H_{\text{fus}}}$$

and if the solute is dilute, it leads to the following approximation

$$\Delta T_f = -\frac{RT_0^2}{\Delta H_{\text{fus}}} x_{\text{solute}}$$

The formula for ΔT_b and ΔT_f are often written in terms of the molality of the solute, $(n_{\text{solute}}/m_{\text{solvent}})$, rather than the mole fraction, since it is easier to measure the mass of the solvent.

Measurements of ΔT_b and ΔT_f can be used to determine the molar mass of an unknown solute. The boiling-point elevation and freezing-point depression formulae can also be used to predict co-existence curves for 2-component phase diagrams.

Osmotic pressure refers to the tendency of a solution to take on additional solvent through osmosis (diffusion through a membrane).
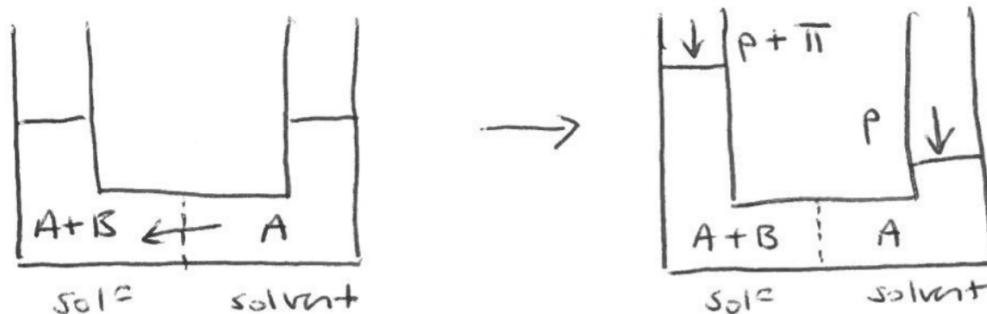
For two liquids separated by a membrane, the chemical potential of the solution is lower than for the pure liquid and these must equalize to reach equilibrium.

This can be done if the pressure on the pure liquid is lowered by diffusion of some liquid through the membrane, building up a pressure head on the solution side. The additional pressure on the solution required to equalize the chemical potential, Π, is called the osmotic pressure.

For this equilibrium,
$$\mu_\ell(P + \Pi) + RT \ln(1 - x_{\text{solute}}) = \mu_\ell^\circ(P)$$
Recall that $\Delta\mu = \int \bar{V} dP = \bar{V}\Delta P$ when the molar volume is independent of P, so

$$\Delta\mu = \mu_\ell(P + \Pi) - \mu_\ell^\circ(P) = \bar{V}\Delta P = \bar{V}\Pi$$

and substituting

$$\boxed{\bar{V}\Pi = RT \ln(1 - x)} \tag{4.8}$$

If the solution is dilute, $\ln(1 - x) \approx -x$ so $\Pi = RTx/\bar{V}$, but $\bar{V} = V/n$ and $x = n_{\text{solute}}/n$. This gives

$$\Pi = RT\frac{n_{\text{solute}}}{V} = RTc$$

where c is the solute concentration.

"Reverse osmosis" is often used to purify water (and other solvents). By applying an external pressure to the solution side, pure solvent can be driven through the membrane.

4.6   Partial Pressures in Two-Component Mixtures

Consider a mixture of two components where there is an equilibrium between the gas and liquid phases. The mole fractions of the two components are x_A and x_B in the liquid phase

and y_A and y_B in the gas phase. We aim to obtain partial pressures of each gas as a function of composition.

To obtain P_T as a function of x_A, start from the total pressure,

$$P_T = P_A + P_B$$

and use Raoult's law of vapour-pressure lowering

$$P_A = P_A^\circ(1 - x_B) = P_A^\circ x_A \quad \text{or} \quad x_A = \frac{P_A}{P_A^\circ}$$

to obtain

$$P_T = x_A P_A^\circ + x_B P_B^\circ = x_A P_A^\circ + (1 - x_A) P_B^\circ$$

and rearranging

$$\boxed{P_T = P_B^\circ + (P_A^\circ - P_B^\circ) x_A} \tag{4.9}$$

so the total pressure is a linear interpolation between P_A° and P_B°.

For P_T as a function of y_A, start from the definition of the partial pressure, $P_A = y_A P_T$,

$$P_T = \frac{P_A}{y_A} = \frac{x_A P_A^\circ}{y_A}$$

but from the result above

$$x_A = \frac{P_T - P_B^\circ}{P_A^\circ - P_B^\circ}$$

Substituting this

$$P_T = \frac{P_A^\circ}{y_A}\left(\frac{P_T - P_B^\circ}{P_A^\circ - P_B^\circ}\right)$$

Solving for P_T gives

$$\boxed{P_T = \frac{P_A^\circ P_B^\circ}{P_A^\circ + (P_B^\circ - P_A^\circ) y_A}} \tag{4.10}$$

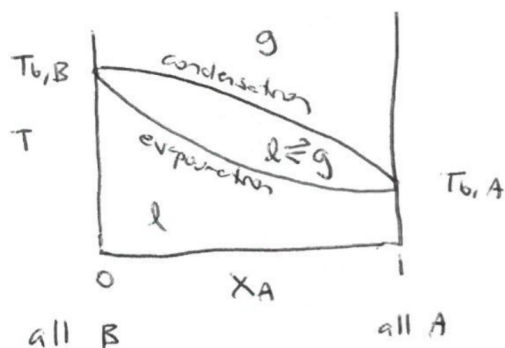which has a hyperbolic dependence on y_A.
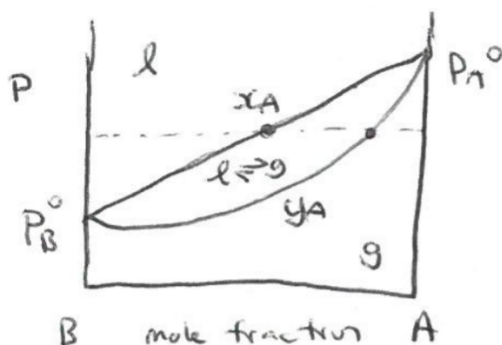
At high pressure, there is a single liquid phase and, at low pressure, there is a single gas phase.

In the intermediate region, there is an equilibrium between the liquid solution and gas mixture.

At a given pressure, the gas phase is enriched in the more volatile component (i.e. $y_A > x_A$).

4.7 Two-Component Phase Diagrams

These are typically given in terms of composition and temperature since pressure changes have very little effect on solid or liquid phases. We will consider liquid-gas phase diagrams first.

At low temperature, there is a single liquid phase and, at high temperature, there is a single gas phase.

In the intermediate region, there is an equilibrium between the liquid solution and the gas mixture.

In the two-phase region, the liquid and gas phases will have different composition depending on the relative boiling points.

The component with lower T_b will be enriched in the gas and the solution will be enriched in the component with higher T_b.

The overall composition is given by X_A and X_B, while the compositions of the liquid and gas phases are (x_A, x_B) and (y_A, y_B), respectively.

Consider heating a system with composition X_A so that the temperature changes along a line of constant composition, called an isopleth.
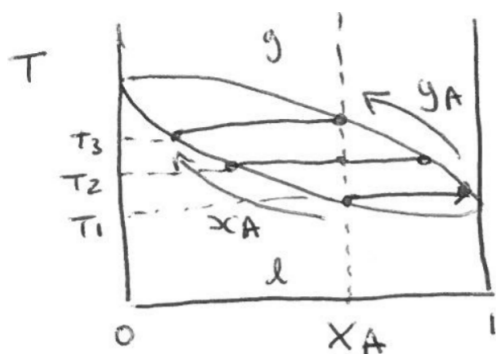
The liquid will have $x_A = X_A$, $x_B = 1 - X_A$ until the isopleth crosses the evaporation curve at T_1.

Then, a gas phase starts to form, with initial composition y_A, where a tie line (horizontal line) at T_1 crosses the condensation curve.

As heating continues, the liquid and gas compositions change according to the evaporation and condensation curves, respectively.

When the isopleth crosses the condensation curve at T_3, all the liquid has evaporated and there is now a single gas phase with composition X_A.

The use of a tie line to determine the two phase compositions is called the Lever rule; the relative amounts of each phase are given by

$$X_{\text{liquid}} = \frac{X_A - y_A}{x_A - y_A} \quad \text{and} \quad X_{\text{gas}} = \frac{x_A - X_A}{x_A - y_A}$$

Fractional distillation makes use of the difference in composition between the liquid and gas phases by repeatedly condensing, separating, and boiling the vapour, which is enriched in the more volatile component

In some cases, the intermolecular interactions prohibit separation by distillation. A minimum in the condensation/evaporation curves will occur if the $A - B$ interactions are significantly weaker than the $A - A$ and $B - B$ interactions, so that the solution is less stable and boils more easily than the pure components.
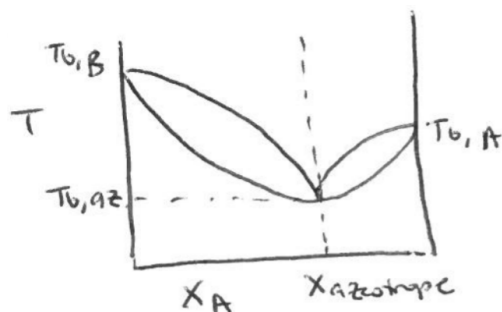
Then, the composition does not change during boiling and the mixture is called an azeotrope (Greek: to boil unchanged).

At $X_{\text{azeotrope}}$, the liquid and gas phases have the same composition, so the mixture cannot be separated by distillation.

An ethanol/water mixture is one example, for $X_{\text{azeotrope}} = 0.89$.

Azeotropes can also form when there is a maximum in the evaporation/condensation curves due to particularly favourable $A - B$ interactions. The solution is more stable and condenses more readily than the pure components.

In cases where the liquids do not mix over the entire temperature and composition range, typical phase diagrams are:
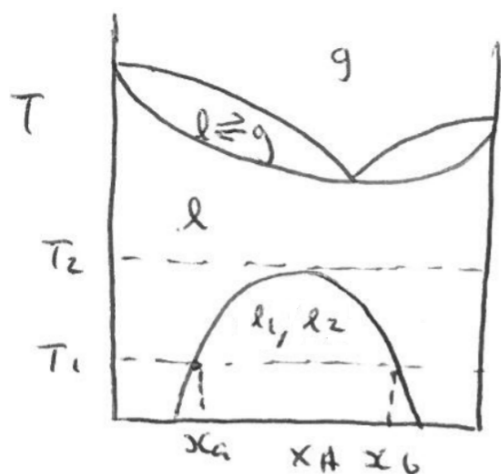
In the 2-phase liquid region, at T_1, one liquid phase will have composition x_a and the other x_b.

The two components form a single solution phase for all compositions at $T > T_2$, called the upper consolute temperature.
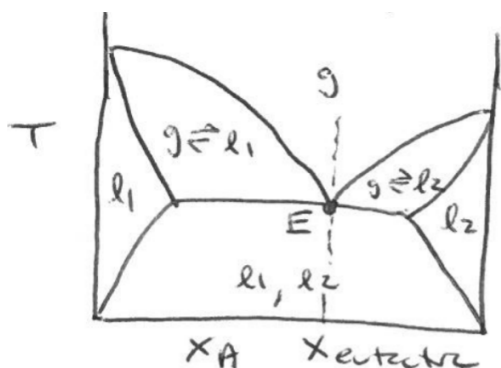
If there is no upper consolute temperature, then there are two distinct $\ell \rightleftharpoons g$ co-existence regions depending on the liquid phase (ℓ_1 or ℓ_2).

The point E is called the eutectic point, at which the 3 phases (g, ℓ_1, ℓ_2) are in equilibrium.

At this one composition, the liquid phase will be a mixture of ℓ_1 and ℓ_2 throughout evaporation.

For solid-liquid phase diagrams, there are 5 typical cases to consider, depending on whether the components form solid solutions or compounds.
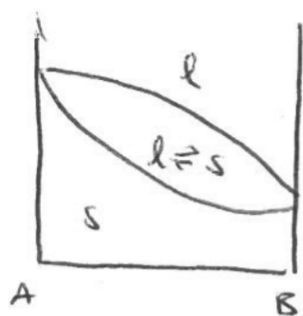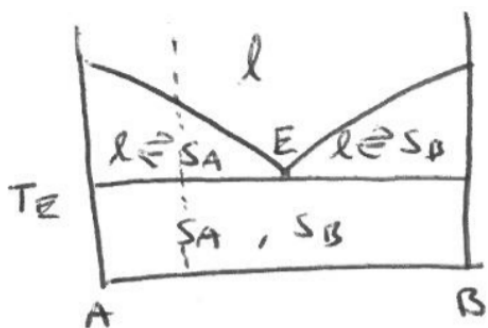

(i) If A and B form a solid solution over the entire composition range, the phase diagram has the same form as the liquid-gas case.
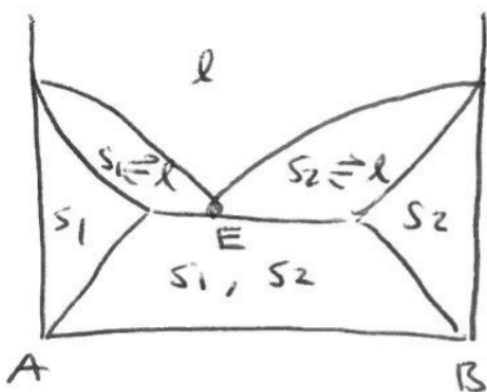

(ii) If A and B are slightly miscible as solids, there will be a mixture of two solid phases, s_1 and s_2.

The phase diagram will resemble the liquid-gas case with no upper consolute temperature.

(iii) A and B are completely immiscible and do not form any solid solution.

For the shown isopleth, component A will initially precipitate from the liquid until T_E is reached. At T_E, component B will also begin to precipitate and will continue until all the liquid has frozen. Below T_E, there is a mechanical mixture of the two solids.
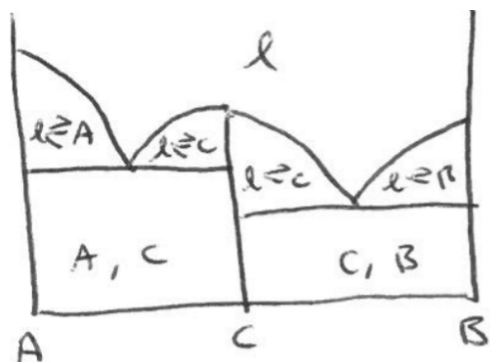
(iv) A and B form a compound, C, which melts congruently (molecules in the solid and liquid are the same).

The phase diagram resembles two case (iii) plots side-by-side.
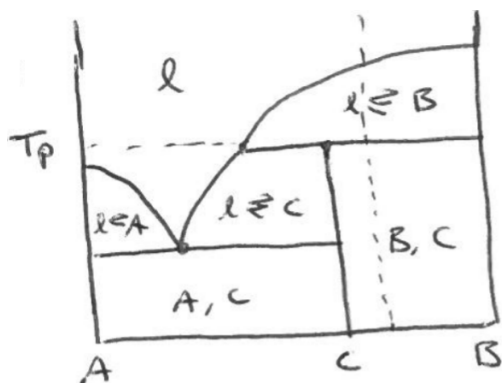
(v) A and B form a compound, C, which melts incongruently (decomposes on melting). These are called peritectic compounds.

For the shown isopleth, when the peritectic compound is heated to T_P, it decomposes into solid B and a liquid solution, containing A and B.

In all cases, the phase diagrams can be constructed from cooling curves (temperature vs. time) according to the points where the curve changes slope.

The temperature will be constant for phase change of a pure compound or azeotrope, eutectic processes, and peritectic processes.

The cooling curve will change slope at the onset of precipitation of a pure solid solution from a liquid solution, condensation of a liquid solution from a gas mixture, and separation of a liquid solution into two distinct liquid phases.

For an example isopleth, the cooling curve is:
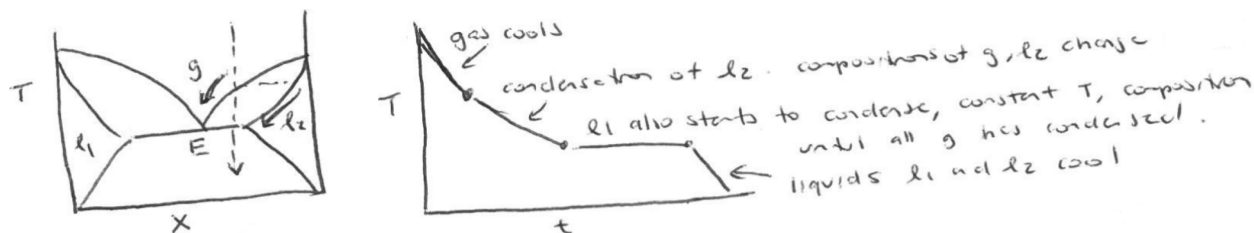
The entire phase diagram can be constructed from cooling curves for a range of compositions by plotting the positions of the temperature breaks.