Example: forming carbon monoxide from methane

(and vice versa)

forward reaction (forms 4 particles)

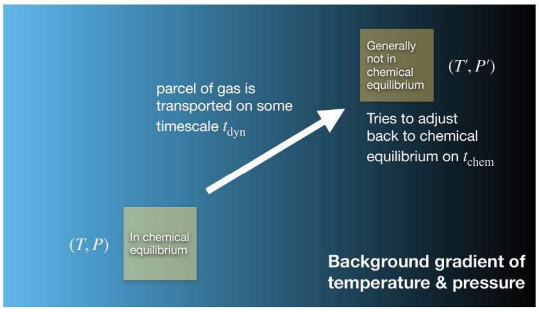
$$CH_4 + H_2O \leftrightarrows CO + 3H_2$$

reverse reaction (forms 2 particles)

Le Chatelier's Principle:

If the pressure is increased, the reverse reaction is favoured as this reduces the number of particles (and hence the pressure)

When is a system in chemical equilibrium?



If $t_{\rm chem} \ll t_{\rm dyn}$, then the parcel of gas adjusts to chemical equilibrium.

If $t_{\rm chem} \gtrsim t_{\rm dyn}$, then it is in chemical disequilibrium.

Equilibrium chemistry versus chemical kinetics

Regime	Treatment	Analogy
$t_{\rm chem} \ll t_{\rm dyn}$	Only local conditions matter Gibbs free energy minimization	Lagrangian approach of Newtonian mechanics (minimising the action)
$t_{\rm chem} \gtrsim t_{\rm dyn}$	Retains memory of previous states Chemical kinetics	Newton's equations of motion (kinematics)

What does energy mean (in chemical reactions)?

work done on the system

$$G = E_{\rm int} + PV - TS$$

Gibbs free energy

internal energy

losses associated with heat

Helmholtz free energy: $F = E_{\rm int} - TS$

Enthalpy: $E_{\rm int} + PV$

If you combine the expression for the Gibbs free energy with the first law of thermodynamics (Problem 6.5.1a), one gets the master equation:

$$dG = V\,dP - S\,dT + \sum_j C_j\,dN_j$$

chemical potential

change in number of particles

Consider a fixed temperature ($dT = 0$) and the number of particles associated with each chemical species to be invariant. Assuming an ideal gas, one obtains (Problem 6.5.1b):

ideal gas constant

$$G = G_0 + \mathcal{R}T \ln\left(\frac{P}{P_0}\right)$$

Gibbs free energy at a reference pressure

reference pressure

Recall this general chemical equation:

$$a_1 X_1 + a_2 X_2 \leftrightarrows b_1 Z_1 + b_2 Z_2$$

We can write down the Gibbs free energy expression four times. (two for the reactants, two for the products). By taking the difference of Gibbs free energy between the products and reactants:

$$\boxed{\Delta G_0 - \Delta G = -\mathcal{R}T \ln K_{\rm eq}}$$

Key concepts:

To achieve chemical equilibrium, the system adjusts itself until $\Delta G = 0$.

ΔG_0 is interpreted as the Gibbs free energy of formation.

$$K_{\rm eq} \equiv \frac{(P_{Z_1}/P_0)^{b_1}\,(P_{Z_2}/P_0)^{b_2}}{(P_{X_1}/P_0)^{a_1}\,(P_{X_2}/P_0)^{a_2}}$$

equilibrium constant

P_{X_i}, P_{Z_i}: partial pressures