Useful relationships in Chemical Thermodynamics

Heat and Work

$$\Delta U = U_f - U_i = q_{to} + w_{on}$$

$$w = -\int pdV$$

$$w = -nRT \int \frac{V_f}{V_i}$$

$$w = -nRT \ln \frac{V_f}{V_i}$$

There are several other analogous ln X_f/X_i relationships in thermodynamics.

Internal Energy and Enthalpy

At Constant V, $\Delta U = q_V$.

At constant p, $\Delta U = q_p + p\Delta V$

Define new state variable

$H = U + PV$

$$\Delta H = \Delta U + p\Delta V$$

$$\Delta H = \Delta U + \Delta nRT$$

Heat Capacities

$$C_V = \frac{dq_V}{dT} = \frac{dU}{dT}$$

$$C_p = \frac{dq_p}{dT} = \frac{dH}{dT}$$

$$C_p - C_V = R$$

$$H = \int_{T_i}^{T_f} C_p dT$$

Entropy

$$S = \frac{dq_{rev}}{T}$$

Isothermal expansion of a gas

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{V_f}{V_i}$$

Temperature dependence

$$\Delta S = C_p \ln \frac{T_f}{T_i} \quad or \quad C_V \ln \frac{T_f}{T_i}$$

Gibb's Energy

$$G = H - TS$$

$$G = U + pV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = Vdp - SdT$$

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

Chemical Potential

$$\mu_x = \left(\frac{\partial G}{\partial n_x}\right)_{T,p,n_{y \neq x},\ldots}$$

or

$$G = \sum_{\text{all } x} n_x \mu_x$$

which for a pure material gives

$$\mu = G / n = G_m$$

Evaporisation

$$\Delta S = \frac{\Delta_{vap} H}{T_{boil}}$$

Chemical Equilibrium

$$\Delta G = -RT \ln K_a$$

$$\ln K_a = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

The Claperyon Equation

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

or

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