

Chemistry 172

IΣII

Winter 2016

1 General Equations

1.1 Entropy Equations

Table 1: Equations for Entropy

Vary Temperature	Vary Pressure	Vary Volume
$\Delta S = C_{v/p} \ln \frac{T_f}{T_i}$	$\Delta S = nR \ln \frac{P_i}{P_f}$	$\Delta S = nR \ln \frac{V_f}{V_i}$

$$S = k \ln W$$

$$S_{\text{surr}} = -q_{\text{reaction}}/T$$

1.2 Enthalpy Equations

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

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

$$\Delta H = \frac{C_p}{\Delta T}$$

$$\Delta U = \frac{C_v}{\Delta T}$$

$$C_p = C_v + nR$$

$$w_{\text{sys}} = - \int_{V_f}^{V_i} PdV$$

Table 2: Equations for Work

Constant Pressure	Constant Temperature	Constant Volume
$w_{\text{sys}} = -P_{\text{ext}}\Delta V$	$w_{\text{sys}} = -nRT \ln \frac{V_f}{V_i}$	0

2 Carnot/Heat Engines

No engine working between two given heat reservoirs can be more efficient than a reversible engine working between these two reservoirs. The cycle is known as the Carnot cycle. No engine can have the a greater efficiency than a Carnot engine because all steps are reversible.

Table 3: Ideal Molecules

Molecule	Translation	Rotation	C_v	C_p	Internal Energy
Atom	3	0	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{3}{2} nRT$
Linear	3	2	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{5}{2} nRT$
Non-Linear	3	3	$3R$	$4R$	$3 nRT$

$$\epsilon = 1 - \frac{Q_c}{Q_h}$$

$$Q_h = W_{\text{by gas}}, \quad Q_c = W_{\text{on gas}}$$

$$Q_{h/c} = nRT_{h/c} \frac{V_2}{V_1}$$

$$\epsilon_C = 1 - \frac{T_c}{T_h} \text{ (Carnot Efficiency)}$$

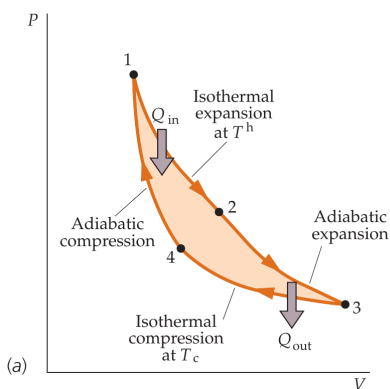


Figure 1: Carnot Cycle

3 Equilibrium

$$\Delta S_{\text{total}} = 0$$

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium, $\Delta G = 0$ and this yields:

$$\Delta S = \Delta H/T$$

Table 4: Gibbs Free Energy

ΔH	ΔS	ΔG	Spontaneous?
<0	>0	<0	yes
>0	<0	>0	no
<0	<0	?	yes if $ T\Delta S < \Delta H$
>0	>0	?	yes if $\Delta H < T\Delta S$

4 Clausius Inequality

$$\Delta U = q + w$$

ΔU is same for paths that start and end point. $w_{rev} > w_{irr}$

$$\Delta U = \text{constant}, q_{irr} > q_{rev}$$

5 Vapor Pressure

Pressure at which the liquid and vapor are in dynamic equilibrium is called the vapor pressure. Once the external pressure meets the vapor pressure at that temperature, the liquid will start to boil. Hence, the vapor pressure is dependent on the temperature, and the boiling point is dependent on external pressure. Note that these two relationships are not the same.

Vapor pressure is also dependent on intermolecular forces.

$$\ln \frac{P'_{vap}}{P^\circ_{vap}} = \frac{\Delta H^\circ_{vap}}{R} \left(\frac{1}{T_B} - \frac{1}{T'} \right)$$

Where X' refers to the new conditions and X° refers to the known values at the substance's boiling point.

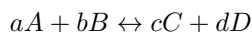
Clausius-Clapeyron Equation:

$$P_{vap} = Ae^{-\Delta H^\circ_{vap}/RT}, A = e^{\Delta H^\circ_{vap}/RT_B}$$

Assumptions:

1. ΔH_{vap} and ΔS_{vap} remain approximately constant.
2. Gas is ideal
3. The molar pressure of the water is much greater than the molar pressure of the gas.

6 Chemical Equilibrium



The most general case for the equilibrium constant would be the fraction of the concentration of the products raised to the power of their coefficients over the concentration of the reactants. The following ratios are also known by the law of mass ratios.

$$K = \frac{\text{products}}{\text{reactants}}$$

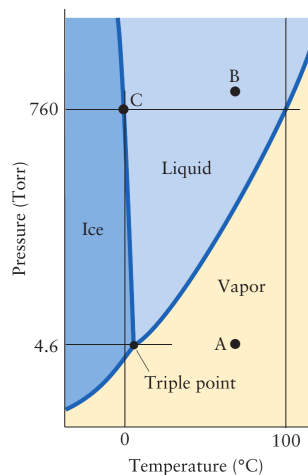


Figure 2: Phase Diagram

6.1 Pressure

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Where P is the partial pressure of the gas.

6.2 Concentration

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Note that solids do not enter the equation here.

6.3 Additional Equations

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where Q is the activity at any time. K can be substituted for Q at equilibrium. At equilibrium, ΔG is zero.

$$K = e^{-\frac{\Delta G^\circ}{RT}}, \text{ (At equilibrium)}$$

Changing to an unknown equilibrium constant, where K', T' are the new conditions:

$$\ln \frac{K'}{K} = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

Note the dependence of K on T. It is not dependant on concentration, pressure, volume, or anything else other than temperature.

7 Acids and Bases

$$\text{pH} = \text{pKa} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Use ICE table to determine changes of concentration. Note that you can use overall change in moles and use the final equilibrium conditions to determine the final moles. From there, x can be obtained and the changes can be calculated.

8 Credits

1. Carnot Cycle, Physics for Science and Engineers
2. Phase Diagram, Chemical Principles