

Chemistry 172

IΣII

Winter 2016

1 General Equations

1.1 Entropy Equations

Table 1: Equations for Entropy

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

$$S = k \ln W$$

$$S_{\text{surr}} = -q_{\text{reaction}}/T = -\frac{\Delta H_{\text{sys}}}{T}$$

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

1.2 Enthalpy Equations

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

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

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

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

$$C_p = C_v + nR$$

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

$$dG = w_{\text{non-exp}}$$

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

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	$3R$	$4R$	$3 nRT$

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 a greater efficiency than a Carnot engine because all steps are reversible.

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

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

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

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

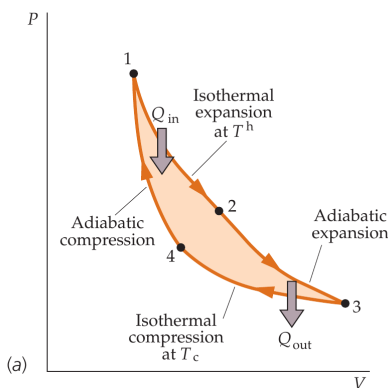


Figure 1: Carnot Cycle

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 at the same point. $w_{rev} > w_{irr}$

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

5 Vapor Pressure

$$T = \frac{\Delta H_{vap}}{\Delta S_{vap}}$$

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.

$$\Delta H^\circ_{vap} - T\Delta S^\circ_{vap} = RT \ln \frac{P^\circ}{P_{vap}}$$

Where P° is 1 bar with P_{vap} being the vapor pressure at temperature T.

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.

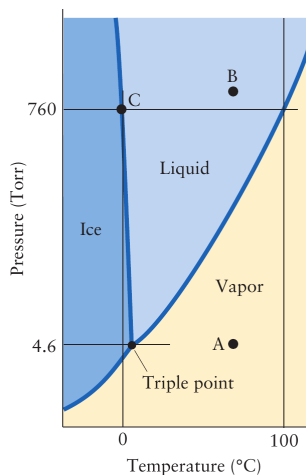
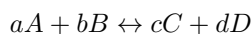


Figure 2: Phase Diagram

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.

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

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.

$$\Delta H - T\Delta S = -RT \ln K$$

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

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

$$\text{pH} = \text{pK}_a + \log[\text{A}^-]/[\text{HA}]$$

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.

pH has nothing to do with how acidic a substance is, it merely refers to the concentration in the solution. Acidity is determined by how strongly the acid dissociates. One way to describe K_a is 'concentration of protons produced per unit concentration of acid'. It is independent of the amount of acid used whereas pH could be dependent on the amount of acid used.

The strongest buffer point is where $\text{pH} = \text{pK}_a$.

Note that when a strong base or acid is added. React the acid/base first before calculating the equilibrium point! Remember that the acid or base completely dissociates, so remember to remove the appropriate amount of H^+ or OH^- (and their salts!) before applying the ICE table.

8 Credits

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

9 Contributors

1. Alex-Ortiz