Physical Chemistry
Formulas and Constants

Compiled by: Mauricio Esguerra Neira

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Some Important Numbers

1 ev = 1.602×10^{-19} J
1 ev = 96.485 KJ/mol
1 hartree = 2624.5996 KJ/mol
1mh = 2625 KJ/mol
physisorption $\approx$ 20KJ/mol
4.8 Kcal/mol
chemisorption $\approx$ 200 KJ/mol
48 Kcal/mol

First Law

$$dE = dQ + dW \tag{1}$$

Second Law

$$dS \geq \frac{dq}{T} \tag{2}$$

Third Law

$$\lim_{T \to 0} (\Delta G - \Delta H) = 0 \tag{3}$$

$$\lim_{T \to 0} -T\Delta S = 0 \tag{4}$$

1 System of Constant Composition [1]

$$U = Q + W \tag{5}$$

$$H = U + PV \tag{6}$$

$$A = U - TS \tag{7}$$

$$G = H - TS \tag{8}$$

Gibbs Equations

$$dU = TdS - PdV \tag{9}$$

$$dH = TdS + VdP \tag{10}$$

$$dA = -SdT - PdV \tag{11}$$

$$dG = -SdT + VdP \tag{12}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \; C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{13}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \; C_P = T\left(\frac{\partial S}{\partial T}\right)_P \tag{14}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \; V = \left(\frac{\partial H}{\partial P}\right)_S \tag{15}$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_V \; -P = \left(\frac{\partial A}{\partial V}\right)_T \tag{16}$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_P \; V = \left(\frac{\partial G}{\partial P}\right)_T \tag{17}$$

Euler's Reciprocity Relation

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{18}$$

Using Euler's Reciprocity Relation one arrives at:

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{19}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{20}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{21}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{22}$$

$$\Delta H^\circ = \Delta U^\circ + RT\sum_i \nu_i(g) \tag{23}$$

Clausius-Clapeyron

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{24}$$

Van der Waals

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \tag{25}$$

Ideal Solutions

$$\mu_i = \mu_i^\circ + RTln\chi_i \tag{26}$$

Kinetic Theory of Gases

Ideal Monoatomic Gas

$$C_V = \frac{3}{2}R \tag{27}$$

$$C_P = \frac{5}{2}R \tag{28}$$

Rate Laws

First Order

$$\frac{d[A]}{dT} = -k_A[A]$$

$$\int \frac{d[A]}{[A]} = -k_A$$

$$ln\frac{[A]}{[A]_0} = -k_A(t2-t1)$$

$$[A] = [A]_0 e^{-k_A t} \tag{29}$$

Second Order

$$r = k[A]^2 \tag{30}$$

$$r = k[A][B] \tag{31}$$

Third Order

$$r = k[A]^3 \tag{32}$$

$$r = k[A]^2[B] \tag{33}$$

$$r = k[A][B][C] \tag{34}$$

Initial Rates of Reaction

The technique of initial rates of reaction is one common technique to determine the order of a reaction by keeping the concentration of one of more reactants fixed, while the concentration of one and only one of the reactants is varied and followed calorimetrically. Typically a graph of log T vs log [concentration] is drawn, and from the slopes of the fitted lines an order is obtained.

References

[1] Ira N. Levine, *Physical Chemistry (Second Edition)*, McGraw Hill, 1983.