

Equations – P-Chem

Kinetics & Electrochemistry

Electrochemical cells, potentials

$$\Delta G = -nFE \quad \Delta G^\circ = -nFE^\circ \quad n \text{ is number of electrons xferred in equation}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln \prod_i [C_i]^i \quad \Delta_r G = \Delta_r G^\circ + RT \ln \prod_i [C_i]^i$$

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (\text{Nernst Equation}) \quad E^\circ = \frac{RT}{nF} \ln K \quad [n \text{ is \#moles } e^- \text{ in std half cell rxn}]$$

$$E = E^\circ - \frac{RT}{nF} \ln \prod_i [C_i]^i \quad @T = 298.15K \quad E = E^\circ - \frac{0.05916}{n} \ln Q$$

$$E^\circ = E_{\text{reduction}}^\circ + E_{\text{oxidation}}^\circ$$

$$w_{\text{electrical}} = \Delta G = -\Delta H \left(1 - \frac{T\Delta S}{\Delta H}\right) = -nEF$$

$$dw (\varphi_2 - \varphi_1) dQ \quad dQ = zFdn \quad (\varphi \text{ is half cell potential})$$

$$\frac{n}{v} = \frac{It}{F} = \frac{C}{F}$$

$$\Delta S^\circ = -\left(\frac{\delta \Delta G^\circ}{\delta T}\right)_p = nF \left(\frac{\delta E^\circ}{\delta T}\right)_p$$

Kinetics

Energy of Activation $k = Ae^{-E_a/RT}$ (k is reaction rate) $\therefore k_2(T_2) = k_1(T_1)e^{-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$

Units of rate order $\text{mol}^{(1-o)} \text{ dm}^{(-3+3o)} \text{ s}^{-1}$ where o = order of rxn

$$\text{rate} = v = \frac{1}{c_i} \frac{d[P]}{dt} = k[A]^\alpha [B]^\beta \dots \quad c_i \text{ is coefficient in stoic. Eq. | overall order} = \alpha + \beta + \dots$$

$$\alpha = \frac{\ln\left(\frac{v_1}{v_2}\right)}{\ln\left(\frac{[A]_1}{[A]_2}\right)}$$

$$\text{eg } 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g}) \quad || \text{ rate} = -\frac{1}{4} \frac{d[\text{NO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt}$$

Rxn Order	Rate Law	Integrated Rate law	Linear plot	Slope of plot	Half-life
Zero	Rate = k	$[A]_t = -kt + [A]_0$	[A] vs t	-k	$\frac{[A]_0}{2k}$
First	Rate = k[A]	$\ln[A]_t = -kt + \ln[A]_0$	ln[A] vs t	-k	$\frac{\ln 2}{k}$
Second	Rate = k[A] ²	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]_t}$ vs t	+k	$\frac{1}{k[A]_0}$
nth (n > 1)	Rate = k[A] ⁿ	$\frac{1}{(n-1)[A]_t^{n-1}} = kt + \frac{1}{(n-1)[A]_0^{n-1}}$	$\frac{1}{(n-1)[A]_t^{n-1}}$ vs t	+k	$\frac{(2^{n-1}-1)}{k(n-1)[A]_0^{n-1}}$

eg $v = -\frac{d[A]}{dt} = \text{rate (above)}$ therefore for 2nd order equation

$$-\frac{d[A]}{dt} = k[A]^2 \quad \rightarrow \quad -\frac{d[A]}{[A]^2} = kdt \quad \rightarrow \quad -\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_0^t kdt \quad \rightarrow \quad \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \quad \rightarrow \quad \frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

Constants

R = Gas constant = $N_A k$ (8.31446 J/Kmol or Pa m³ /K mol) = 0.0831445 (dm³ bar /K mol)
= (0.0820574 dm³ atm /K mol) = (62.364 dm³ Torr/K mol) = (1.98721 cal/K mol)

C_s water = 4.184 ($\frac{J}{g K}$) = 1 $\frac{cal}{g K}$; C_m water = 75.4 ($\frac{J}{mol K}$); k = Boltzmann's constant (1.38065x10⁻²³ J/K)

atm = 1.01325 bar = 101325 Pa = 760 torr ; bar = 1.0x10⁵ Pa torr = mmHg = 133.322 Pa

F = Faraday's constant = 96,485 C/mol = N_A x e⁻ charge

Legend

d = distance, Collision diam

V = volume

H = Enthalpy (J)

U = Internal energy

M = molar mass (Kg/mol)

W = number of microstates

λ = number density (N/V)

π_T = Internal pressure ($\frac{J}{m^3}$)

H° = Std Enthalpy (J)

C_{V,s} = C_s = Specific Heat Capacity ($\frac{J}{<unit>K}$)

Q = Rxn quotient

R = Gas constant = N_Ak (8.31446 J/Kmol)

E = Energy; Cell potential (V)

A = area, Helmholtz free energy

V_m = molar volume (V/n)

G = Gibbs free energy

w = work (J)

F = force (N; Kg m/s²)

N = total molecules

v = electrons/molecule, rxn rate

α = expansion coefficient

G° = Std Gibbs free energy

C_{V,m} = C_m = Molar Heat Capacity, V

R = Thermodynamic Equilibrium Const (= Q_{Equil})

k = Boltzmann's constant (1.38065x10⁻²³ J/K)

φ = half cell potential (V)

p = pressure (N/m²)

V_m⁰ = molar vol of ideal gas

A = Helmholtz free energy

q = heat energy (J)

n = moles (mol)

N_A = Avogadro's number

J = Joules (Nm or kg m²/s²)

K_T = compressibility coefficient

A° = Std Helmholtz free energy

C_{V,m} = Molar Heat Cap, const p,

C = Columb (6.24x10¹⁸ e⁻)

z is charge xferred (electron=-1)