Physical Chemistry Cheat Sheet

Comprehensive Formulas, Laws, and Constants

Thermodynamics

First Law:

$$\Delta U = q + w$$

For an infinitesimal change: $dU = dqv - pdV$

Expansion Work:

$$w = -\int_{V_1}^{V_2} p_{\text{ext}} dV$$

* **Isothermal Reversible Expansion:**

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -nRT \ln\left(\frac{p_1}{p_2}\right)$$

* **Free Expansion ($p_{\text{ext}} = 0$):** $w = 0$

Enthalpy (H):

$$H = U + pV \implies dH = dU + d(pV)$$

At constant pressure: $dH = q_p$

Heat Capacities:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V, \quad C_p = \left(/\frac{\partial H}{\partial T}\right)_p$$

For ideal gases: $C_p - C_v = nR$

Second Law Entropy (S):

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$dS = \frac{dq_{\text{rev}}}{T}$$

* **Phase Transition:** $\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}}$ * **Temperature Dependence:**

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

Gibbs Free Energy (G):

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

* **Spontaneity Criteria (at constant T, p):** * $\Delta G < 0$ (Spontaneous) * $\Delta G = 0$ (Equilibrium) * $\Delta G > 0$ (Non-spontaneous)

Chemical Potential Equilibrium:

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

$$\Delta G^\circ = -RT \ln K$$

Chemical Kinetics

Rate Law: For $aA + bB \to$ Products, Rate $= k[A]^x[B]^y$

Integrated Rate Equations:

* **Zero Order ($x = 0$):**

$$[A]_t = -kt + [A]_0$$

Half-life: $t_{1/2} = \frac{[A]_0}{2k}$

* **First Order ($x = 1$):**

$$\ln[A]_t = -kt + \ln[A]_0 \iff [A]_t = [A]_0 e^{-kt}$$

Half-life: $t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k}$

* **Second Order ($x = 2$):**

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Half-life: $t_{1/2} = \frac{1}{k[A]_0}$

Arrhenius Equation:

$$k = Ae^{-E_a/RT}$$

Linearized form:

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

Two-temperature form:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Collision Transition State Theory: * Activation energy E_a is the threshold energy. * Eyring equation: $k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT}$

Quantum Chemistry

Fundamental Postulates: * Time-independent Schrödinger Equation:

$$\hat{H}\psi = E\psi$$

* Momentum Operator: $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$ * Hamiltonian Operator: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

Particle in a 1D Box ($0 \leq x \leq L$): * **Wavefunction:**

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \ldots$$

* **Energy Levels:**

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Harmonic Oscillator (Vibrational):

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega, \quad v = 0, 1, 2, \ldots$$

Zero-point energy ($v = 0$): $E_0 = \frac{1}{2}\hbar\omega$

Hydrogen Atom: * Radial and angular separation of variables. * Energy levels depend solely on principal quantum number n:

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

Electrochemistry

Faradayś Laws of Electrolysis:

$$m = Z \cdot I \cdot t = \frac{M \cdot Q}{n \cdot F}$$

Nernst Equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

At 298 K:

$$E = E^\circ - \frac{0.0591}{n} \log Q \; ext(inVolts)$$

Electrochemical Cells:

$$\Delta G = -nFE_{\text{cell}}$$

At equilibrium ($Q = K, E_{\text{cell}} = 0$):

$$\log K = \frac{nE^\circ}{0.0591}$$

Conductivity Molar Conductivity: * Resistivity ρ, Conductivity $\kappa = \frac{1}{\rho}$ * Molar Conductivity:

$$\Lambda_m = \frac{\kappa \cdot 1000}{C}$$

* **Kohlrauschś Law:**

$$\Lambda_m^\circ = \sum \nu_+ \lambda_+^\circ + \sum \nu_- \lambda_-^\circ$$

Solutions Colligative Prop.

Concentration Terms: * Molarity (M): $\frac{\text{Moles of solute}}{\text{Volume of solution (L)}}$ * Molality (m): $\frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$ * Mole Fraction (x_i): $\frac{n_i}{\sum n_j}$

Raoultś Law:

$$p_A = x_A p_A^\circ, \quad P_{\text{total}} = p_A + p_B$$

Colligative Properties (with vant́ Hoff factor i): * Relative Lowering of Vapour Pressure:

$$\frac{p_A^\circ - p_A}{p_A^\circ} = i \cdot x_B$$

* **Elevation of Boiling Point:**

$$\Delta T_b = i \cdot K_b \cdot m$$

* **Depression of Freezing Point:**

$$\Delta T_f = i \cdot K_f \cdot m$$

* **Osmotic Pressure (Π):**$\Pi = i \cdot CRT$

Gases Statistical Basics

Ideal Gas Law:

$$PV = nRT$$

Van der Waals Real Gas Equation:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Kinetic Theory Speeds: * Root Mean Square Speed:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

* Average Speed:

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}}$$

* Most Probable Speed:

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

Physical Constants Reference: * Gas Constant (R): 8.314 J mol^{-1}K^{-1} * Faraday Constant (F): 96485 C mol^{-1} * Planckś Constant (h): 6.626×10^{-34} J s * Boltzmann Constant (k_B): 1.381×10^{-23} J K^{-1}