CHECKLIST OF KEY EQUATIONS

FOCUS 1

TOPIC 1A Work and heat

Property or process	Equation	Comment	Equation number
Work of raising a weight	work = mgh	At surface of Earth	1
Expansion work	$w = -p_{ex}\Delta V$	Constant external pressure	2
	$w = -nRT\ln(V_f/V_i)$	Reversible, isothermal expansion, perfect gas	5
Heat capacity	$C = q/\Delta T$	Preliminary definition*	6a
Boltzmann distribution	$N_2/N_1 = e^{-(\varepsilon_2-\varepsilon_1)/kT} = e^{-\Delta\varepsilon/kT}$		7

* The definition is developed in Topics 1B and 1D.

TOPIC 1B Internal energy and enthalpy

Property or process	Equation	Comment	Equation number
Internal energy change	$\Delta U = w + q$	Definition	1
	$\Delta U = q_V$	No non-expansion work	3
Heat capacity at constant volume	$C_V = \mathrm{d}U/\mathrm{d}T$	Definition, constant volume	4b
Enthalpy	$H = U + pV$	Definition	5
Change in enthalpy	$\Delta H = \Delta U + p\Delta V$	Constant pressure	6b
	$\Delta H = q_p$	No non-expansion work	8
Heat capacity at constant pressure	$C_p = \mathrm{d}H/\mathrm{d}T$	Definition, constant pressure	9b
Relation between molar heat capacities	$C_{p,m} - C_{V,m} = R$	Perfect gas	10

TOPIC 1C Calorimetry

Property	Equation	Comment	Equation number
Calorimeter constant	$C = q/\Delta T$	Determined empirically	1
Electrical heating	$q = I\Delta\phi\Delta t$	I in amperes, $\Delta\phi$ in volts	2
Enthalpy and internal energy	$\Delta H_m = \Delta U_m + \Delta\nu_{gas}RT$	Gases regarded as perfect	3

TOPIC 1D Fundamental processes

Property	Equation	Comment	Equation number
Forward and reverse processes	$\Delta_{forward}H^{\ominus}(T) = -\Delta_{reverse}H^{\ominus}(T)$	Same temperature	1
Composite processes	$\Delta_{sub}H^{\ominus}(T) = \Delta_{fus}H^{\ominus}(T) + \Delta_{vap}H^{\ominus}(T)$	Same temperature	2

TOPIC 1E Chemical change

Property	Equation	Comment	Equation number
Standard reaction enthalpy	$\Delta_r H = \sum_{\text{Products}} \nu H_m - \sum_{\text{Reactants}} \nu H_m$	Definition	1a
	$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus$	Calculation	1b
Heat capacity difference	$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$	Definition	2b
Temperature dependence of standard reaction enthalpy	$\Delta_r H^\ominus(T_f) = \Delta_r H^\ominus(T_i) + \Delta_r C_p^\ominus \times (T_f - T_i)$	Kirchhoff's law; $\Delta_r C_p^\ominus$ independent of temperature	3

FOCUS 2

TOPIC 2A Entropy

Property	Equation	Comment	Equation number
Entropy change	$\Delta S = q_{rev}/T$	Definition	1
Entropy change on heating	$\Delta S = \int_{T_i}^{T_f} (C/T)\mathrm{d}T$		3b
	$\Delta S = C\ln(T_f/T_i)$	If C independent of temperature	3c
Entropy of phase transition	$\Delta_{trs}S(T_{trs}) = \Delta_{trs}H(T_{trs})/T_{trs}$	trs = vap, fus,…	4a,b
Entropy change of surroundings	$\Delta S_{sur} = -\Delta H/T$	At constant pressure	5

TOPIC 2B Entropy in biology

Property	Equation	Comment	Equation number
Standard entropy of reaction	$\Delta_r S^\ominus = \sum_{Products} \nu S_m^\ominus - \sum_{Reactants} \nu S_m^\ominus$	Definition	1
Standard entropy change of surroundings	$\Delta_r S_{sur}^\ominus = -\Delta_r H^\ominus/T$	Constant pressure	2
Hydrophobicity index	$\pi = \log_{10}\{s(\mathrm{RX})/s(\mathrm{HX})\}$	Definition	3

TOPIC 2C The Gibbs energy

Property	Equation	Comment	Equation number
Gibbs energy	$G = H - TS$	Definition; also referred to as 'free energy'	3
Standard reaction Gibbs energy	$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$	Definition	6a
	$\Delta_r G^\ominus = \sum_{Products} \nu G_m^\ominus - \sum_{Reactants} \nu G_m^\ominus$	Calculation	6b
Maximum non-expansion work	$\Delta G = w_{non\text{-}exp,max}$	Constant temperature and pressure	7

FOCUS 3

TOPIC 3A Water in transition

Property	Equation	Comment	Equation number
Variation of Gibbs energy with pressure and temperature	$dG = Vdp - SdT$	Constant composition	1
Variation of Gibbs energy with pressure	$G_m(p_f) = G_m(p_i) + (p_f - p_i)V_m$	Incompressible substance	3
	$G_m(p_f) = G_m(p_i) + RT\ln(p_f/p_i)$	Perfect gas	4

TOPIC 3B The thermodynamic properties of water

Property	Equation	Comment	Equation number
Clapeyron equation	$dp/dT = \Delta_{trs}H/T\Delta_{trs}V$		1
Clausius–Clapeyron equation	$d\ln p/dT = \Delta_{vap}H/RT^2$	Vapour is a perfect gas	2
Capillary rise	$h = 2\gamma/\rho gr$	Hemispherical meniscus	3

TOPIC 3C The thermodynamic description of aqueous solutions

Property	Equation	Comment	Equation number
Chemical potential	$\mu_J(g) = \mu_J^{\ominus}(g) + RT\ln(p_J/p^{\ominus})$	Perfect gas	2b
Raoult's law	$p_W = x_W p_W^*$	Ideal solution	3
Chemical potential of water	$\mu_W(aq) = \mu_W^*(l) + RT\ln x_W$	Ideal solution	4a
	$\mu_W(aq,h) = \mu_W^*(l) + RT\ln x_W + M_W gh$	In a gravitational field	4b
Henry's law	$[S] = K_H p_S$	Ideal–dilute solution	5
Chemical potential of solute	$\mu_S(aq) = \mu_S^* + RT\ln([S]/c^{\ominus})$	Ideal–dilute solution	6a
	$\mu_S(aq) = \mu_S^* + RT\ln[S] + zF\phi$	In electric field	6c
Activity	$a_W = \gamma_W x_W$	Of water	8
	$a_S = \gamma_S[S]/c^{\ominus}$	Of solute	8

TOPIC 3D Water at equilibrium in solution

Property	Equation	Comment	Equation number
Elevation of boiling point	$\Delta T_b = K_b b_S$	Empirical relation	1
Depression of freezing point	$\Delta T_f = K_f b_S$	Empirical relation	1
van 't Hoff equation	$\Pi \approx [S]RT$	Ideal solution	2
Water potential	$\Psi = (\mu_W - \mu_W^{\ominus})/V_W$	Definition	3
	$\Psi = P - \Pi + \rho_W gh$		4

FOCUS 4

TOPIC 4A The thermodynamic background

Property	Equation	Comment	Equation number
Gibbs energy of reaction	$\Delta_r G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$	Evaluated at a specific stage of the reaction	1c
Condition for equilibrium	$\Delta_r G = 0$	Constant temperature, pressure	2
Standard Gibbs energy of reaction	$\Delta_r G^\ominus = \{cG_m^\ominus(C) + dG_m^\ominus(D)\} - \{aG_m^\ominus(A) + bG_m^\ominus(B)\}$	Definition	4b
Reaction quotient	$Q = a_C^c a_D^d / a_A^a a_B^b$	Definition	6
Reaction Gibbs energy	$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$		7
Equilibrium constant	$K = Q_{equilibrium} = (a_C^c a_D^d / a_A^a a_B^b)_{equilibrium}$	Definition	8
Thermodynamic relation	$\Delta_r G^\ominus = -RT \ln K$		9
Condition for K becoming >1	$T = \Delta_r H^\ominus / \Delta_r S^\ominus$	For an endothermic reaction	10

* The definitions refer to a reaction of the form a A + b B → c C + d D.

TOPIC 4B The standard reaction Gibbs energy

Property	Equation	Comment	Equation number
Standard Gibbs energy of reaction	$\Delta_r G^\ominus = \sum_{Products} \nu G_m^\ominus - \sum_{Reactants} \nu G_m^\ominus$	Definition	2
	$\Delta_r G^\ominus = \sum_{Products} \nu \Delta_f G^\ominus - \sum_{Reactants} \nu \Delta_f G^\ominus$	Implementation	4
Relation between standards	$\Delta_r G^{\ominus\prime} = \Delta_r G^\ominus + 7\nu RT \ln 10$	For reactants + ν H_3O^+ → products	5
Relation between equilibrium constants	$K' = K \times 10^{-7\nu}$	For reactants + ν H_3O^+ ⇌ products	7

* Quantities without a prime refer to conventional (thermodynamic) standard states; those with a prime refer to biochemical standard states (pH = 7).

TOPIC 4C The response of equilibria to the conditions

Property	Equation	Comment	Equation number
van 't Hoff equation	$\ln K_2 = \ln K_1 + (\Delta_r H^\ominus / R)(1/T_1 - 1/T_2)$	Integrated form	3

TOPIC 4E Proton transfer equilibria

Property	Equation	Comment	Equation number
pH	$\mathrm{pH} = -\log_{10}\ a_{\mathrm{H_3O^+}}$	Definition	2
Acidity constant	$K_\mathrm{a} = a_{\mathrm{H_3O^+}} a_{\mathrm{A^-}} / a_{\mathrm{HA}}$	Definition	3a
	$\mathrm{p}K_\mathrm{a} = -\log_{10}\ K_\mathrm{a}$		4
Basicity constant	$K_\mathrm{b} = a_{\mathrm{HB^+}} a_{\mathrm{OH^-}} / a_\mathrm{B}$	Definition	5a
Relation between constants	$\mathrm{p}K_\mathrm{a} + \mathrm{p}K_\mathrm{b} = \mathrm{p}K_\mathrm{w}$	Conjugate acid/base pair	7b
Autoprotolysis	$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_\mathrm{w}$		8
pH of amphiprotic salt	$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K_{\mathrm{a}1} + \mathrm{p}K_{\mathrm{a}2})$	Approximate relation	9
Fraction deprotonated	$f_{\mathrm{deprotonated}} = [\mathrm{A^-}]_{\mathrm{at\ equilibrium}} / [\mathrm{HA}]_{\mathrm{as\ prepared}}$	Definition	10a
Fraction protonated	$f_{\mathrm{protonated}} = [\mathrm{HB^+}]_{\mathrm{at\ equilibrium}} / [\mathrm{B}]_{\mathrm{as\ prepared}}$	Definition	10b

* For ideal solutions, replace a_J by $[\mathrm{J}]/c^\ominus$.

TOPIC 4F Buffer solutions

Property	Equation	Comment	Equation number
Henderson–Hasselbalch equation	$\mathrm{pH} = \mathrm{p}K_\mathrm{a} - \log_{10}([\mathrm{acid}]/[\mathrm{base}])$	Ideal solution; [acid] and [base] little changed from 'as prepared'.	1

TOPIC 4G Ligand binding equilibria

Property	Equation	Comment	Equation number
Fractional saturation	$f = N_{\mathrm{bound}} / N_\mathrm{P}$	Definition	1a
	$f = [\mathrm{L}]/(K_\mathrm{d} c^\ominus + [\mathrm{L}])$	One ligand type	1b
Scatchard equation	$f/[\mathrm{L}] = 1/K_\mathrm{d} c^\ominus - f/K_\mathrm{d} c^\ominus$		2
Relation between equilibrium constants	$K_\mathrm{d} = \hat{K}_\mathrm{d} / N_{\mathrm{sites}}$	For first ligand binding	4
Microscopic binding	$\hat{f} = [\mathrm{L}]/(\hat{K}_\mathrm{d} c^\ominus + [\mathrm{L}])$		5a
	$f = N_{\mathrm{sites}} \hat{f}$		5b
Measure of cooperativity	$g = \Delta_{\mathrm{bind}} G^\ominus(\mathrm{L'\ to\ PL}) - \Delta_{\mathrm{bind}} G^\ominus(\mathrm{L'\ to\ P})$	$g = g'$	7
	$g' = \Delta_{\mathrm{bind}} G^\ominus(\mathrm{L\ to\ PL'}) - \Delta_{\mathrm{bind}} G^\ominus(\mathrm{L\ to\ P})$		
Multisite binding	$\ln\{f/(n-f)\} = n \ln([\mathrm{L}]/c^\ominus) - \ln K_\mathrm{d}$		9
Polydentate binding	$K_\mathrm{d}(\mathrm{L-L'}) = K_\mathrm{d}(\mathrm{L}) K_\mathrm{d}(\mathrm{L'})$	Independent centres	10

FOCUS 5

TOPIC 5A Ion transport across membranes

Property	Equation	Comment	Equation number
Activity coefficient	$\log_{10}\gamma = -Az^2I^{1/2}$	Limiting law	3
Ionic strength	$I = \frac{1}{2}\sum_i z_i^2 c_i / c^\ominus$	Definition	4
Extended Debye–Huckel equation	$\log_{10}\gamma = -Az^2I^{1/2}/(1+BI^{1/2})$		5a
Davies equation	$\log_{10}\gamma = -Az^2I^{1/2}/(1+BI^{1/2}) + CI$	Empirical constants	5b
Electrochemical potential	$\mu_J = \mu_J^\ominus + RT\ln a_J + z_J F\phi$	Definition	8
Permeability coefficient	$P_J = D_J K_J / L$	Definition	15

TOPIC 5B Electron transfer reactions

Property	Equation	Comment	Equation number
Relation between the cell potential and $\Delta_r G$	$-\nu F E_{cell} = \Delta_r G$	Reversible conditions	2
Standard cell potential	$E_{cell}^\ominus = -\Delta_r G^\ominus / \nu F$	Definition	3a
Nernst equation	$E_{cell} = E_{cell}^\ominus - (RT/\nu F)\ln Q$		3b
Equilibrium constant	$\ln K = \nu F E_{cell}^\ominus / RT$		4
Electrode potentials	$E_{cell} = E_R - E_L$	Definition	5
Biochemical standard potential	$E^{\ominus\prime}(\mathrm{Ox/Red}) = E^\ominus(\mathrm{Ox/Red}) - 7\nu_p RT(\ln 10)/\nu F$		6
Equilibrium constant	$\ln K_1 = \nu\{E^\ominus(A_{ox}/A_{red}) - E^\ominus(B_{ox}/B_{red})\}F/RT$	Reaction 1	7a
	$\ln K_2 = \nu_a\nu_b\{E^\ominus(A_{ox}/A_{red}) - E^\ominus(B_{ox}/B_{red})\}F/RT$	Reaction 2	7b
Standard reaction entropy	$\Delta_r S^\ominus = \nu F\, dE_{cell}^\ominus/dT$		8
Standard reaction enthalpy	$\Delta_r H^\ominus = -\nu F(E_{cell}^\ominus - dE_{cell}^\ominus/dT)$		9

TOPIC 5C Electron transport chains

Property	Equation	Comment	Equation number
Reaction Gibbs energy	$\Delta_r G = -\nu F\{E(Ox_2/Red_2) - E(Ox_1/Red_1)\}$	Matching electron numbers	1a
	$\Delta_r G = -\nu_a\nu_b F\{E(B_{ox}/B_{red}) - E(A_{ox}/A_{red})\}$	Based on individual half-reactions	1b
Gibbs energy gradient	$\Delta G_m = F\Delta\phi - RT(\ln 10)\Delta\mathrm{pH}$		2b
Proton motive force	$\Delta p = -\Delta G_m/F$	Definition	3a
	$\Delta p = (RT/F)(\ln 10)\Delta\mathrm{pH} - \Delta\phi$		3b

FOCUS 6

TOPIC 6A Reaction rates

Property	Equation	Comment	Equation number
Instantaneous reaction rate	$v(\mathrm{J}) = \lvert \mathrm{d[J]}/\mathrm{d}t \rvert$	Definition	1b
Unique rate	$v = (1/\nu_\mathrm{J}) \lvert \mathrm{d[J]}/\mathrm{d}t \rvert$	Definition	Summary of 2
Reaction order	$v = k_\mathrm{r}[\mathrm{A}]^x[\mathrm{B}]^y \cdots$	xth-order in A, yth-order in B, . . . and overall order $x + y + \cdots$	Summary of 4

TOPIC 6B The rate laws of single-step reactions

Property	Equation	Comment	Equation number
Concentration of reactant	$[\mathrm{A}] = [\mathrm{A}]_0 - k_\mathrm{r}t$ for $k_\mathrm{r}t \le [\mathrm{A}]_0$, $[\mathrm{A}] = 0$ for $k_\mathrm{r}t > [\mathrm{A}]_0$	Zeroth-order reaction	1b
	$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - k_\mathrm{r}t$	First-order reaction	3b
	$[\mathrm{A}] = [\mathrm{A}]_0 \mathrm{e}^{-k_\mathrm{r}t}$		3c
	$1/[\mathrm{A}] = 1/[\mathrm{A}]_0 + k_\mathrm{r}t$	Second-order reaction	6b
	$[\mathrm{A}] = [\mathrm{A}]_0/(1 + k_\mathrm{r}t[\mathrm{A}]_0)$		6c
Half-life	$t_{1/2} = [\mathrm{A}]_0/2k_\mathrm{r}$	Zeroth-order reaction	In text
	$t_{1/2} = (\ln 2)/k_\mathrm{r}$	First-order reaction	4
	$t_{1/2} = 1/k_\mathrm{r}[\mathrm{A}]_0$	Second-order reaction	7
Equilibrium constant	$K = k_\mathrm{r}/k'_\mathrm{r}$	First-order in both directions	11

TOPIC 6C The rate laws of multi-step reactions

Property	Equation	Comment	Equation number
$\mathrm{A} \xrightarrow{k_{\mathrm{r},1}} \mathrm{I} \xrightarrow{k_{\mathrm{r},2}} \mathrm{P}$	$[\mathrm{A}] = f_\mathrm{A}(t)[\mathrm{A}]_0$, $f_\mathrm{A}(t) = \mathrm{e}^{-k_{\mathrm{r},1}t}$		1a
	$[\mathrm{I}] = f_\mathrm{I}(t)[\mathrm{A}]_0$, $f_\mathrm{I}(t) = (k_{\mathrm{r},1}/(k_{\mathrm{r},2} - k_{\mathrm{r},1}))(\mathrm{e}^{-k_{\mathrm{r},1}t} - \mathrm{e}^{-k_{\mathrm{r},2}t})$		1b
	$[\mathrm{P}] = f_\mathrm{P}(t)[\mathrm{A}]_0$, $f_\mathrm{P}(t) = 1 + (1/(k_{\mathrm{r},2} - k_{\mathrm{r},1}))(k_{\mathrm{r},1}\mathrm{e}^{-k_{\mathrm{r},2}t} - k_{\mathrm{r},2}\mathrm{e}^{-k_{\mathrm{r},1}t})$		1c
Time at which [I] is greatest	$t_\mathrm{max} = (1/(k_{\mathrm{r},2} - k_{\mathrm{r},1}))\ln(k_{\mathrm{r},2}/k_{\mathrm{r},1})$		2
A^- and HA different reactivities	$1/k_{\mathrm{r,eff}} = 1/k_{\mathrm{r},2} + [\mathrm{H_3O^+}]/K_\mathrm{a}k_{\mathrm{r},2}$	A^- active	10a
	$1/k_{\mathrm{r,eff}} = 1/k_{\mathrm{r},2} + K_\mathrm{a}/k_{\mathrm{r},2}[\mathrm{H_3O^+}]$	HA active	10b
Kinetic control	$[\mathrm{P_2}]/[\mathrm{P_1}] = k_{\mathrm{r},2}/k_{\mathrm{r},1}$		11

TOPIC 6D The values of rate constants

Property	Equation	Comment	Equation number
Activation and diffusion control	$k_r = k_a k_d/(k_d' + k_a)$		1
Diffusion control	$k_r = k_d$	$k_a >> k_d'$	2a
Activation control	$k_r = k_a k_d/k_d'$	$k_a << k_d'$	2b
Temperature coefficient	$Q_{10}(T) = v(T + 10\,\mathrm{K})/v(T)$	Definition	4a
	$Q_{10}(T) = k_r(T + 10\,\mathrm{K})/k_r(T)$	For reactions with rate law $v = k_r[\mathrm{A}]^x[\mathrm{B}]^y \ldots$	4b
Arrhenius law	$\ln k_r = \ln A - E_a/RT$	General form	5b
	$k_r = A\mathrm{e}^{-E_a/RT}$	Alternative form	5c
Temperature coefficient and activation energy	$\ln Q_{10}(T) = (E_a/RT)\{1 - T/(T + 10\,\mathrm{K})\}$	For reactions that follow the Arrhenius law	6b
Eyring equation	$k_a = \kappa(kT/h)K^{\ddagger}$	Transition-state theory	8
Activation Gibbs energy	$\Delta^{\ddagger}G^{\ominus} = -RT \ln K^{\ddagger}$	Definition	9a
Activation enthalpy and entropy	$\Delta^{\ddagger}G^{\ominus} = \Delta^{\ddagger}H^{\ominus} - T\Delta^{\ddagger}S^{\ominus}$	Definition	9b
Kinetic isotope effect	$k_r(\mathrm{H})/k_r(\mathrm{D}) = \mathrm{e}^{\delta E/RT}$	E_a is increased to $E_a + \delta E$	11
Kinetic salt effect	$\log_{10} k_a = \log_{10} k_a^{\circ} + 2Az_A z_B I^{1/2}$	Dilute solution (low ionic strength)	12

FOCUS 7

TOPIC 7A Enzyme action

Property	Equation	Comment	Equation number
Molar rate	$v_m = dn_P/dt$	Definition; $v_m = Vv$	1a
Specific rate	$v_s = v_m/m_E$	Definition	1c
Specific activity	$a_s = v_{s,max}$	Definition	1d
	$a_s = v_{max}/M[E]_{total}$		1e
Michaelis constant	$K_M = (k'_{r,1} + k_{r,2})/k_{r,1}$	Definition	2
Michaelis–Menten equation	$v = v_{max}[S]/(K_M + [S])$		5a
Lineweaver–Burk equation	$1/v = 1/v_{max} + K_M/v_{max}[S]$		6
Fractional rate	$v/v_{max} = f_{ES_iS_2}$	Ternary complex mechanism	9
Turnover frequency	$k_{cat} = k_{r,2} = v_{max}/[E]_{total}$	Michaelis–Menten model, $k_{cat} = Ma_s$	14
Catalytic efficiency	$\eta = k_{cat}/K_M$	Michaelis–Menten model	15

TOPIC 7B Enzyme inhibition

Property	Equation	Comment	Equation number
Inhibition parameters	$v_{max}^{inhibited} = v_{max}/(1 + [I]/K_{d,ESI})$ $K_M^{inhibited} = \{(1 + [I]/K_{d,EI})/(1 + [I]/K_{d,ESI})\}K_M$	Definition; pre-equilibrium approximation	1
Rate with inhibition	$v = v_{max}^{inhibited}[S]/(K_M^{inhibited} + [S])$	Definition; pre-equilibrium approximation	2a
Lineweaver–Burk equation with inhibition	$1/v = 1/v_{max}^{inhibited} + (K_M^{inhibited}/v_{max}^{inhibited}) \times 1/[S]$		2b
	y-intercept $= (1 + [I]/K_{d,ESI})/v_{max}$ slope $= (1 + [I]/K_{d,EI})K_M/v_{max}$		2c

TOPIC 7C Diffusion in biological systems

Property	Equation	Comment	Equation number
Flux	$J = N/A\Delta t$	Definition	1a
Fick's first law	$J = -D\mathrm{d}c/\mathrm{d}x \quad J_\mathrm{m} = -D\mathrm{d}c_\mathrm{m}/\mathrm{d}x$		2
Diffusion equation	$\partial c/\partial t = D\partial^2 c/\partial x^2$	In one dimension	3
Diffusion coefficient	$D = D_0 \mathrm{e}^{-E_\mathrm{a}/RT}$	Activated process	5
Stokes–Einstein relation	$D = kT/f$	f is the frictional coefficient	6
Frictional force	$F = fs$		7
Stokes' law	$f = 6\pi\eta a$	a is the hydrodynamic radius	-
Mean square distance	$\langle r^2\rangle^{1/2} = (6Dt)^{1/2}$	Random walk in 3D	8
Einstein–Smoluchowski equation	$D = d^2/2\tau$		9
Drift speed	$s = ez\mathcal{E}/f$	In an electric field $\mathcal{E}$	10a
Electrophoretic mobility	$s = u\mathcal{E}$	Definition	10b
	$u = ez/6\pi\eta a$	Assuming Stokes' law	10c
Partition constant	$\kappa = [\mathrm{A}]_\mathrm{outer}/[\mathrm{A}]_\mathrm{bulk}$	Definition	13
Diffusion flux	$J_\mathrm{m} = (\kappa D/L)[\mathrm{A}]_\mathrm{bulk}$	Linear gradient	14a
Net diffusion flux	$J_\mathrm{m} = (D/L)(\kappa_\mathrm{outer}[\mathrm{A}]_\mathrm{bulk,outer} - \kappa_\mathrm{inner}[\mathrm{A}]_\mathrm{bulk,inner})$		14b
	$J_\mathrm{m} = P_\mathrm{A}([\mathrm{A}]_\mathrm{bulk,outer} - [\mathrm{A}]_\mathrm{bulk,inner})$	Assumes $\kappa_\mathrm{outer} = \kappa_\mathrm{inner}$	14c
Facilitated flux	$J_\mathrm{m} = J_\mathrm{m,max}[\mathrm{A}]_\mathrm{bulk}/([\mathrm{A}]_\mathrm{bulk} + K_\mathrm{d})$		15

TOPIC 7D Electron transfer

Property	Equation	Comment	Equation number
Gibbs energy of activation	$\Delta^\ddagger G^\ominus = (\Delta_\mathrm{reorg}G^\ominus + \Delta_\mathrm{r}G^\ominus)^2/4\Delta_\mathrm{reorg}G^\ominus$	$\mathrm{D} + \mathrm{A} \rightarrow \mathrm{D}^+ + \mathrm{A}^-$	3
Rate constant	$k_\mathrm{r} = \kappa(kT/h)\mathrm{e}^{-\beta r}\mathrm{e}^{-\Delta^\ddagger G/RT}$	Transition-state theory	4
Experimental test	$\ln k_\mathrm{r} = -\beta r + \mathrm{constant}$	For molecules with a fixed r	5
Marcus cross-relation	$k_\mathrm{r,et} = (k_\mathrm{r,DD}k_\mathrm{r,AA}K_\mathrm{DA})^{1/2}$	Assumes $Z_\mathrm{DA}/(Z_\mathrm{DD}Z_\mathrm{AA})^{1/2} \approx 1$	7

FOCUS 8

TOPIC 8A The principles of quantum theory

Property	Equation	Comment	Equation number
Bohr frequency condition	$\Delta E = h\nu$	h is Planck's constant	1
de Broglie relation	$\lambda = h/p$		3
Schrödinger equation	$-(\hbar^2/2m)(\mathrm{d}^2\psi/\mathrm{d}x^2) + V\psi = E\psi$	$\hbar = h/2\pi$	4a
	$\hat{H}\psi = E\psi$	$\hat{H}$ is an operator	4b
Position–momentum uncertainty relation	$\Delta p \Delta x \geq \frac{1}{2}\hbar$		5

TOPIC 8B The quantum mechanics of motion

Property	Equation*	Comment	Equation number
Particle in a box			
Energy	$E_n = n^2(h^2/8mL^2)$	One dimension	1a
Wavefunction	$\psi_n(x) = (2/L)^{1/2}\sin(n\pi x/L)$		1c
Angular momentum	$J = pr$	In 2D	7
Rotation in 2D	$E_{m_l} = m_l^2\hbar^2/2I$		10
Rotation in 3D			
Energy	$E_{l,m_l} = l(l+1)\hbar^2/2I$		12
Angular momentum	$J = \{l(l+1)\}^{1/2}\hbar$		13a
z-Component	$J_z = m_l\hbar$		13b
Hooke's law	Restoring force $= -k_f x$		14a
Parabolic potential energy	$V(x) = \frac{1}{2}k_f x^2$		14b
Harmonic oscillator	$E_v = (v+\frac{1}{2})h\nu, \quad \nu = (1/2\pi)(k_f/m)^{1/2}$		15

* For allowed values of the quantum numbers, see the preceding table.

TOPIC 8C Atomic orbitals

Property	Equation	Comment	Equation number
Energy levels	$E_{n,l,m_l} = -Z^2\mathcal{R}/n^2$	Independent of l, m_l	2
Wavefunctions	$\psi_{n,l,m_l}(r,\theta,\phi) = \psi_{l,m_l}(\theta,\phi)\psi_{n,l}(r)$		3
Radial distribution function	$P(r) = 4\pi r^2\psi^2$	For s orbitals	6

FOCUS 9

TOPIC 9B Molecular orbital theory: diatomic molecules

Property	Equation	Comment	Equation number
Linear combination	$\psi = c_A\psi_A + c_B\psi_B$	$c_A^2 = c_B^2$ in a homonuclear diatomic molecule	1a
Overlap integral	$S = \int \psi_A \psi_B \mathrm{d}\tau$	Integration over all space	2
Bond order	$b = \frac{1}{2}(n - n^*)$	Definition	4

FOCUS 10

TOPIC 10A Molecular interactions

Property	Equation	Comment	Equation number
Coulomb potential energy	$E_p = Q_1Q_2/4\pi\varepsilon r$	$\varepsilon = \varepsilon_r\varepsilon_0$	1b
Dipole moment and electronegativity	$\mu/\mathrm{D} \approx \Delta\chi$	Pauling electronegativities	2
Charge–dipole interaction	$E_p = -(\mu_1 Q_2/4\pi\varepsilon_0 r^2)\cos\theta$	Orientation as in (7)	4b
Dipole–dipole interaction	$E_p = (\mu_1\mu_2/4\pi\varepsilon_0 r^3)(1-3\cos^2\theta)$	Orientation as in (8)	5
	$E_p = -2\mu_1^2\mu_2^2/3(4\pi\varepsilon_0)^2 kTr^6$	Rotating molecules	6
Polarizability	$\mu = \alpha\mathcal{E}$	Definition	7
Polarizability volume	$\alpha' = \alpha/4\pi\varepsilon_0$	Definition	8
Dipole–induced-dipole interaction	$E_p = -\mu_1^2\alpha_2'/4\pi\varepsilon_0 r^6$		9
London formula	$E_p = -\frac{3}{2}(\alpha_1'\alpha_2'/r^6)I_1I_2/(I_1+I_2)$	Dispersion interaction	10a
Lennard-Jones (12,6) potential energy	$E_p = -A/r^6 + B/r^{12}$	$A = 4\varepsilon\sigma^6$ and $B = 4\varepsilon\sigma^{12}$	12

TOPIC 10B Macromolecular structure

Property	Equation	Equation number
Distribution of ends	$f(r) = 4\pi(a/\pi^{1/2})^3 r^2 \mathrm{e}^{-a^2r^2}$, $a = (3/2Nl^2)^{1/2}$	1
Contour length	$R_c = Nl$	2
Root mean square separation	$R_{rms} = N^{1/2}l$	3
Radius of gyration	$R_g = (N/6)^{1/2}l$	4
Conformational entropy	$\Delta S = -\frac{1}{2}Nk\ln\{(1+\nu)^{1+\nu}(1-\nu)^{1-\nu}\}$, $\nu = \delta L/R_c$	5a

* All the entries refer to a fully flexible three-dimensional chain with N links of length l.

TOPIC 10C Conformational stability and molecular aggregation

Property	Equation	Comment	Equation number
Cooperativity modelling	$K_{intra}(i) = K_{inter}\{\mathrm{X}\}_{effective}C_f^{i-1}/c^{\ominus}$		4
Gibbs–Helmholtz equation	$\mathrm{d}(G/T)/\mathrm{d}T = -H/T^2$		5
Surfactant packing parameter	$N_s = V_{tail}/A_{head}l_{tail}$	Definition	7

TOPIC 10D Computer-aided simulation

Property	Equation	Comment	Equation number
Contribution to the conformational energy	$E_{p,stretch} = \frac{1}{2}k_{f,stretch}(R-R_e)^2$	Bond stretching	1
	$E_{p,bend} = \frac{1}{2}k_{f,bend}(\theta-\theta_e)^2$	Bond bending	2
	$E_{p,torsion} = \frac{1}{2}A\{1+\cos(n\phi-\phi_0)\}$	Bond torsion	3
	$E_{p,electrostatic} = Q_iQ_j/4\pi\varepsilon r_{ij}$, $\varepsilon = \varepsilon_r\varepsilon_0$	Electrostatic interactions	4
	$E_{p,Lennard\text{-}Jones} = -A_{ij}/r_{ij}^6 + B_{ij}/r_{ij}^{12}$	Dispersive and repulsive interactions	5
	$E_{p,H\text{-}bond} = -C_{ij}/r_{ij}^{10} + D_{ij}/r_{ij}^{12}$	Hydrogen bonding	6

FOCUS 11

TOPIC 11A General features of spectroscopy

Property	Equation	Comment	Equation number
Beer–Lambert law	$I = I_0 10^{-\varepsilon[J]L}$	Uniform composition	3
Absorbance	$A = \log_{10}(I_0/I)$	Definition	4a
Transmittance	$T = I/I_0$	Definition	4b
Transition dipole moment	$\boldsymbol{\mu}_{fi} = \int \psi_f \boldsymbol{\mu} \psi_i \, d\tau$	Definition	9
Rate of stimulated absorption	$Rate = N_l B_{l\to u} I(\nu)$		10a
Rate of stimulated emission	$Rate = N_u B_{u\to l} I(\nu)$		10b
Relation between coefficients	$A_{u\to l} = (8\pi h\nu^3/c^3) B_{u\to l}$, $B_{u\to l} = B_{l\to u}$		11

TOPIC 11B Vibrational spectroscopy

Property	Equation	Comment	Equation number
Vibrational energy levels	$E_\upsilon = (\upsilon + \frac{1}{2})h\nu$, $\upsilon = 0, 1, 2, \ldots$	Harmonic approximation	2a
	$\nu = (1/2\pi)(k_f/\mu)^{1/2}$, $\mu = m_A m_B/(m_A + m_B)$		2b
Selection rule	$\Delta\upsilon = \pm 1$		3
Number of normal modes	$N_{vib} = 3N - 6$	Nonlinear molecules	5
	$N_{vib} = 3N - 5$	Linear molecules	

TOPIC 11D Photoactivation and its consequences

Property	Equation	Comment	Equation number
Primary quantum yield	$\phi_E = N_E/N_{\text{photons absorbed}}$	E denotes an event [definition]	1
	$\phi_E = \upsilon_{E,\text{induced}}/I_{abs}$	Implementation	3
Fluorescence lifetime	$\tau_{F,0} = 1/(k_F + k_{ISC} + k_{IC})$	No quencher	6
	$\tau_{F,Q} = 1/(k_F + k_{ISC} + k_{IC} + k_Q[Q])$	With quencher	9b
Fluorescence quantum yield	$\phi_{F,0} = k_F/(k_F + k_{ISC} + k_{IC})$	No quencher	7
	$\phi_{F,Q} = k_F/(k_F + k_{ISC} + k_{IC} + k_Q[Q])$	With quencher	9a
Concentration dependence of quenching	$\phi_{F,0}/\phi_{F,Q} = 1 + \tau_{F,0} k_Q[Q]$	Stern–Volmer equation	10a
Energy transfer efficiency	$\eta_T = 1 - \phi_{F,Q}/\phi_{F,0}$	Definition	11
	$\eta_T = R_0^6/(R_0^6 + R^6)$	Förster theory	12

TOPIC 11E Nuclear magnetic resonance

Property	Equation	Comment	Equation number
Energy of nucleus in a magnetic field	$E_{m_I} = -\gamma_N \hbar \mathcal{B}_0 m_I$	γ_N is the magnetogyric ratio	1
Nuclear magneton	$\mu_N = e\hbar/2m_p$	Definition	2a
Resonance condition	$h\nu = \gamma_N \hbar \mathcal{B}_0$, or $\nu = \gamma_N \mathcal{B}_0/2\pi$		6
Scalar spin–spin coupling	$E_{\text{spin-spin}} = hJm_A m_X$		10
Karplus equation	${}^3J_{HH} = A + B\cos\phi + C\cos 2\phi$	Empirical	11
Enhancement parameter	$\eta = (I - I_0)/I_0$	NOE; definition	13

TOPIC 11F Electron paramagnetic resonance

Property	Equation	Comment	Equation number
Magnetic moment of electron	$\mu_z = \gamma_e s_z$, $\gamma_e = -g_e e/2m_e$	z-component	1
Energy of an electron in a magnetic field	$E_{m_s} = -\gamma_e \hbar \mathcal{B}_0 m_s$	Free electron	2
Bohr magneton	$\mu_B = e\hbar/2m_e$	Definition	3
Resonance condition	$h\nu = g\mu_B \mathcal{B}_0$		7
McConnell equation	$a = Q\rho$	Empirical statement	11
Dipolar coupling energy	$E_{m_s(1),m_s(2)} = hDm_s(1)m_s(2)$, $hD = (\mu_0 \hbar^2 \gamma_e^2/4\pi r^3)(1 - 3\cos^2\theta)$	Electrons aligned in z-direction	12

FOCUS 12

TOPIC 12A Scattering by individual molecules

Property	Equation	Comment	Equation number
Rayleigh ratio	$R(\theta) = (I(\theta)/I_0) \times r^2$	Definition	1
	$R(\theta) = KMc_{\text{mass}}$		3
Form factor	$P(\theta) \approx 1 - A \sin^2 \frac{1}{2}\theta, \quad A = 16\pi^2 R_g^2/3\lambda^2$	$A << 1$	5a
Radius of gyration	$R_g = \left((1/N) \sum_{i=1}^{N} r_i^2 \right)^{1/2}$	Definition in scattering theory	5b
Guinier approximation	$I(q) = I(0) e^{-\frac{1}{3}q^2 R_g^2}, \ \ln\{I(q)/I(0)\} = -\frac{1}{3}q^2 R_g^2$	$q = (4\pi/\lambda)\sin\frac{1}{2}\theta$	7
Intensity correlation function	$g_2(\tau) = \langle I(t) I(t+\tau) \rangle / \langle I(t) \rangle^2$	Definition	8

TOPIC 12B Cooperative scattering: X-ray diffraction

Property	Equation	Comment	Equation number
Separation of planes	$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$	Orthorhombic lattice	1
Bragg's law	$\lambda = 2d \sin\theta$		2a
Structure factor	$F_{hkl} = \sum_{j=1}^{N} f_j e^{i\phi_{hkl}(j)}$, $\phi_{hkl}(j) = 2\pi(hx_j + ky_j + lz_j)$	Definition	3
Fourier synthesis of electron density	$\rho(\boldsymbol{r}) = (1/V) \sum_{h,k,l} F_{hkl} e^{-i\phi_{hkl}(r)}$	V is volume of unit cell	4b

FOCUS 13

TOPIC 13A Ultracentrifugation

Property	Equation	Comment	Equation number
Sedimentation constant	$S = s/r\omega^2$	Definition	1
	$S = (1 - \rho v_s)MD/RT$	Based on Stokes–Einstein equation	2
Equilibrium distribution	$\ln c(r) = \ln c(r_0) + \{(1 - \rho v_s)M\omega^2/2RT\}(r^2 - r_0^2)$		3