

$$\text{Relative uncertainty} = \frac{\text{absolute uncertainty}}{\text{magnitude of measurement}}$$

$$\text{Percent relative uncertainty} = 100 \times \text{relative uncertainty}$$

Table 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function ^a	Uncertainty ^b
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10} \frac{e_x}{x} \approx 0.434 29 \frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302 6 e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty,

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n - 1}}$$

$$\bar{x} = \frac{\sum_i x_i}{n}$$

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$$

$$z = \frac{x - \mu}{\sigma} \approx \frac{x - \bar{x}}{s}$$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \quad (4-8)$$

where $|\bar{x}_1 - \bar{x}_2|$ is the absolute value of the difference (a positive number) and

$$s_{\text{pooled}} = \sqrt{\frac{\sum_{\text{set 1}} (x_i - \bar{x}_1)^2 + \sum_{\text{set 2}} (x_j - \bar{x}_2)^2}{n_1 + n_2 - 2}} = \sqrt{\frac{s_1^2 (n_1 - 1) + s_2^2 (n_2 - 1)}{n_1 + n_2 - 2}} \quad (4-9)$$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}} \quad (4-8a)$$

$$\text{Degrees of freedom} = \left\{ \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\left(\frac{s_1^2/n_1}{n_1 + 1} + \frac{s_2^2/n_2}{n_2 + 1} \right)} \right\} - 2 \quad (4-9a)$$

$$s_d = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n - 1}} \quad (4-10)$$

$$s_d = \sqrt{\frac{(-3.0 - \bar{d})^2 + (4.8 - \bar{d})^2 + \dots + (0.2 - \bar{d})^2 + (-11.6 - \bar{d})^2}{11 - 1}} = 6.7_{48}$$

Once you have the mean and standard deviation, compute $t_{\text{calculated}}$ with the formula

$$t_{\text{calculated}} = \frac{|\bar{d}|}{s_d} \sqrt{n} \quad (4-11)$$

$$F_{\text{calculated}} = \frac{s_1^2}{s_2^2}$$

$$Q_{\text{calculated}} = \frac{\text{gap}}{\text{range}}$$

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

$$s_y = \sqrt{\frac{\sum (d_i^2)}{n-2}}$$

Standard deviation of slope and intercept

$$\begin{cases} s_m^2 = \frac{s_y^2 n}{D} \\ s_b^2 = \frac{s_y^2 \sum (x_i^2)}{D} \end{cases}$$

$$\% \text{ recovery} = \frac{C_{\text{spiked sample}} - C_{\text{unspiked sample}}}{C_{\text{added}}}$$

$$R^2 = \frac{[\sum (x_i - \bar{x})(y_i - \bar{y})]^2}{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}$$

Signal detection limit:

$$y_{\text{dl}} = y_{\text{blank}} + 3s$$

Detection limit:

$$\text{Minimum detectable concentration} = \frac{3s}{m}$$

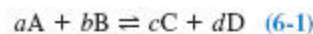
$$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}}$$

$$\text{Standard deviation of x-intercept} = \frac{s_y}{|m|} \sqrt{\frac{1}{n} + \frac{\bar{y}^2}{m^2 \sum (x_i - \bar{x})^2}} \quad (5-10)$$

Response factor:

$$\frac{\text{Area of analyte signal}}{\text{Concentration of analyte}} = F \left(\frac{\text{area of standard signal}}{\text{concentration of standard}} \right) \quad (5-11)$$

$$\frac{A_X}{[X]} = F \left(\frac{A_S}{[S]} \right)$$

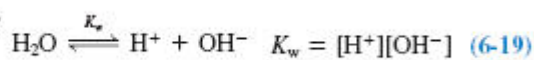


Equilibrium constant:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (6-2)$$

Free energy and equilibrium: $K = e^{-\Delta G^\circ/RT} \quad (6-6)$ Free energy: $\Delta G = \Delta H - T\Delta S \quad (6-5)$

Autoprotolysis of water:



$$\text{pH} + \text{pOH} = -\log(K_w) = 14.00 \text{ at } 25^\circ\text{C} \quad (6-21)$$

Dissociation of weak acid:



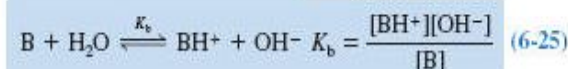
Relation between K_a and K_b for a conjugate pair:

$$K_a \cdot K_b = K_w \quad (6-35)$$

General relation between K_a and K_b :

$$K_{a1} \cdot K_{b2} = K_w \quad (6-36)$$

Base hydrolysis:



$$K_{a2} \cdot K_{b1} = K_w \quad (6-37)$$

Corrected absorbance = $\left(\frac{\text{total volume}}{\text{initial volume}} \right)$ (observed absorbance) $(7-7)$ p function: $\text{pX} = -\log_{10}[\text{X}] \quad (7-8)$

Mass balance for M: $C_M^0 \cdot V_M = \underbrace{[\text{M}^+](V_M + V_X^0)}_{\text{Total moles of added M}} + \text{mol MX}(s) \quad (7-16)$

Moles of M in solution Moles of M in precipitate

Mass balance for X: $C_X^0 \cdot V_X^0 = \underbrace{[\text{X}^-](V_M + V_X^0)}_{\text{Total moles of added X}} + \text{mol MX}(s) \quad (7-17)$

Moles of X in solution Moles of X in precipitate

General form of equilibrium constant:

$$K = \frac{\mathcal{A}_C^c \mathcal{A}_D^d}{\mathcal{A}_A^a \mathcal{A}_B^b} = \frac{[\text{C}]^c \gamma_C^c [\text{D}]^d \gamma_D^d}{[\text{A}]^a \gamma_A^a [\text{B}]^b \gamma_B^b} \quad (8-5)$$

$$\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log[\text{H}^+] \gamma_{\text{H}^+} \quad (8-8)$$

Extended Debye-Hückel equation:

$$\log \gamma = \frac{-0.51z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu}/305)} \quad (\text{at } 25^\circ\text{C}) \quad (8-6)$$

Henderson-Hasselbalch equation for an acid:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) \quad (9-16)$$

Fraction of dissociation of an acid:

$$\alpha = \frac{[\text{A}^-]}{[\text{A}^-] + [\text{HA}]}$$

Henderson-Hasselbalch equation for a base:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{B}]}{[\text{BH}^+]} \right) \quad (9-17)$$

\leftarrow $\text{p}K_a$ applies to this acid

Intermediate form of diprotic acid: $[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$ (10-11) Intermediate form of diprotic acid: $pH = \frac{1}{2}(pK_1 + pK_2)$ (10-12)

$$[H^+] \approx \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}} \quad (10-14)$$

$$M + L \rightleftharpoons ML \quad \beta_1 = \frac{[ML]}{[M][L]} \quad (12-13)$$

$$M + 2L \rightleftharpoons ML_2 \quad \beta_2 = \frac{[ML_2]}{[M][L]^2} \quad (12-14)$$

Isoionic point: $[H^+] = \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$ (10-22) Isoelectric point: $pH = \frac{1}{2}(pK_1 + pK_2)$ (10-23)

$$[OH^-] = \left(\frac{10.00 - 3.00}{10.00} \right) (0.02000 \text{ M}) \left(\frac{50.00}{50.00 + 3.00} \right) = 0.0132 \text{ M} \quad (11-1)$$

← Initial volume of OH⁻
← Total volume of solution

Fraction of OH⁻ remaining
Initial concentration of OH⁻
Dilution factor

Fraction of titration for weak acid by strong base: $\phi = \frac{C_b V_b}{C_a V_a} = \frac{\alpha_{A^-} - \frac{[H^+] - [OH^-]}{C_a}}{1 + \frac{[H^+] - [OH^-]}{C_a}}$ (11-9) Gran plot equation: $V_b 10^{-pH} = \frac{\gamma_{HA}}{\gamma_{A^-}} K_a (V_e - V_b)$ (11-5)

Formation constant: $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \quad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$ (12-5)

Conditional formation constant: $K'_f = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$ (12-6)

$$\alpha_{Zn^{2+}} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4} \quad (12-17) \quad K'_f = \alpha_{Zn^{2+}} \alpha_{Y^{4-}} K_f \quad (12-18)$$

Davies equation: $\log \gamma = -0.51z^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right)$ (at 25°C) (13-18)

Relation between charge and moles: $q = n \cdot F$ (14-2) Relation between work and voltage: $\text{Work} = E \cdot q$ (14-3)

Work done on surroundings = $-\Delta G$ (14-4) Ohm's law: $I = \frac{E}{R}$ (14-6)

Relation between free-energy difference and electric potential difference: $\Delta G = -nFE$ (14-5) Nernst equation: $E = E^\circ - \frac{RT}{nF} \ln \frac{A_b}{A_a}$ (14-13)

Nernst equation for a complete cell: $E = E_+ - E_-$ (14-16) $E^\circ = \frac{0.05916}{n} \log K$ (at 25°C) (14-23)

Table 11-6 Titration equations for spreadsheets

CALCULATION OF α

Monoprotic system s

$$\alpha_{\text{HA}} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a}$$

$$\alpha_{\text{A}^-} = \frac{K_a}{[\text{H}^+] + K_a}$$

$$\alpha_{\text{BH}^+} = \frac{[\text{H}^+]}{[\text{H}^+] + K_{\text{BH}^+}}$$

$$\alpha_{\text{B}} = \frac{K_{\text{BH}^+}}{[\text{H}^+] + K_{\text{BH}^+}}$$

SYMBOLS

K_a = acid dissociation constant of HA

K_{BH^+} = acid dissociation constant of BH^+ ($= K_w/K_b$)

Diprotic system s

$$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

$$\alpha_{\text{HA}^-} = \frac{[\text{H}^+]K_1}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

$$\alpha_{\text{A}^{2-}} = \frac{K_1K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

$$\alpha_{\text{BH}_3^+} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

$$\alpha_{\text{BH}^+} = \frac{[\text{H}^+]K_1}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

$$\alpha_{\text{B}} = \frac{K_1K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

SYMBOLS

K_1 and K_2 for the acid are the acid dissociation constants of H_2A and HA^- , respectively.

K_1 and K_2 for the base refer to the acid dissociation constants of BH_3^+ and BH^+ , respectively: $K_1 = K_w/K_{b2}$; $K_2 = K_w/K_{b1}$

Triprotic system s

$$\alpha_{\text{H}_3\text{A}} = \frac{[\text{H}^+]^3}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

$$\alpha_{\text{H}_2\text{A}^-} = \frac{[\text{H}^+]^2K_1}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

$$\alpha_{\text{HA}^{2-}} = \frac{[\text{H}^+]K_1K_2}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

$$\alpha_{\text{A}^{3-}} = \frac{K_1K_2K_3}{[\text{H}^+]^3 + [\text{H}^+]^2K_1 + [\text{H}^+]K_1K_2 + K_1K_2K_3}$$

Table 11-6 part 2

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Electric potential difference for ion-selective electrode:

$$E = \text{constant} + \frac{0.05916}{n} \log \mathcal{A}_o \text{ (volts at } 25^\circ\text{C)} \quad (15-3)$$

Selectivity coefficient:

$$k_{\text{A,X}} = \frac{\text{response to X}}{\text{response to A}} \quad (15-7)$$

Response of ion-selective electrode:

$$E = \text{constant} \pm \beta \frac{0.05916}{n} \log \left[\mathcal{A}_A + \sum_X (k_{\text{A,X}} \mathcal{A}_X) \right] \quad (15-8)$$

$$\begin{aligned} \left(\begin{array}{l} \text{Indicator transition} \\ \text{range versus calomel} \\ \text{electrode (S.C.E.)} \end{array} \right) &= \left(\begin{array}{l} \text{transition range} \\ \text{versus standard hydrogen} \\ \text{electrode (S.H.E.)} \end{array} \right) - E(\text{calomel}) \quad (16-15) \\ &= (1.088 \text{ to } 1.206) - (0.241) \\ &= 0.847 \text{ to } 0.965 \text{ V (versus S.C.E.)} \end{aligned}$$

Relation of moles to current and time:

$$\text{Moles reacted} = \frac{I \cdot t}{nF} \quad (17-3)$$

$$E = \underbrace{E(\text{cathode}) - E(\text{anode}) - IR}_{\text{These terms include the effects of concentration polarization}} - \text{overpotentials} \quad (17-6)$$

Relation of charge to current and time:

$$q = I \cdot t$$

Coulombs Amperes · Seconds

The number of moles of electrons is

$$\text{Moles of } e^- = \frac{\text{coulombs}}{\text{coulombs/mole}} = \frac{I \cdot t}{F}$$