ENCLOSURE TO EXAM TMT4252 ELECTROCHEMISTRY JUNE 2022: FORMULAS[1]

$$\frac{I}{A} = i = i_f + \frac{C}{A}\frac{dE}{dt} \tag{1}$$

For $\mathrm{O} + \mathrm{e}^- \rightleftharpoons \mathrm{R}$ or $\mathrm{O} + \mathrm{e}^- \rightleftharpoons \mathrm{R}$:

$$i_\mathrm{f} = i_\mathrm{n}\left[-\frac{c_\mathrm{O}^\mathrm{s}}{c_\mathrm{O}^\mathrm{b}}\exp\left\{\frac{-\alpha F}{RT}\eta\right\} + \frac{c_\mathrm{R}^\mathrm{s}}{c_\mathrm{R}^\mathrm{b}}\exp\left\{\frac{(1-\alpha)F}{RT}\eta\right\}\right] \tag{2}$$

$$\frac{1}{i_\mathrm{f}} = \frac{1}{i_\mathrm{kin}} + \frac{1}{i_\mathrm{rem}} + \frac{1}{i_\mathrm{lim}} \tag{3}$$

with

$$i_{kin} = i_n\left(b^{1-\alpha} - b^{-\alpha}\right) \tag{4}$$

$$i_{rem} = (1-b)\, i_\mathrm{lim}^\mathrm{cath} \tag{5}$$

$$i_{lim} = \left(\frac{b-1}{b}\right) i_\mathrm{lim}^\mathrm{an} \tag{6}$$

$$b = \exp\left\{F\eta/RT\right\} \tag{7}$$

$$i_\mathrm{n} = Fk^{0'}\left(c_\mathrm{O}^\mathrm{b}\right)^{1-\alpha}\left(c_\mathrm{R}^\mathrm{b}\right)^{\alpha} \tag{8}$$

$$\eta = E - E_\mathrm{n} \tag{9}$$

$$E_n = \frac{-\Delta G}{nF} \tag{10}$$

$$E^0 = \frac{-\Delta G^0}{nF} \tag{11}$$

If

$$\nu_A A + \nu_B B + \cdots + ne^- \rightleftharpoons \nu_Z Z + \nu_Y Y + \cdots$$

then

$$E_n = E^0 - \frac{RT}{nF}\ln\left\{\frac{a_Z^{\nu_Z} a_Y^{\nu_Y}\cdots}{a_A^{\nu_A} a_B^{\nu_B}\cdots}\right\} \tag{12}$$

or

$$E_n = E^{0'} - \frac{RT}{nF}\ln\left\{\frac{\left(c_Z/c^0\right)^{\nu_Z}\left(c_Y/c^0\right)^{\nu_Y}\cdots}{\left(c_A/c^0\right)^{\nu_A}\left(c_B/c^0\right)^{\nu_B}\cdots}\right\} \tag{13}$$

$$E^{0'} = E^0 - \frac{RT}{nF}\ln\left\{\frac{\gamma_Z^{\nu_Z}\gamma_Y^{\nu_Y}\cdots}{\gamma_A^{\nu_A}\gamma_B^{\nu_B}\cdots}\right\} \tag{14}$$

$$a_\pm = \left(a_+^{\nu_+} a_-^{\nu_-}\right)^{1/(\nu_+ + \nu_-)};\ \gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/(\nu_+ + \nu_-)} \tag{15}$$

[1]Formulas for use at the exam. To be attached the problem sets.

$$\gamma_\pm = \exp\left\{\frac{z_+ z_- \sqrt{\mu/\mu_{DH}}}{1 + (R_c/\beta)}\right\}$$

$$\mu = \frac{1}{2}\sum_i z_i^2 c_i \tag{17}$$

$$\mu_{DH} = \left(2\pi N_A\right)^2\left(2RT\epsilon/F^2\right)^3 \tag{18}$$

$$\mu_{DH}^{aq} = 727\ \mathrm{mmol\ dm^{-3}\ at\ 298\ K} \tag{19}$$

$$\beta = \sqrt{\frac{RT\epsilon}{2F^2\mu}};\quad \beta_{25\,^\circ\mathrm{C}}^{aq} = \frac{9.622\ \mathrm{nm}}{\sqrt{\mu/\ \mathrm{mmol\ dm^{-3}}}} \tag{20}$$

$$j_i(x) = -D_i\frac{dc_i}{dx} \tag{21}$$

$$j_i(x) = -u_i c_i\frac{d\phi}{dx} \tag{22}$$

$$j_i(x) = \left(-\frac{c_i(x) D_i}{RT}\right)\frac{d\tilde{\mu}_i}{dx} = -D_i\frac{dc_i}{dx} - \frac{z_i F}{RT}D_i c_i(x)\frac{d\phi}{dx} \tag{23}$$

$$\tilde{\mu}_i = \mu^0 + RT\ln a_i + z_i F\phi \tag{24}$$

$$z_i F D_i = RT u_i \tag{25}$$

$$j_i = \pm\frac{\nu_i i_i}{nF} \tag{26}$$

$$\kappa = F\sum_i z_i u_i c_i \tag{27}$$

$$u_i = \frac{v_{av}}{\left|\vec{E}\right|} \overset{Stoke}{=} \frac{z_i Q_0}{6\pi\eta R_i} \tag{28}$$

$$R_{disk} = \frac{1}{4\kappa r_{disk}} \tag{29}$$

$$R_{hemi} = \frac{1}{2\pi\kappa}\left[\frac{1}{r_{hemi}} - \frac{1}{r_{RE}}\right] \tag{30}$$

$$R_{trough} = \frac{L}{\kappa A} \tag{31}$$

$$t_j = \frac{i_j}{i} = \frac{z_j u_j c_j}{\sum_i z_i u_i c_i} = \frac{c_j\lambda_j}{\sum_i c_i\lambda_i} \tag{32}$$

$$\Lambda = \frac{\kappa}{c} = \sum_i \nu_i\lambda_i \tag{33}$$

$$\lambda_i = z_i F u_i \tag{34}$$

$$j_i(x) = -D_i\frac{dc_i}{dx} - \frac{z_i F}{RT}D_i c_i(x)\frac{d\phi}{dx} + c_i(x)\, v(x) \tag{35}$$

$$j_i^s = m_i \left(c_i^s - c_i^b\right) \tag{36}$$

Experiment	m_i
RDE	$0.62 D_i^{2/3} \omega^{1/2} \nu^{-1/6}$
hemispherical micro-electrode	D_i / r_{hemi}
disk micro-electrode	$4D_i / (\pi r_{disk})$
thin-layer cell (steady state)	$2D_i / L$
Nernst layer	D_i / δ
macro-electrode	$\sqrt{D_i / (\pi t)}$
growing spherical electrode	$\sqrt{7D_i / (3\pi t)}$

$$\Delta E = (E_{WE} - E_{SHE}) - (E_{RE} - E_{SHE}) \tag{37}$$

$$\Delta G - W \leq 0 \tag{38}$$

$$\Delta\phi = \phi^L - \phi^R = \frac{RT}{F\left(u_+ - u_-\right)} \left(\frac{u_+}{z_+} - \frac{u_-}{z_-}\right) \ln\left\{\frac{c^R}{c^L}\right\} \tag{39}$$

$$\Delta\phi = \phi^{inner} - \phi^{outer} = \frac{RT}{z_i F} \ln\left\{\frac{c_i^{outer}}{c_i^{inner}}\right\} \tag{40}$$

$$i = i_f + \frac{C}{A}\frac{dE}{dt} \tag{41}$$

$$q = -\frac{d\sigma}{dE}; \text{ Lippmann equation} \tag{42}$$

$$\frac{C}{A} = \frac{dq}{dE} = -\frac{d^2\sigma}{dE^2} \tag{43}$$

$$\begin{aligned} \frac{1}{C_S} &= \frac{1}{C_H} + \frac{1}{C_{GC}} \\ &= \frac{x_H}{A\epsilon_H} + \frac{\sqrt{RT/2F^2\epsilon c}}{A\cosh\left\{F\left(E - E_{zc}\right)/2RT\right\}} \end{aligned} \tag{44}$$

$$\theta_i = K c_i \tag{45}$$

$$\frac{1}{\theta_i} = 1 + \frac{1}{B c_i} \tag{46}$$

$$I = \frac{F^2 A v \Gamma_{max}}{4RT} \cosh^{-2}\left\{\frac{F}{2RT}\left(E - E_{peak}\right)\right\} \tag{47}$$

$$\sum_i z_i c_i = 0 \tag{48}$$

$$\vec{E} = -\vec{\nabla}\phi \tag{49}$$

$$\Phi = \oint_S \vec{E} \cdot \vec{n}\, dS = \frac{Q_1 + Q_2 + Q_3 + \ldots}{\epsilon} \tag{50}$$

$$\nabla^2 \phi\left(x, y, z\right) = -\frac{\rho\left(x, y, z\right)}{\epsilon} \tag{51}$$

$$\frac{c_i\left(x\right)}{c_i^b} = \exp\left\{-\frac{z_i F\left[\phi\left(x\right) - \phi_b\right]}{RT}\right\} \tag{52}$$

$$\nabla^2 \phi\left(x, y, z\right) = 0 \tag{53}$$

$$I = \frac{\Delta E}{R} \exp\left(\frac{-t}{RC}\right) \tag{54}$$

$$I = vC + \left[\left(\frac{E_i}{R} - vC\right) \exp\left(\frac{-t}{RC}\right)\right] \tag{55}$$

$$E = h\nu = \frac{hc}{\lambda} \tag{56}$$

$$c = \nu\lambda \tag{57}$$