1\. A) Doolittle equation, $\eta = A e^{B(\frac{1}{f}-1)}$

$$\ln \eta(T) = \ln A + B\left(\frac{1}{f(T)} - 1\right)$$

$$\ln \eta(T_0) = \ln A + B\left(\frac{1}{f(T_0)} - 1\right)$$

$f(T) = f(T_0) + \alpha_f (T - T_0)$

$$\ln[\eta(T)/\eta(T_0)] = B\left[\frac{1}{f(T)} - \frac{1}{f(T_0)}\right] = B\left[\frac{1}{f(T_0)+\alpha_f(T-T_0)} - \frac{1}{f(T_0)}\right]$$

$$= B\left\{\frac{\cancel{f(T_0)} - \cancel{f(T_0)} - \alpha_f(T-T_0)}{f(T_0)[f(T_0)+\alpha_f(T-T_0)]}\right\} = -\frac{[B/f(T_0)]\cdot(T-T_0)}{\frac{f(T_0)}{\alpha_f} + (T-T_0)}$$

$$\therefore \log\frac{\eta(T)}{\eta(T_0)} = -\frac{\frac{B}{2.303 f(T_0)}\cdot(T-T_0)}{\frac{f(T_0)}{\alpha_f} + (T-T_0)} = -\frac{C_1^0 (T-T_0)}{C_2^0 + (T-T_0)}, \quad C_1^0 = \frac{B}{2.303 f(T_0)}, \quad C_2^0 = \frac{f(T_0)}{\alpha_f}$$

Hence, $f(T_1) = f(T_0) + \alpha_f (T_1 - T_0)$

$$C_1^1 = \frac{B}{2.303 f(T_1)} = \frac{B}{2.303[f(T_0)+\alpha_f(T_1-T_0)]} = \frac{B/2.303\cdot f(T_0)}{1 + \frac{\alpha_f(T_1-T_0)}{f(T_0)}} = \frac{C_1^0}{1 + \frac{(T_1-T_0)}{C_2^0}} = \frac{C_1^0 C_2^0}{C_2^0 + (T_1-T_0)}$$

$$C_2^1 = \frac{f(T_1)}{\alpha_f} = \frac{f(T_0) + \alpha_f(T_1-T_0)}{\alpha_f} = \frac{f(T_0)}{\alpha_f} + (T_1 - T_0) = C_2^0 + (T_1 - T_0)$$

$$C_2^0 = C_2^1 + (T_0 - T_1)$$

$$C_1^0 C_2^0 = \frac{B}{2.303\alpha_f} = C_1^1 C_2^1, \quad C_1^0 = \frac{C_1^1 C_2^1}{C_2^0} = \frac{C_1^1 C_2^1}{C_2^1 + T_0 - T_1}$$

B) VFT equation can be written as $\log\frac{\eta(T)}{\eta(T_0)} = B'\left(\frac{1}{T-T_\infty} - \frac{1}{T_0 - T_\infty}\right)$

$$B'\left(\frac{1}{T-T_\infty} - \frac{1}{T_0-T_\infty}\right) = B'\left(\frac{T_0 - \cancel{T_\infty} - T + \cancel{T_\infty}}{(T-T_\infty)(T_0-T_\infty)}\right) =$$

$$= -\frac{B'(T-T_0)}{(T_0-T_\infty)(T-T_\infty)} = -\frac{\frac{B'}{(T_0-T_\infty)}\cdot(T-T_0)}{T - T_\infty + T_0 - T_0} = -\frac{\frac{B'}{(T_0-T_\infty)}(T-T_0)}{(T_0-T_\infty)+(T-T_0)}$$

$$= -\frac{\alpha(T-T_0)}{\beta + (T-T_0)}, \quad \log\frac{\eta(T)}{\eta(T_0)} = -\frac{\alpha(T-T_0)}{\beta+(T-T_0)}$$ which is WLF equation

c) $\log \frac{\eta(255)}{\eta(205)} = -\frac{16.6(50)}{104.4+50} = -5.38$

$$\eta(255) = 10^{12}\,Pa\cdot s \cdot 10^{-5.38} = 4.21\cdot 10^{6}\,Pa\cdot s$$
$$\eta(305) = 10^{12}\,Pa\cdot s \cdot 10^{-8.12} = 7.56\cdot 10^{3}\,Pa\cdot s$$
$$\eta(355) = 10^{12}\,Pa\cdot s \cdot 10^{-9.79} = 1.63\cdot 10^{2}\,Pa\cdot s$$

2. Under isobaric conditions, $\alpha\, dT = \frac{dL_o}{L_o}$, $\alpha \int_{T_o}^{T} dT = \int_{L_o^*}^{L_o} \frac{dL_o}{L_o}$

$\alpha \neq f(T)$

$$\alpha(T-T_o) = \ln \frac{L_o(T)}{L_o^*(T_o)}$$
$$L_o(T) = L_o^*(T_o)\, e^{\alpha(T-T_o)}$$
$$\varepsilon = \frac{L}{L_o} - 1, \quad L = L_o(1+\varepsilon), \quad \left(\frac{\partial L}{\partial T}\right)_{P,\varepsilon} = (1+\varepsilon)\left(\frac{\partial L_o}{\partial T}\right)_{P,\varepsilon}$$
$$= (1+\varepsilon) L_o^*(T_o)\,\alpha\, e^{\alpha(T-T_o)}$$
$$= (1+\varepsilon)\alpha L_o(T) = \alpha L(T)$$

Since $df = \left(\frac{\partial f}{\partial T}\right)_{P,L} dT + \left(\frac{\partial f}{\partial L}\right)_{P,T} dL$

$$\left(\frac{\partial f}{\partial T}\right)_{P,\varepsilon} = \left(\frac{\partial f}{\partial T}\right)_{P,L} + \left(\frac{\partial f}{\partial L}\right)_{P,T} \cdot \underbrace{\left(\frac{\partial L}{\partial T}\right)_{P,\varepsilon}}_{=\ \alpha L(T)}$$

$$\therefore \left(\frac{\partial f}{\partial T}\right)_{P,L} = \left(\frac{\partial f}{\partial T}\right)_{P,\varepsilon} - \alpha L(T)\left(\frac{\partial f}{\partial L}\right)_{P,T} \quad \text{Q.E.D.}$$

3. Equilibrium swelling condition is $\Delta\mu_1 = \Delta\mu_{1,m} + \Delta\mu_{1,e} = 0$

$$\Delta\mu_{1,e} = \left(\frac{\partial \Delta A}{\partial n_1}\right)_{T,P} = \left\{\frac{\partial}{\partial n_1}\left[\frac{3}{2}\frac{\rho RT}{M_s}(\lambda^2 - 1)\right]\right\}_{T,P}$$

isotropic swelling, $\lambda_x = \lambda_y = \lambda_z = \lambda$

Note that $\lambda^3 = 1/\phi_2$ (swell ratio) $= 1 + n_1 \overline{V}_1$

$$\lambda^2 = (1+n_1\overline{V}_1)^{2/3}, \quad \left(\frac{\partial \lambda^2}{\partial n_1}\right)_{T,P} = \frac{2}{3}(1+n_1\overline{V}_1)^{-\frac{1}{3}} \cdot \overline{V}_1 = \frac{2}{3}\phi_2^{1/3}\cdot \overline{V}_1$$

$$\Delta\mu_{1,e} = \frac{3}{2}\frac{\rho RT}{M_S}\cdot\frac{2}{3}\phi_2^{1/3}\bar{V}_1 = \frac{\rho RT}{M_S}\bar{V}_1\phi_2^{1/3}$$

$$\Delta\mu_1 = RT\left[-\cancel{\phi_2} - \frac{1}{2}\phi_2^2 \cdots + \cancel{\phi_2} + \chi_1\phi_2^2\right] + \frac{\rho RT}{M_S}\bar{V}_1\phi_2^{1/3} = 0$$

when $\phi_2 << 1$ (large swell ratio limit)

$$\phi_2^2\left(\chi_1 - \frac{1}{2}\right) + \frac{\rho\bar{V}_1}{M_S}\cdot\phi_2^{1/3} = 0$$

Equilibrium swell at large swelling limit

$$\frac{\rho\bar{V}_1}{M_S} = \left(\frac{1}{2} - \chi_1\right)\phi_2^{5/3},\ \text{hence } G = \frac{\rho RT}{M_S} = \frac{RT}{\bar{V}_1}\left(\frac{1}{2} - \chi_1\right)\phi_2^{5/3}$$

Q.E.D.

4. $$\Delta\bar{S} = \int_{T_{ref}}^{T}\bar{C}_p\, d\ln T = \int_{T_{ref}}^{T}\frac{\bar{C}_p}{T}dT$$

T_1 : Tg of polymer 1 in pure state

T_2 : Tg of " 2 "

$\bar{S}_{total} = X_1\bar{S}_1 + X_2\bar{S}_2$, $\bar{C}_{pi}$ molar heat capacity of "i"

Melt state: $\bar{S}_{melt} = X_1\bar{S}_{1,melt} + X_2\bar{S}_{2,melt}$

$$= X_1\left\{\bar{S}^o_{1,melt} + \int_{T_1}^{T_g}\bar{C}_{p1,melt}\, d\ln T\right\} + X_2\left\{\bar{S}^o_{2,melt} + \int_{T_2}^{T_g}\bar{C}_{p2,melt}\, d\ln T\right\}$$

Glass State: $\bar{S}_{glass} = X_1\bar{S}_{1,glass} + X_2\bar{S}_{2,glass}$

$$= X_1\left\{\bar{S}^o_{1,glass} + \int_{T_1}^{T_g}\bar{C}_{p1,glass}\, d\ln T\right\} + X_2\left\{\bar{S}^o_{2,glass} + \int^{T_g}\bar{C}_{p2,glass}\, d\ln T\right\}$$

$\overline{S}_{melt} = \overline{S}_{glass}$ for each component

$$\overline{S}^o_{1,melt}(T_1) = \overline{S}^o_{1,glass}(T_1)$$

$$\overline{S}^o_{2,melt}(T_2) = \overline{S}^o_{2,glass}(T_2)$$

Also $\overline{S}_{melt}(T_g) = \overline{S}_{glass}(T_g)$

$$X_1 \cancel{\overline{S}^o_{1,melt}} + X_2 \cancel{\overline{S}^o_{2,melt}} + X_1 \int_{T_1}^{T_g} \overline{C}_{p1,melt}\, d\ln T + X_2 \int_{T_2}^{T_g} \overline{C}_{p2,melt}\, d\ln T$$

$$= X_1 \cancel{\overline{S}^o_{1,glass}} + X_2 \cancel{\overline{S}^o_{2,glass}} + X_1 \int_{T_1}^{T_g} \overline{C}_{p1,glass}\, d\ln T + X_2 \int_{T_2}^{T_g} \overline{C}_{p2,glass}\, d\ln T$$

$$X_1 \int_{T_1}^{T_g} (\overline{C}_{p1,melt} - \overline{C}_{p1,glass})\, d\ln T + X_2 \int_{T_2}^{T_g} (\overline{C}_{p2,melt} - \overline{C}_{p2,glass})\, d\ln T = 0$$

$$X_1 \Delta\overline{C}_{p,1} (\ln T_g - \ln T_1) + X_2 \Delta\overline{C}_{p,2} (\ln T_g - \ln T_2) = 0$$

$$n_1 \Delta\overline{C}_{p,1} (\ln T_g - \ln T_1) + n_2 \Delta\overline{C}_{p,2} (\ln T_g - \ln T_2) = 0$$

$$\left(\frac{m_1}{\cancel{M_1}}\right)(\Delta c_{p,1} \cdot \cancel{M_1})(\ln T_g - \ln T_1) + \frac{m_2}{\cancel{M_2}}(\Delta c_{p,2} \cdot \cancel{M_2})(\ln T_g - \ln T_2) = 0$$

specific heat capacity difference

$$w_1 (\Delta c_{p,1})(\ln T_g - \ln T_1) + w_2 (\Delta c_{p,2})(\ln T_g - \ln T_2) = 0$$

weight fraction $= \dfrac{m_1}{m_1 + m_2}$

$$\ln T_g = \frac{w_1 (\Delta c_{p,1}) \ln T_1 + w_2 (\Delta c_{p,2}) \ln T_2}{w_1 \Delta c_{p,1} + w_2 \Delta c_{p,2}}$$

Q.E.D.

B) If $T_1 \approx T_2$ and $\Delta c_{p,1} = \Delta c_{p,2}$

$\ln T_g = w_1 \ln T_1 + w_2 \ln T_2$ since denominator $= 1 = w_1 + w_2$

$\Delta c_{p,1} = \Delta c_{p,2}$

$$w_1 \ln T_1 + w_2 \ln T_2 - (w_1 + w_2) \ln T_g = 0$$

$$w_1 \ln\left(\frac{T_1}{T_g}\right) + w_2 \ln\left(\frac{T_2}{T_g}\right) = 0$$

since $T_1 \approx T_2$, $T_1 \lesssim T_g \lesssim T_2$, $\frac{T_1}{T_g} \lesssim 1$, $\frac{T_2}{T_g} \gtrsim 1$

$\ln\left(\frac{T_1}{T_g}\right) \approx \frac{T_1}{T_g} - 1$, $\ln\left(\frac{T_2}{T_g}\right) \approx \frac{T_2}{T_g} - 1$, $\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \ldots$

$w_1 \frac{T_1}{T_g} - w_1 + w_2 \frac{T_2}{T_g} - w_2 = 0$, $T_g = w_1 T_1 + w_2 T_2$ Q.E.D.