Chem 654, Spring 2003
Problem Set

#7, 04/25/03

Problem Set 7. due 05/05/03

1. A) If the WLF equation with the reference temperature T_o is switched to another reference temparature T_1 whereby it now reads as

$$\log\frac{\eta(T)}{\eta(T_1)} = -\frac{C_1^1(T-T_1)}{C_1^2+T-T_1} \tag{1}$$

then there should exist relationships between C_1^o, C_2^o & T_o and C_1^1, C_2^1 & T_1. Show that

$$C_1^o = \frac{C_1^1 \cdot C_2^1}{C_2^1 + T_o - T_1} \tag{2}$$

and

$$C_1^o \cdot C_2^o = C_1^1 \cdot C_2^1 \tag{3}$$

B) Prove that WLF equation can also be derived from Vogel-Fulcher-Tammann(VFT) equation, commonly found in the physics literature,

$$\log\eta(T) = A' + \frac{B'}{T-T_\infty} \tag{4}$$

where A' and B' are temperature independent constants and T_∞ is a system dependent characteristic temperature.

C) For poly(isobutylene), the following are given if the reference temperature is chosen to be $T_g = 205K$: $C_g^1 = 16.6$~~K~~ & $C_g^2 = 104.4K$. Calculate the viscosity of this polymer at 255K, 305K, and 355K if $\eta(T_g) = 10^{13}$ poise $= 10^{12}$ Pa·s.

2. Prove the following identity for a rubber sample under the assumption that the linear expansion coefficient α is independent of temperature.

$$\left(\frac{\partial f}{\partial T}\right)_{P,L} = \left(\frac{\partial f}{\partial T}\right)_{P,\varepsilon} - \alpha L\left(\frac{\partial f}{\partial L}\right)_{P,T} \tag{5}$$

where

$$\varepsilon \equiv \frac{L-L_o}{L_o} \tag{6}$$

and

$$\alpha \equiv \frac{1}{L_o}\left(\frac{\partial L_o}{\partial T}\right)_P \neq f(T), \text{ i.e., independent of T} \tag{7}$$

such that

$$L_o(T) = L_o^* e^{\alpha(T-T_o)} \quad \text{where } L_o^* = L_o(T_o) \tag{8}$$

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3. Combining the Flory-Huggins theory with the ideal rubber elasticity, the modulus of a highly swollen rubber network can be derived from the chemical potential change of the solvent component for the mixing $\Delta\mu_{1,m}$ and elastic terms $\Delta\mu_{1,e}$. The Flory-Huggins gives the first and the ideal rubber elasticity the second term:

$$\Delta\mu_1 = \Delta\mu_{1,m} + \Delta\mu_{1,e} \qquad (9)$$

where

$$\Delta\mu_{1,m} = RT[\ln(1 - \phi_2) + \phi_2 + \chi_1\phi_2^2] \qquad (10)$$

$$\Delta\mu_{1,e} = \left(\frac{\partial \Delta A}{\partial n_1}\right) \text{, where } \Delta A = -T\Delta S = \frac{1}{2}\frac{\rho RT}{M_s}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (11)$$

Prove that under isotropic equilibrium swelling, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$ and $\lambda^3 = 1/\phi_2 = 1 + n_1\overline{V}_1$, the modulus of highly swollen network, $\phi_2 << 1$, is given by

$$G = \frac{\rho RT}{M_s} = \frac{RT}{\overline{V}_1}\left(\frac{1}{2} - \chi_1\right)\phi_2^{5/3} \qquad (12)$$

4. A) For a compatible blend of polymer 1 and polymer 2, derive the following formula for Tg of the blend,

$$\ln T_g = \frac{w_1(\Delta C_{P,1})\ln T_1 + w_2(\Delta C_{P,2})\ln T_2}{w_1(\Delta C_{P,1}) + w_2(\Delta C_{P,2})} \qquad (13)$$

where w_1 and w_2 are weight fractions, T_1 and T_2 are the glass transition temperatures, and $(\Delta C_{P,1})$ and $(\Delta C_{P,2})$ are the specific heat capacity differences between the melt and glassy states of polymers 1 and 2, respectively. You may assume that the total entropy of the blend is given by

$$\overline{S} = X_1\overline{S}_1 + X_2\overline{S}_2 \qquad (14),$$

and

$$S_{glass} = S_{melt} \qquad (15)$$

B) Also, show that if T_1 and T_2 are close, and $(\Delta C_{P,1}) = (\Delta C_{P,2})$, Eq.(9) reduces to

$$T_g = w_1T_1 + w_2T_2 \qquad (16)$$

Cf. Couchman, *Phys. Lett.* **70A**, 155(1979).