Solutions to

Chem 664	Problem Set #12	Due: December 10, 2003

A. 7.13

B. 7.14

C. 7.17

D. 7.23

E. 7.24

F. 7.36

G. 7.37

Solutions to PS#12

due 12/10/03

A(7.13) (i) Both rubber bands in mechanical equilibrium are stretched by the same tension force, but since the higher temperature rubber band stretches more, it has a higher true stress

(ii) Engineering stress is defined by the ratio of the force to the original cross-section area. force the engineering stress is the same for the two bands

(iii) The length of band A is

$$L_A = \lambda_A L_o \, , \quad L_o = 10\,cm$$
$$_B = \lambda_B L_o$$

$$L_A + L_B = L_o(\lambda_A + \lambda_B) = 80\,cm$$

$$\lambda_A + \lambda_B = 8, \quad \lambda_B = \frac{38}{10} = 3.8$$

$$\lambda_A = 8 - 3.8 = 4.2$$

$$\sigma_A = RT_A\nu\left(\lambda_A - \frac{1}{\lambda_A^2}\right) = RT_B\nu\left(\lambda_B - \frac{1}{\lambda_B^2}\right) = \sigma_B$$

$$T_B = T_A\left(\lambda_A - \frac{1}{\lambda_A^2}\right)\Big/\left(\lambda_B - \frac{1}{\lambda_B^2}\right) = 283K\,\frac{4.2 - \left(\frac{1}{4.2}\right)^2}{3.8 - \left(\frac{1}{3.8}\right)^2}$$
$$= \underline{\underline{314K}}$$

B(7.14) (i) $\sigma = \sigma_{enthalpy} + \sigma_{entropy}$

$$\to T\frac{\partial\sigma}{\partial T} = 303K\frac{(1.5\cdot 10^6)}{30K}\,dyn/cm^2$$
$$\cong 1.5\cdot 10^7\,dyn/cm^2 = 1.52\,10^6\,Pa$$
$$= 1.52\,MPa$$

$$\to (1.65 - 1.52)\cdot 10^7\,\frac{dyn}{cm^2} = 1.3\cdot 10^6\,dyn/cm^2$$
$$= 1.3\cdot 10^5\,Pa$$

$$\sigma_E/\sigma = \frac{1.3}{15.2 + 1.3} \cong 0.079$$
$$\cong 8\%$$

(ii) $$G_s = \frac{\sigma_{entropy}}{\lambda - \lambda^{-2}} = \frac{1.52\,MPa}{2 - \frac{1}{4}} \cong 0.87\,MPa$$

(iii) $$G_s = \nu RT = \frac{\rho}{M_s}RT, \quad M_s = \frac{\rho RT}{G_s} = \frac{1.1\cdot 10^3\,\frac{kg}{m^3}\cdot 8.3\,\frac{J}{mol\cdot K}\cdot 303K}{0.87\cdot 10^6\,N/m^2}$$
$$= 3.2\,kg/mol$$

C(7.17)

$$dA = -SdT - PdV + f\,dL$$
$$= -SdT - PdV + \underbrace{f_x dL_x}_{f_x L_{x0} d\lambda \Leftarrow L_x = \lambda L_{x0}}$$

$$\left(\frac{\partial A}{\partial \lambda}\right)_{T,V} = f_x L_{x0}, \quad \sigma_{xx} = \frac{f_x}{L_x L_y} = \frac{1}{L_{x0} L_y L_z}\left(\frac{\partial A}{\partial \lambda}\right)_{T,V}$$

$L_y = L_{y0}/\sqrt{\lambda}$, $L_z = L_{z0}/\sqrt{\lambda}$ since $L_x L_y L_z = L_{x0} L_{y0} L_{z0}$

$$\therefore \sigma_{xx} = \frac{\sqrt{\lambda}\cdot\sqrt{\lambda}}{L_{x0} L_{y0} L_{z0}}\left(\frac{\partial A}{\partial \lambda}\right)_{T,V} = \frac{\lambda}{V}\left(\frac{\partial A}{\partial \lambda}\right)_{T,V} = \left[\frac{\partial (A/V)}{\partial \ln \lambda}\right]_{T,V}$$

D(7.23) (i)

$N = 100$
$b^3 = 30\,\text{Å}^3$

$$\underset{\text{dry state modulus}}{G(1)} = \frac{kT}{b^3 N} = \frac{1.38\cdot 10^{-23}\,\frac{J}{mol\cdot K}\cdot 298\cdot K}{30\cdot 10^{-30}\,m^3\cdot 10^2}$$
$$\cong 1.38\cdot 10^6\,N/m^2 = 1.38\,MPa$$

(ii) $Q \approx N^{3/8} = (10^2)^{3/8} = 5.6$

(iii) $Q \approx N^{3/5} = 10^{6/5} = 15.8$

(iv) $$G(1/Q) = \frac{kT}{b^3 Q^{2.3}} = \frac{1.38\cdot 10^{-23}\cdot 298}{30\cdot 10^{-30}\cdot (15.8)^{2.3}} \cong 2.4\cdot 10^5\,Pa$$
$$= 0.24\,MPa$$

E(7.24)
(i) $$\Pi_{gel} = -\left(\frac{\partial \Delta A}{\partial V}\right) = -\left[\left(\frac{\partial \Delta A_{mix}}{\partial V}\right) + \left(\frac{\partial \Delta A_{el}}{\partial V}\right)\right]$$

$$\Pi_{chain} \approx \frac{kT}{b^3}\phi^{9/4} \approx -\frac{\partial \Delta A_{mix}}{\partial V}$$

$$\Delta A_{el}/\text{chain} \approx kT\left(\frac{(\lambda R_0)^2}{R_{ref}^2}\right) \approx kT\left(\frac{\phi_0}{\phi}\right)^{5/12}$$

Since $\lambda = (\phi_0/\phi)^{1/3}$ $\quad R_0/R_{ref} = (\phi_0/\phi)^{-1/8}$

$\phi = b^3 N / V$

$\uparrow$ pervaded vol of a network strand

$$\frac{\partial \Delta A_{el}}{\partial V} \approx kT \left(\frac{\phi_0}{b^3 N}\right)^{5/12} \frac{\partial V^{5/12}}{\partial V} \approx kT \left(\frac{\phi_0}{b^3 N}\right)^{5/12} V^{-7/12}$$

$$\approx \frac{kT}{b^3 N} \phi_0^{5/12} \phi^{7/12}$$

$\uparrow$ $V \approx b^3 N / \phi$

$$\Pi_{gel} \approx \frac{kT}{b^3} \phi^{9/4} - \frac{kT}{b^3 N} \phi_0^{5/12} \phi^{7/12}$$

(ii) $\Pi_{gel} < -\frac{\partial \Delta A_{el}}{\partial V} < 0$

Elastic contribution is always larger than Π_{gel}, i.e., elasticity resists swelling

(iii) $\Pi_{gel} = 0 \Rightarrow \phi \approx \phi_0^{1/4} / N^{3/5}$

Equil. swell ratio $Q \approx N^{3/5} / \phi_0^{1/4} = 1/\phi$

At this point no further swelling takes place.

F(7.36) (i) $\eta = \int_{-\infty}^{\infty} t G(t) \, d\ln t \cong 4.4 \cdot 10^7 \ Pa \cdot s$

$$J_{eq} = \frac{1}{\eta^2} \int_{-\infty}^{\infty} t^2 G(t) \, d\ln t \cong 1.6 \cdot 10^{-6} \ Pa^{-1}$$

$$\tau \approx \eta J_e \cong 70 \ s$$

(ii) Max in $tG(t)$ is at $t \cong 60.6 \ s \cong \tau$

$t^2 G(t)$ max is at $t \cong 155 \ s \cong 2 \times \tau$

G(7.37)

(i) Steady state is established in the latter half of the time period, hence

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{20\,Pa}{0.0018\,s^{-1}} \cong 1.1 \cdot 10^{4}\,Pa \cdot s$$

0.18/100s

$$J_e = \frac{\gamma_0}{\sigma} = \frac{0.2}{20\,Pa} = 10^{-2}\,Pa^{-1}$$ where $\gamma_0 = 0.2$ is the extrapolated strain at $t=0$

$$\tau \approx \eta J_e = \frac{\gamma_0}{\dot{\gamma}} \cong 110\,s$$

(ii) $$D \approx \frac{R_g^2}{\tau} \approx \frac{(400\,\text{Å})^2}{110\,s} \simeq 1500\,\text{Å}^2/s = 1.5 \cdot 10^{-13}\,cm^2/s$$