

Chemistry 2850 Practice Test 2 Solutions

1. The entropy of a perfect crystal approaches a universal constant as the temperature approaches absolute zero.
2. ΔG gives the maximum **non- PV** work at constant temperature and pressure.
3. (a) $d(\Delta G^\circ) = \Delta V^\circ dP - \Delta S^\circ dT$
(b) The sign of the change in ΔG° will be the same as the sign of ΔV° .
(c) Increasing ΔG° decreases the equilibrium constant. This would occur if $\Delta V^\circ > 0$, i.e. if the products occupied a larger volume than the reactants. Le Chatelier's principle would predict that an increase in pressure would favor the direction of a reaction which tends to decrease the volume, i.e. decrease the equilibrium constant, so the effect of increasing pressure on the equilibrium constant is consistent with the principle.
- 4.

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P.$$

For an ideal gas, $V = nRT/P$, so we have

$$\alpha = \frac{P}{nRT} \frac{nR}{P} = \frac{1}{T}.$$

5. The equilibrium expression, neglecting factors of the standard concentration, is

$$K = \frac{[\text{tetramer}]}{[\text{dimer}]^2}.$$

Since K is very large, we might guess that the reaction goes more-or-less to completion. However, if you try to do a calculation on this basis, you will find that a significant amount of the original dimer is left at equilibrium, i.e. that the reaction does *not* go to completion. The reason is that the concentrations involved in this problem are relatively small. In these cases, we have to do an initial-change-final table:

	[dimer]/mol L ⁻¹	[tetramer]/mol L ⁻¹
Initial	50×10^{-6}	0
Change	$-2x$	x
Final	$50 \times 10^{-6} - 2x$	x

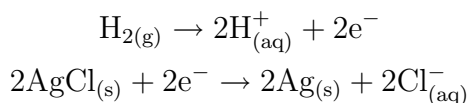
Note that the initial concentration of dimers is $50 \mu\text{mol/L}$ because the solution was made to a *monomer* concentration of $100 \mu\text{mol/L}$.

Our equilibrium expression is then

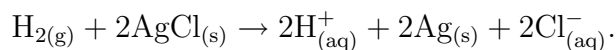
$$\begin{aligned}
 3.3 \times 10^5 &= \frac{x}{(50 \times 10^{-6} - 2x)^2} \\
 \therefore 3.3 \times 10^5 (50 \times 10^{-6} - 2x)^2 &= x. \\
 \therefore 3.3 \times 10^5 (2.5 \times 10^{-9} - 2 \times 10^{-4}x + 4x^2) &= x. \\
 \therefore 8.25 \times 10^{-4} - 66x + 1.32 \times 10^6 x^2 &= x. \\
 \therefore 8.25 \times 10^{-4} - 67x + 1.32 \times 10^6 x^2 &= 0. \\
 \therefore x &= \frac{67 \pm \sqrt{67^2 - 4(8.25 \times 10^{-4})(1.32 \times 10^6)}}{2(1.32 \times 10^6)}.
 \end{aligned}$$

We get two solutions, $x = 3.0 \times 10^{-5}$ and $x = 2.1 \times 10^{-5}$. The first solution is physically meaningless since it would make the final concentration of dimer negative. The correct solution is therefore the second one. The equilibrium concentrations are therefore [tetramer] = $21 \mu\text{mol/L}$ and dimer = $50 \times 10^{-6} - 2(2.1 \times 10^{-5}) = 8 \times 10^{-6} \text{ mol/L} \equiv 8 \mu\text{mol/L}$.

6. The half-reactions are



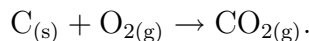
For this cell, $\mathcal{E}^\circ = 0.222\ 33 - 0\ \text{V} = 0.222\ 33\ \text{V}$, and $z = 2$. The overall reaction is



Therefore

$$\begin{aligned}
 \mathcal{E} &= \mathcal{E}^\circ - \frac{RT}{zF} \ln Q \\
 &= \mathcal{E}^\circ - \frac{RT}{zF} \ln \left(\frac{(a_{\text{H}^+})^2 (a_{\text{Cl}^-})^2}{a_{\text{H}_2}} \right) \\
 &= 0.222\ 33\ \text{V} - \frac{(8.314\ 472\ \text{J K}^{-1}\text{mol}^{-1})(298.15\ \text{K})}{2(96\ 485.3383\ \text{C/mol})} \ln \left(\frac{(0.03)^2 (0.004)^2}{1} \right) \\
 &= 0.455\ 28\ \text{V}.
 \end{aligned}$$

7. The formation reaction is



The standard entropy change is

$$\begin{aligned}
 \Delta_f S^\circ &= S^\circ_{(\text{CO}_2)} - (S^\circ_{(\text{C})} + S^\circ_{(\text{O}_2)}) \\
 &= 213.785 - (5.74 + 205.152)\ \text{J K}^{-1}\text{mol}^{-1} \\
 &= 2.89\ \text{J K}^{-1}\text{mol}^{-1}. \\
 \therefore \Delta_f G^\circ &= \Delta_f H^\circ - T\Delta_f S^\circ \\
 &= -393.51\ \text{kJ/mol} - (298.15\ \text{K})(2.89 \times 10^{-3}\ \text{kJ K}^{-1}\text{mol}^{-1}) \\
 &= -394.37\ \text{kJ/mol}.
 \end{aligned}$$

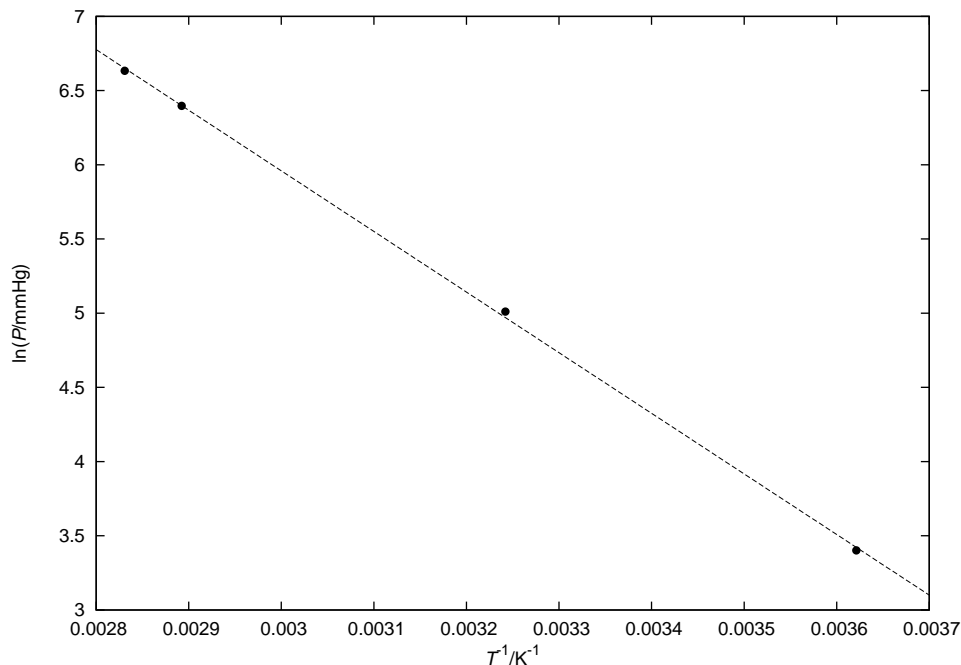


Figure 1: Plot of $\ln P$ vs $1/T$ where P is the vapor pressure of benzene.

8. The process is $l \rightarrow g$ with equilibrium constant

$$K = a_g/a_l = a_g = P/P^\circ.$$

Note that

$$\frac{d(\ln K)}{d(1/T)} = \frac{d(\ln(P/P^\circ))}{d(1/T)} = \frac{d}{d(1/T)} (\ln P - \ln P^\circ) = \frac{d(\ln P)}{d(1/T)} = -\frac{\Delta H^\circ}{R}$$

since P° is a constant. This little derivation just shows that we can plot the logarithm of the pressure directly without going through the intermediate step of calculating the equilibrium constant. Of course, it wouldn't be wrong to calculate the equilibrium constant first, and then plotting $\ln K$ vs $1/T$.

My plot is shown in figure 1. The plot is reasonably linear, with a slope of -4085 K. Therefore

$$\Delta H^\circ = -R(\text{slope}) = -(8.314472 \text{ J K}^{-1}\text{mol}^{-1})(-4085 \text{ K}) = 33.96 \text{ kJ/mol}.$$