

# Physical Chemistry I

## FINAL EXAM SOLUTIONS

Work any 8. Identify the 2 not to be graded!

1. In last year's final, students were asked to derive an expression for the isothermal Joule-Thompson Coefficient that turned out to be very simple:

$$\mu_T = (\partial H / \partial p)_T = V - T(\partial V / \partial T)_p \quad \text{which you may assume for the purposes of this problem.}$$

Using the *full* expression for the Van der Waals gas, show that an excellent approximation to  $\mu_T$  is given by

$$\mu_T = nb - 2an/RT$$

or, for a single mole,

$$\mu_T = b - (2a/RT)$$

(The approximations that reduce the final expression to this are that  $V/(V-nb) \sim 1$  and  $2an^2 \ll nRTV$ , both of which are excellent. And remember the trick to set  $p = \text{stuff}$  so that partials with  $p$  fixed will set the partials of *stuff* to zero.)

$$(p + an^2/V^2)(V - nb) = nRT$$

$$p = nRT/(V-nb) - an^2/V^2$$

$$0 = (\partial p / \partial T)_p = nR/(V-nb) - [nRT/(V-nb)^2](\partial V / \partial T)_p + [2an^2/V^3](\partial V / \partial T)_p$$

$$(\partial V / \partial T)_p = \{ nR/(V-nb) \} / \{ [nRT/(V-nb)^2] - 2an^2/V^3 \}$$

$$T(\partial V / \partial T)_p = \{ nRT/(V-nb) \} / \{ [nRT/(V-nb)^2] - 2an^2/V^3 \}$$

$$V = nb + (V-nb) \quad \text{so}$$

$$V - T(\partial V / \partial T)_p = nb + (V-nb) - T(\partial V / \partial T)_p$$

$$= nb + \{ [(V-nb)nRT/(V-nb)^2 - 2an^2(V-nb)/V^3] - nRT/(V-nb) \} / \{ [nRT/(V-nb)^2] - 2an^2/V^3 \}$$

$$= nb - 2an^2(V-nb)/V^3 / [nRT/(V-nb)^2 - 2an^2/V^3]$$

$$= nb - 2an^2(V-nb)^3/V^3 / [nRT - 2an^2(V-nb)^2/V^3]$$

$$\sim nb - 2an^2 / [nRT - 2an^2/V] \sim nb - 2an^2/nRT = \mathbf{nb - 2an/RT = \mu_T}$$

2. Using that last expression for  $\mu_T$ , obtain  $\Delta H$  for the isothermal compression of a mole of ethane at 298 K from 1 atm to 100 atm. For ethane,  $a = 5.562 \text{ atm L}^2 \text{ mol}^{-1}$  and  $b = 0.06380 \text{ L mol}^{-1}$ .

$$\Delta H \sim \Delta p \times (\partial H / \partial p)_T = \Delta p \times \mu_T = \Delta p \times (b - 2a/RT)$$

$$\Delta H \sim 99 \text{ atm} \times (0.06380 \text{ L} - [2 \times 5.562 \text{ atm L}^2 / \{0.08206 \text{ atm L} / \text{mol K} \times 298 \text{ K}\}])$$

$$\Delta H \sim - 38.9 \text{ atm L} (8.314 \text{ J} / 0.08206 \text{ atm L}) = \mathbf{- 3.94 \text{ kJ}}$$

3. The conductivity of a 0.0312 M solution of a weak base is  $1.53 \times 10^{-4} \text{ S cm}^{-1}$ . If the sum of the limiting ionic conductances of  $\text{BH}^+$  and  $\text{OH}^-$  is  $237.0 \text{ S cm}^2 / \text{mol}$ , what is the value of the base constant,  $K_b$ ?

$$\kappa = \Lambda^\circ c$$

$$\Lambda^\circ = \nu_+ \lambda_+ + \nu_- \lambda_- = 237.0 \text{ S cm}^2 / \text{mol}$$

$$c = \kappa / \Lambda^\circ = 1.53 \times 10^{-4} \text{ S cm}^{-1} / 237.0 \text{ S cm}^2 \text{ mol}^{-1} = 6.45 \times 10^{-7} \text{ mol/mL}$$

$$c = 6.45 \times 10^{-4} \text{ M} = [\text{BH}^+] = [\text{OH}^-]$$

$$[\text{B}] = 0.0312 - c = 0.0306$$

$$K_b = [\text{BH}^+][\text{OH}^-] / [\text{B}] = (6.45 \times 10^{-4})^2 / 0.0306 = \mathbf{1.36 \times 10^{-5}}$$

4. One liter of a 0.1 M solution of substance A mixes *ideally* with 3 liters of a 0.05 M solution of substance B at 25°C. What is  $\Delta_{\text{mix}}S$ ? And  $\Delta_{\text{mix}}H$ ?

Water mixing with water represents no entropy change, but moles of A mixing with moles of B surely does. And we have 0.1 moles of A and 0.15 moles of B for a total of 0.25 moles of solute. That's  $n$ . And the final mole fraction of A is  $X_A = 0.1/0.25 = 0.4$  meaning that  $X_B = 0.6$ .

$$\Delta_{\text{mix}}S = -nR(X_A \ln X_A + X_B \ln X_B) = -\frac{1}{4} \text{ mol } 8.314 \text{ J/mol K } (0.4 \ln 0.4 + 0.6 \ln 0.6)$$

$$\Delta_{\text{mix}}S = \mathbf{+ 1.40 \text{ J/K}}$$

$$\Delta_{\text{mix}}H = \mathbf{0.00}$$
 by definition of *ideal mixture*.

5. In the older literature, pressures are in mm Hg and logarithms are to the base 10. Fortunately, T is still in Kelvins! In such an article, you find the vapor pressure curve of some substance listed as

$$\log_{10}(p) = 7.9741 - (1318.9 / T)$$

Obtain its normal boiling point temperature and  $\Delta_{\text{vap}}H$  there.

First thing first; we ought to convert to natural logarithm via  $\ln(x) = 2.3026 \log(x)$ , so

$$\ln(p) = 18.361 - (3036.9/T)$$

Even without that, the normal boiling point is easy;  $p = 760 \text{ mm Hg}$ . So

$$\begin{aligned} \ln(760) &= 18.361 - (3036.9/T) \\ T &= 3036.9 / [18.361 - \ln(760)] = \mathbf{258.95 \text{ K}} = -14.20^\circ\text{C} \end{aligned}$$

Now oddly enough, we don't have to change to bars or atmospheres to proceed to the enthalpy of vaporization. That's because a conversion factor inside the logarithm just becomes an *additive* term, altering the magnitude of the 18.361 but not changing the slope with respect to  $1/T$ , which, by the Clausius-Clapeyron equation, is  $\Delta_{\text{vap}}H$ .

$$\Delta_{\text{vap}}H/R = -d(\ln p)/d(1/T) = 3036.9$$

$$\Delta_{\text{vap}}H = 8.3145 \text{ J/mol K} \times 3036.9 = \mathbf{25.250 \text{ kJ/mol}}$$

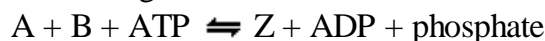
6. A biological cell at 37°C needs to run the hypothetical reaction:



and gets it to be spontaneous by using an enzyme that couples that reaction with



Find the equilibrium constant the cell manages for



(All values pertain to 37°C.)

$$\Delta_{\text{overall}}G^\circ = + 23.8 - 31.9 = - 8.1 \text{ kJ/mol}$$

$$K = e^{-\Delta_{\text{overall}}G^\circ / RT} = e^{8100 \text{ J/mol} / (8.314 \text{ J/mol K} \times 310 \text{ K})} = \mathbf{23.2} > 1$$

7. The following data are for isopropanol (I) in benzene (B) at 25°C.

$X_I$	0	0.059	0.521	0.924	1
$P_I(\text{torr})$	0	12.9	30.5	42.2	44.0
$P_B(\text{torr})$	94.4	86.6	75.3	24.2	0

(a) Does this solution exhibit positive, negative, or no deviation from ideality?

Were the solution ideal, we'd expect  $p_{0.5}$  to be  $\frac{1}{2}$  way from 0 to  $p^*$ , but  $30.5 > 22.0$  and  $75.3 > 47.7$  for  $X_I \sim 0.5$ , hence the deviations are quite **positive**. We wouldn't have expected otherwise from the mixture of an organic (no hydrogen bonding) and an alcohol (lots of hydrogen bonding).

(b) Estimate  $K_{\text{Henry}}$  for both substituents. Are they consistent with your answer to (a)?

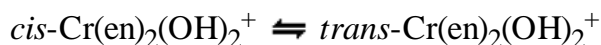
$$p_{\text{solute}} \sim K_H X_{\text{solute}}$$

$$K_H \sim p_{\text{solute}} / X_{\text{solute}}$$

$$K_H(I) \sim 12.9 \text{ torr} / 0.059 = \mathbf{219 \text{ torr}} \gg 44 \text{ torr (positive deviation)}$$

$$K_H(B) \sim 24.2 \text{ torr} / (1-0.924) = \mathbf{318 \text{ torr}} \gg 94.4 \text{ (positive deviation)}$$

8. The reaction



is first order in both directions. At 25°C, the equilibrium constant is 0.16 and the rate constant  $k_1 = 3.3 \times 10^{-4} \text{ s}^{-1}$ . In an experiment starting from the pure *cis* form, how long would it take for **half** the equilibrium amount of the *trans* isomer to be formed?

(Of course  $[cis] + [trans] = A_0$ , the original concentration of *cis*. So there's really only one variable to solve the rate equation for,  $[trans] = x$ , as a function of time.)

Let  $x = [trans]$  and  $A_0$  be  $[cis]_0$ , the initial *cis* concentration, then

$$dx/dt = k_1[cis] - k_{-1}[trans] = k_1(A_0 - x) - k_{-1}x = k_1A_0 - (k_1 + k_{-1})x$$

$$dx / [k_1A_0 - (k_1 + k_{-1})x] = dt \text{ which integrates to}$$

$$-\ln[k_1A_0 - (k_1 + k_{-1})x] \Big|_0^x / (k_1 + k_{-1}) = t \Big|_0^t$$

$$\ln\{ [k_1A_0 - (k_1 + k_{-1})x] / [k_1A_0] \} = - (k_1 + k_{-1})t$$

$$[k_1A_0 - (k_1 + k_{-1})x] = k_1A_0 e^{- (k_1 + k_{-1}) t}$$

or

$$x = A_0 \left[ \frac{k_1}{k_1 + k_{-1}} \right] \left( 1 - e^{- (k_1 + k_{-1}) t} \right)$$

Although we know that  $k_1[cis]_{eq} = k_{-1}[trans]_{eq}$ , or rather  $K = [trans] / [cis] = k_1/k_{-1}$ , we can actually arrive at that by setting  $t$  to infinity (where equilibrium has been established). Then

$$x = [trans]_{eq} = A_0 \left[ \frac{k_1}{k_1 + k_{-1}} \right]$$

$$[cis]_{eq} = A_0 - x = A_0 \left\{ 1 - \frac{k_1}{k_1 + k_{-1}} \right\} = A_0 \left[ \frac{k_{-1}}{k_1 + k_{-1}} \right]$$

$$\text{hence } [trans]_{eq} / [cis]_{eq} = k_1 / k_{-1} = K \text{ } \textit{deja vu}$$

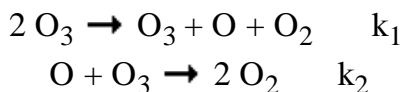
$$\text{So } k_{-1} = k_1 / K = 3.3 \times 10^{-4} \text{ s}^{-1} / 0.16 = 2.1 \times 10^{-3} \text{ s}^{-1} \text{ and } k_1 + k_{-1} = 2.39 \times 10^{-3} \text{ s}^{-1}$$

That's all we need to establish  $t_{1/2}$  where  $x = \frac{1}{2}A_0 \left[ \frac{k_1}{k_1 + k_{-1}} \right]$

$$t_{1/2} = - \left[ 1 / (k_1 + k_{-1}) \right] \ln \left\{ \left[ k_1A_0 - \frac{1}{2}A_0(k_1 + k_{-1}) \frac{k_1}{k_1 + k_{-1}} \right] / k_1A_0 \right\}$$

$$t_{1/2} = - \left[ 1 / (k_1 + k_{-1}) \right] \ln \left( \frac{1}{2} \right) = 0.693 / 2.39 \times 10^{-3} \text{ s}^{-1} = \mathbf{290 \text{ s} < 5 \text{ min.}}$$

9. The following mechanism has been proposed for the thermal decomposition of pure ozone in the gas phase:



Derive the rate equation.

$$-d[\text{O}_3]/dt = k_1 [\text{O}_3]^2 + k_2 [\text{O}] [\text{O}_3]$$

$$d[\text{O}]/dt = k_1 [\text{O}_3]^2 - k_2 [\text{O}]_{ss} [\text{O}_3] \sim 0$$

$$[\text{O}]_{ss} = k_1 [\text{O}_3]^2 / (k_2 [\text{O}_3]) = (k_1 / k_2) [\text{O}_3]$$

$$-d[\text{O}_3]/dt = k_1 [\text{O}_3]^2 + k_2 (k_1/k_2) [\text{O}_3]^2 = 2 k_1 [\text{O}_3]^2$$

since steady state in this mechanism means that every reaction 1 is followed immediately by reaction 2 at the same rate, and each consumes one  $\text{O}_3$ .

10. In Alaska, you put heating elements on your car's engine at night not only to keep the block from cracking in the intense cold but also, perhaps, to keep the battery warm. The battery ads that tout "*cold cranking amps*" do so to encourage buyers in cold climates. What's the deal? How does a lead acid battery's voltage change between  $25^\circ\text{C}$  and, say,  $-25^\circ\text{C}$ ? Bear in mind that a "battery" means a collection of cells in series to add their voltages. In an automobile "battery," there are 6 cells. (Which is why you have to top off the distilled water in each of six little holes. Have you remembered to do that lately?)

In case you don't remember it, an auto battery reacts Pb and  $\text{PbO}_2$  to produce  $\text{PbSO}_4$  from each in sulfuric acid solution. For our purposes, we'll let the acid activity be 1, but in real batteries it's more concentrated.

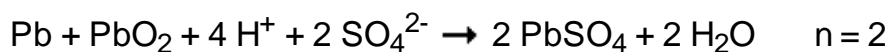
Species	$\Delta_f G^\circ$ (kJ/mol)	$\Delta_f H^\circ$ (kJ/mol)	$S^\circ$ (J/mol K)
Pb	0	0	64.81
$\text{PbO}_2(\text{s})$	-217.33	-277.4	68.6
$\text{PbSO}_4(\text{s})$	-811.24	-981.39	147
$\text{H}^+(\text{aq})$	0	0	0
$\text{SO}_4^{2-}(\text{aq})$	-744.53	-909.27	20.1
$\text{H}_2\text{O}(\text{aq})$	-237.13	-285.83	69.91

$$-nFE^\circ = \Delta G^\circ$$

$$E^\circ = -\Delta G^\circ / nF$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$dE^\circ/dT = -(d\Delta G^\circ/dT) / nF = +\Delta S^\circ / nF$$



$$\Delta S^\circ = 2(147) + 2(69.91) - 64.81 - 68.6 - 4(0) - 2(20.1) = 260 \text{ J/mol K}$$

$$dE^\circ/dT = \Delta S^\circ / nF = 260 \text{ J/mol K} / [2 \times 96,450 \text{ C/mol}] = +1.35 \text{ mV/K}$$

$$\Delta E^\circ \sim (dE^\circ/dT) \Delta T = 1.35 \text{ mV/K} (-50 \text{ K}) = -0.067 \text{ V per cell}$$

$$\Delta E^\circ \sim 6(0.067) = \mathbf{-0.40\ V}$$
 per battery

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