

Columbia University in the City of New York
New York, N.Y. 10027

Chemistry C2407x
Third Exam
December 3, 1998

Total Points: 150

75 Minutes

1998
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Answer Key Exam 3, Chemistry C2407 1998

Problem 1: (35 points) [Oxtoby Problem 7.57] Imagine that 2.00 moles of argon gas, confined by a moveable, frictionless piston in a cylinder at a constant pressure of 1.00 atm and a temperature of 398 K, is cooled to 298 K. Argon is an ideal gas with a molar heat capacity $C_p = (5/2)R$, where $R = 8.314 \text{ J/K}^\circ$.

a)(10 points) Calculate the work done on the system, w . Show all reasoning clearly.

$$w = -\int p_{\text{ex}} dV$$

$$p_{\text{ex}} \text{ is constant} \Rightarrow w = -p_{\text{ex}} \int dV$$

$$w = -p_{\text{ex}}(V_f - V_i)$$

$$V_i = 2R(398)/p_{\text{ex}}$$

$$V_f = 2R(298)/p_{\text{ex}}$$

$$w = -(p_{\text{ex}}/p_{\text{ex}})(2R)(298-398) = 200R$$

$$w = 1662.8 \text{ Joules}$$

b)(10 points) Calculate the heat absorbed by the system, q . Show all reasoning clearly.

$$dq/dT = C_p \text{ at constant pressure (per mole)}$$

$$q = \int C_p dT = C_p \int dT \text{ when } C_p \text{ is constant}$$

$$q = C_p (T_f - T_i) \text{ per mole}$$

$$C_p = [(5/2)R/\text{mole}]$$

$$q = (2 \text{ moles})(5/2)R(298-398)$$

$$q = -4157 \text{ Joules}$$

c)(10 points) Calculate the energy change for the system, ΔE . Show all reasoning clearly.

$$\Delta E = q + w$$

$$w = 1662.8 \text{ joules (part a)}$$

$$q = -4157 \text{ joules (part b)}$$

$$\Delta E = [-4157 + 1662.8] \text{ joules}$$

$$\Delta E = -2494.2 \text{ joules}$$

Alternate approach:

$$E = (3/2)RT/\text{mole for an ideal gas}$$

$$\Delta E = (2 \text{ moles})[(3/2)R(298-398)]$$

$$\Delta E = -300R$$

$$\Delta E = -2494.2 \text{ joules}$$

d)(5 points) Calculate the enthalpy change for the system, ΔH . Show all reasoning clearly.

We showed in class (see free formula sheet) that $\Delta H = q_p$

Since p is constant here, $q = q_p$

From part b, $q = -4157$ joules $= q_p$

$\Delta H = q_p = -4157$ joules

Problem 2: (30 Points) [Much in common with Oxtoby problem 8.33] At the normal boiling point of water, $\Delta H_{\text{vap}} = 40.7$ kJ/mole. In the following, assume that the volume of one mole of liquid water is negligible compared to that of one mole of water vapor, which can be treated as an ideal gas.

a) (5 points) Determine q , the heat absorbed by the system in the reversible conversion of one mole of liquid water to one mole of water vapor at its boiling point. Show all reasoning clearly.

We showed in class (see free formula sheet) that $\Delta H = q_p$

But $\Delta H = \Delta H_{\text{vap}} = 40.7$ kJ/mole

Therefore, $q_p = \Delta H_{\text{vap}} = 40.7$ kJ/mole

b) (10 points) Determine the work, w , done by the system in converting one mole of liquid water to one mole of water vapor at the boiling point. Show all reasoning clearly.

$$w = -\int p_{\text{ex}} dV$$

p_{ex} is constant at one atm $\Rightarrow w = -p_{\text{ex}} \int dV$

$$w = -p_{\text{ex}}(V_f - V_i)$$

$V_i = 0$ (see instructions with problem)

$$w = -p_{\text{ex}}(V_f)$$

$$V_f = R(373)/p_{\text{ex}}$$

$$w = -(p_{\text{ex}}/p_{\text{ex}})(R)(373) = -373 R$$

$$w = -3101 \text{ Joules}$$

c) (5 points) What is ΔE for this process? Show all reasoning clearly.

$$\Delta E = q + w$$

$$w = -3101 \text{ joules (part b)}$$

$$q = +40,700 \text{ joules (part a)}$$

$$\Delta E = [40,700 - 3101] \text{ joules}$$

$$\Delta E = 37,599 \text{ joules}$$

d) (10 points) Determine ΔS for this process. Show all reasoning clearly.

$$\Delta S = \int (1/T) dq_{\text{rev}}$$

But this is an isothermal process ($T = 373$ K)

$$\Delta S = (1/T) \int dq_{\text{rev}}$$

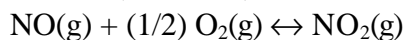
$$\Delta S = (1/T) q_{\text{rev}}$$

$$\text{Here } q_{\text{rev}} = q_p = \Delta H_{\text{vap}} = 40.7 \text{ kJ/mole}$$

$$\Delta S = (40,700 \text{ joules/mole})/373 \text{ K}$$

$$\Delta S = 109 \text{ joules/mole deg}$$

Problem 3: (35 Points) Consider the chemical reaction:



The following table of thermodynamic quantities may be useful:

	$\text{DH}^\circ_f(25^\circ\text{C})$	$\text{S}^\circ(25^\circ\text{C})$	$\text{DG}^\circ_f(25^\circ\text{C})$	$\text{C}_p(25^\circ\text{C})$
	(kJ/mole)	(J/K° mole)	(kJ/mole)	(J/K° mole)
NO	90.25	210.65	86.55	29.84
NO ₂	33.18	239.95	51.29	37.20
O ₂	0	205.03	0	29.36
N ₂	0	191.50	0	29.12

a) (5 points) Determine ΔG° for the reaction forming NO₂ from NO and O₂ at 25°C. Show all reasoning clearly!

$$\Delta G^\circ = \Delta G^\circ_f(\text{NO}_2) - \Delta G^\circ_f(\text{NO}) - (1/2)\Delta G^\circ_f(\text{O}_2)$$

$$\Delta G^\circ = [51,290 - 86,550 - (1/2)(0)] \text{ Joules}$$

$$\Delta G^\circ = -35,260 \text{ Joules}$$

b) (5 points) Determine ΔH° for the reaction forming NO₂ from NO and O₂ at 25°C. Show all reasoning clearly!

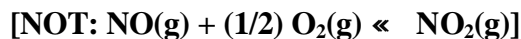
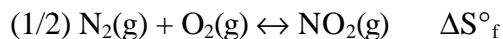
$$\Delta H^\circ = \Delta H^\circ_f(\text{NO}_2) - \Delta H^\circ_f(\text{NO}) - (1/2)\Delta H^\circ_f(\text{O}_2)$$

$$\Delta H^\circ = [33,180 - 90,250 - (1/2)(0)] \text{ Joules}$$

$$\Delta H^\circ = -57,070 \text{ Joules}$$

c) (10 points) What is the entropy of formation, ΔS°_f , for NO₂ (1 atm and 25°C). Show all reasoning clearly.

The relevant reaction for determining an entropy of formation is:



$$\Delta S^\circ_f = S^\circ(25^\circ\text{C}, \text{NO}_2) - S^\circ(25^\circ\text{C}, \text{O}_2) - (1/2)S^\circ(25^\circ\text{C}, \text{N}_2)$$

$$\Delta S^\circ_f = [239.95 - 205.03 - (1/2)(191.50)] \text{ Joules/K}^\circ\text{-mole}$$

$$\Delta S^\circ_f = -60.83 \text{ Joules/K}^\circ\text{-mole}$$

- d) (10 points)** Suppose a mixture of NO, NO₂, and O₂ is contained in a closed vessel at 25°C with the partial pressures of each gas equal to one atm. In which direction (toward NO or toward NO₂) will the reaction

$$\text{NO}(\text{g}) + (1/2) \text{O}_2(\text{g}) \leftrightarrow \text{NO}_2(\text{g})$$
go spontaneously? Show all reasoning clearly.

At least two ways to approach this problem. Can either calculate the equilibrium constant or ΔG for the reaction:

$$\Delta G = \Delta G^\circ + RT \ln(P_{\text{NO}_2}) - RT \ln(P_{\text{NO}}) - (1/2) RT \ln(P_{\text{O}_2})$$

But each partial pressure is 1 atm and $\ln(1) = 0$

So, $\Delta G = \Delta G^\circ$

From part a above: $\Delta G^\circ = -35,260$ Joules

So, $\Delta G = \Delta G^\circ < 0$

Reaction is spontaneous in direction written (toward NO₂)

If calculate equilibrium constant:

$$\ln K_p = -\Delta G^\circ / RT$$

T = 298 K, $-\Delta G^\circ = 35,260$ Joules, R = 8.314 Joules/mole-deg

$$\ln K_p = (35,260)/(8.314)(298) = 14.232$$

$$K_p = e^{14.232} \gg 1$$

When all partial pressures are 1 atm, the ratio

$$P_{\text{NO}_2} / P_{\text{NO}}(P_{\text{O}_2})^{1/2} = 1$$

But this ratio must equal $e^{14.232}$ if the system is to reach equilibrium!

To do this must increase NO₂ and decrease NO and O₂ or shift to right toward NO₂!

- e) (5 points)** If the temperature of an equilibrium mixture of NO, O₂, and NO₂ is increased, in which direction (toward NO or toward NO₂) will the equilibrium shift? Show all reasoning clearly.

$$\ln K_p = -\Delta G^\circ / RT = -\Delta H^\circ / RT + \Delta S^\circ / R$$

T dependence is contained in ΔH° term (assumes ΔH° and ΔS° are roughly independent of T)

However, $\Delta H^\circ = -57,070$ Joules is negative (see part b above)

As increase T, term in $-\Delta H^\circ / RT$ is positive and gets smaller

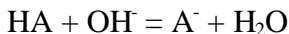
Thus, $\ln K_p$ decreases as T increases, and K_p decreases as T increases

Thus, the equilibrium shifts to the left (toward NO) as T increases.

Problem 4: (50 Points) [A challenging problem that has much in common with Oxtoby problems 10.45, 10.49, 10.54 and 10.55 and the titration recitation exercise.] A solution of an unknown monobasic, weak acid, HA, was titrated with 0.100 M NaOH base. The equivalence point was reached when 36.12 mL of base had been added to the solution. Then

18.06 mL of 0.100 M HCl was added to the solution, the pH measured, and found to be 4.92. NaOH is a strong base and HCl is a strong acid.

a)(10 points) How many moles of the acid HA were contained in the original solution before the titration began? Show all reasoning and calculations clearly!



At the equivalence point: moles base added = initial moles of acid
 Moles base added = (0.100 moles/liter)(36.12 mL)(1 liter/1000 mL)
 Moles of base added = (3.612/1000) moles
 Moles of base added = 3.612 millimoles = 3.612×10^{-3} moles
 Original moles of HA = 3.612×10^{-3} moles

b)(15 points) How many moles of HA are contained in solution after the addition of the HCl and the NaOH? (Use appropriate approximations.) Show all reasoning and calculations clearly!

At the equivalence point have almost all A^- with no HA

HCl converts A^- into HA almost quantitatively

The table below gives the number of millimoles of each substance at various points:

A^-	+	H_3O^+	=	HA	+	H_2O
3.612		≈ 0		≈ 0		(Equiv. Point)
3.612		1.806		≈ 0		(Add HCl)
3.612 - 1.806	≈ 0		1.806			(Reaction)
1.806 + x		x		1.806 - x		(Final)

This is a buffer with large amounts of both HA and A^-

Therefore, expect $x \ll 1.806$ millimoles \Rightarrow

Moles HA = 1.806×10^{-3}

c)(10 points) How many moles of the conjugate base of HA, A^- , are contained in solution after the addition of the HCl and the NaOH? (Use appropriate approximations.) Show all reasoning and calculations clearly!

At the equivalence point have almost all A^- with no HA

HCl converts A^- into HA almost quantitatively

The table below gives the number of millimoles of each substance at various points:

A^-	+	H_3O^+	=	HA	+	H_2O
3.612		≈ 0		≈ 0		(Equiv. Point)
3.612		1.806		≈ 0		(Add HCl)
3.612 - 1.806	≈ 0		1.806			(Reaction)

1.806+x

x

1.806-x

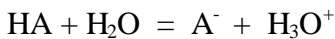
(Final)

This is a buffer with large amounts of both HA and A⁻

Therefore, expect $x \ll 1.806$ millimoles \Rightarrow

Moles A⁻ = 1.806×10^{-3}

d)(15 points) Determine the acid ionization constant K_a for the weak unknown acid HA. Show all reasoning clearly.



$$K_a = [\text{A}^-][\text{H}_3\text{O}^+]/[\text{HA}]$$

Millimoles of A⁻ = millimoles of HA = 1.806 millimoles \Rightarrow

$$[\text{HA}] = [\text{A}^-] = 1.806 \times 10^{-3}/V$$

V = total volume of solution after addition of **both** base and acid

V is unknown in the problem

At these conditions, pH = 4.92 \Rightarrow

$$[\text{H}_3\text{O}^+] = 10^{-4.92}$$

$$K_a = \{1.806 \times 10^{-3}/V\} \{10^{-4.92}\} / \{1.806 \times 10^{-3}/V\}$$

Thus, even though V is unknown in the problem, it drops out \Rightarrow

$$K_a = 10^{-4.92} = 1.202 \times 10^{-5}$$

$$\text{p}K_a = 4.92$$

The End