Chemistry 1A, Fall 2006

Midterm 3, Version A Nov 14, 2006

(90 min, closed book)

- There are 24 Multiple choice questions worth 3.75 points each.
- There are 5 short answer questions.
- For the multiple choice section, fill in the Scantron form AND circle your answer on the exam.
- Put your final answers in the boxes provided. Answers outside the boxes may not be considered in grading.
- The homework and chemquizzes that each question is based upon is listed after the question e.g. [HW 1.13, CQ 7.3]

Question	Page	Points	Score
Question 25 - 27	8	13	
Question 28	9	12	
Question 29	10	25	
Total		50	

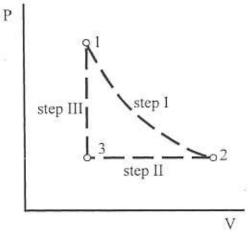
NOTE:1) All thermodynamic variables refer to the system unless otherwise stated.
2) The symbol "↔" will be used to denote potential equilibrium reactions.

For questions 1 – 6 consider the following three step process shown on the PV diagram for one mole of an ideal gas initially at 1 atm pressure and 273K.

Step I: The gas expands isothermally from 22.4 L to 44.8 L (point 1 to 2 on the PV diagram).

Step II: The gas is cooled and compressed back to its original volume (point 2 to 3 on the PV diagram).

Step III: The gas is warmed back to its original pressure and volume (point 3 to point 1 on the PV diagram).



Which is true of the gas for step I? [CQ 23.1]

A) $\Delta T > 0$

B) $\Delta T = 0$

C) $\Delta T < 0$

D) q = 0

E) none of these

2.) What is the temperature (K) of the gas at point 3?

A) 273

B) 425

C) 373

D) 137

E) 57

- 3.) Which is true of the gas for step I? [CQ 23.1]
- A) Work is done on the gas with no heat transfer.
- B) The gas does work with no heat transfer.
- The gas does work and absorbs heat.
- D) Work is done on the gas and it releases heat.
- E) Cannot be determined.

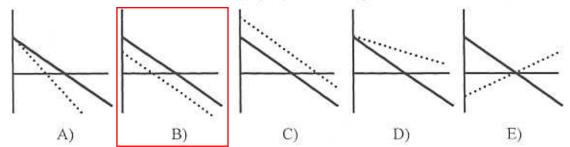
- 4.) Which is true of the gas for step II? [HW 6.5]
- A) Work is done on the gas with no heat transfer.
- B) The gas does work with no heat transfer.
- C) The gas does work and absorbs heat.
- D) Work is done on the gas and it releases heat.
- E) Cannot be determined.
- 5.) Which is true of the gas for step III? [HW 6.11]
- A) Heat is absorbed and no work is done.
- B) Heat is released and no work is done.
- C) Heat is absorbed and work is done on the gas.
- D) Heat is absorbed and the gas does work.
- E) Cannot be determined.
- 6.) Which is the correct arrangement of the three points (1, 2, 3) in the PV diagram from highest to lowest internal energy E? [CQ 23.1 HW 6.5]
- A) 3 > 2 > 1
- B) 3 = 2 > 1
- C) 1 > 3 > 2
- D) 1 = 2 > 3
- E) 1 > 2 = 3

For questions 7 – 16 consider the following table of data for reactions among two unknown diatomic molecules X₂ and Y₂.

Rxn Number	Reaction	K (equilibrium)	Temp (K)
I	$2 \text{ XY } (g) \leftrightarrow X_2 (g) + Y_2 (g)$	377	300
		32	500
		5	1000
II	$X_2(g) \leftrightarrow 2X(g)$	1.0 x 10 ⁻⁵	1000
	120	1.7×10^{-3}	1200
III	$Y_2(g) \leftrightarrow 2 Y(g)$	3.4 x 10 ⁻⁵	1000

- Which reaction(s) in the table are spontaneous at 1000K starting from the standard state? [CQ 31.1 HW 9.15, 9.101]
- A) I
- B) II
- C) III
- D) All three
- E) None
- 8.) Which is true of ΔH° for reaction II?
- A) ΔH° > 0
- B) $\Delta H^{\circ} = 0$
- C) $\Delta H^{\circ} < 0$
- Cannot be determined from the information given.
- Which is true of ΔS° for reaction II? [HW 7.29]
- A) $\Delta S^{\circ} > 0$
- B) $\Delta S^{\circ} = 0$
- C) $\Delta S^{\circ} < 0$
- D) Cannot be determined from the information given.
- 10.) What is the value of ΔG° (kJ) for reaction III at 1000K? [HW 9.15]
- A) 33
- B) -45
- C) 22
- D) 86
- E) -11
- 11.) Which is true of reaction I?
- A) $\Delta H^{\circ} > 0$
- B) $\Delta H^{\circ} = 0$
- C) ΔH° < 0</p>
- Cannot be determined from the information given.

12.) Which is the best plot of ΔG° vs. T for reactions II and III (reaction II is the solid line, reaction III is the dotted line)? [CQ 31.2, 9.101]



- What is the value of K (the equilibrium constant) at 1000K for the reaction: XY (g) ↔ X (g) + Y (g)? [HW 9.25]
- A) 4.1 x 10⁻⁵
- B) 5.5 x 10⁻¹⁰
- C) 7.0 x 10⁻³
- D) 1.2 x 10⁻¹⁰
- E) 2.3 x 10⁻⁶
- 14.) Which is true for reaction II at 1000K when 1 atm X₂ and 1 atm X are present? [HW 9.17, CQ 31.1]
- A) K = 1
- B) $\Delta G^{\circ} = 0$
- C) Q = 1
- D) Q = K
- E) Q < K</p>
- 15.) For which partial pressure of X atoms is $\Delta G = 0$ at 1000K for reaction II when 1.00 atm of X_2 is present [HW 9.17]?
- A) 1.00 atm
- B) 2.00 atm
- C) 1.1 x 10⁵ atm
- D) 3.2 x 10⁻³ atm
- E) 3.4 x 10⁻⁵ atm
- 16.) Which is true for the relative bond enthalpies X-X and Y-Y? [HW 9.39]
- A) X-X > Y-Y
- B) X-X = Y-Y
- C) X-X < Y-Y
- D) Cannot be determined from the information given.

Consider two compounds in their gas phase: ethanol (CH₃CH₂OH) and dimethyl ether (CH₃OCH₃) and their combustion in oxygen to form carbon dioxide and *liquid* water for questions 17 - 27. Unless instructed otherwise, you should use standard enthalpies and Hess's Law to calculate enthalpies of reaction.

Compound	Abbreviation	ΔH° _f (formation) (kJ/mol)	ΔH° _c (combustion) (kJ/mol)
ethanol (g) (CH ₃ CH ₂ OH)	EtOH		-1271
dimethyl ether (g) (CH ₃ OCH ₃)	DiMe		-1328
carbon dioxide (g) (CO ₂)		-394	
water (l) (H ₂ O)		-286	

17.)	What is the coefficient of O2 in the balanced chemical reaction for the combustion
571	of one (1) mole of dimethyl ether?

C) 3

18.) How much heat (kJ) is released when 50 g of ethanol is reacted with excess oxygen [HW 6.47]?

D) 4

E) 5

A) 1271

A) 1

- B) 1382
- C) 1492
- D) 1555
- E) 1645
- 19.) Which of the following is responsible for the sign of ΔH°_c (the enthalpy of combustion) for ethanol?
- A) Breaking C-H and C-C bonds.
- B) Breaking O-H bonds.
- C) Forming C-H bonds and C-C bonds.

B) 2

- D) Forming O-C and O-H bonds.
- E) Condensation of the water formed.
- 20.) Which statement(s) (I IV) below are true regarding ΔH^{*}_i for the gas phase isomerization shown [HW 6.56, 6.61]?

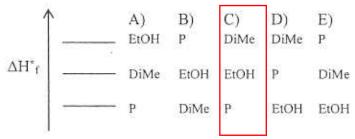
- I $\Delta H^*_i = \Delta H^*_c(CO_2) \Delta H^*_f(EtOH)$
- $\Pi \quad \Delta H^{\circ}_{i} = \Delta H^{\circ}_{f}(DiMe) \Delta H^{\circ}_{f}(EtOH)$
- III $\Delta H^*_i = \Delta H^*_f(CO_2) \Delta H^*_f(H_2O)$
- IV $\Delta H_i^e = \Delta H_c^e(EtOH) \Delta H_c^e(DiMe)$
 - A) I only B) I and II C) II only D) II and IV E) III only

 What is ΔH^{*}; (kJ) for the gas phase isomerization reaction shown? [HW 6.61. CQ24.21

$$CH_3CH_2OH(g) \rightarrow CH_3OCH_3(g)$$

- A) -48

- B) -13 C) +22 D) +57 E) +102
- Which is the arrangement of ethanol (EtOH), dimethyl ether (DiMe) and the combustion products (P) in terms of relative ΔH° [CQ 24.2]?



- 23.) Which combustion would release more energy? [CQ 25.4]
- A) 1.0 mole ethanol in excess O₂?
- B) 1.0 mole of dimethyl ether in excess O₂?
- C) 1.5 mole ethanol in excess O₂.
- D) 0.5 mole dimethyl ether in excess O₂.
- A and B release the same amount of energy.
- 24.) If you consume ethanol at 25°C it reacts with oxygen in your body to form carbon dioxide and water (both of which you exhale). The products you exhale then cool to carbon dioxide gas and liquid water at 25°C. How does this process compare with the combustion of ethanol in the laboratory where the products and reactants are also compared at 25°C?
- A) The laboratory combustion has a larger ΔH.
- B) The reaction in your body has a larger ΔH.
- C) The free energy released by the reaction in your body is larger.
- ΔG and ΔH are the same for the laboratory combustion and in your body.
- E) No comparison of energy functions for different the two processes can be made.

The table from page 6 is repeated here for your exam-taking convenience.

Compound	Abbreviation	ΔH* _f (formation) (kJ/mol)	ΔH° _c (combustion) (kJ/mol)
ethanol (g) (CH ₃ CH ₂ OH)	EtOH		-1271
dimethyl ether (g) (CH ₃ OCH ₃)	DiMe		-1328
carbon dioxide (g) (CO ₂)		-394	
water (1) (H ₂ O)		-286	

$$\Delta H_c^0 = \sum \Delta H_f^0 \text{ (products)} - \sum \Delta H_f^0 \text{ (reactarits)}$$

$$\Delta H_c^0 = 2(CO_2) + 3(H_2O) - (EtOH)$$

$$-1271 = 2(-394) + 3(-286) - EtOH$$

$$375 = -EtOH$$

$$\Delta H^{\circ}_{f} = -375 \frac{kJ}{Mol}$$

= 4726 - 5748

Formula +1
magnitude
$$\Delta H_c^a + 2$$
sign $\Delta H_c^a + 0.5$
units $\Delta H_c^a + 0.5$
inventory of bonds +1

$$\Delta H^{\circ}_{c} = -1022 \frac{kJ}{\text{mol Exch}}$$

27.) (4 pt) Does the value of ΔH*_c for ethanol calculated from average bond enthalpies agree with the value in the table (explain in 20 words or less)?

Explanation:	No	+1
explanation:	reason	
No, bond enthalpies are averages over	1603011	
nany molecules so they seldom agree		
Mary morecules so mey second		
exactly with Hess's Law or experiment.		

- 28.) A 1.00 kg block of iron is dropped into a small copper kettle (mass 300.0 g) containing, and in thermal equilibrium with, 100.0 g of water at 25°C. The maximum final temperature reached in the kettle, water, iron system is 55°C. The heat capacity of iron metal is 0.45 J/gK; copper metal is 0.51 J/gK. The heat capacity of water is 4.184 J/gK [HW 6.15]
- A) (4 pt) How much heat is transferred from the iron?

$$\Delta T = 55 - 25 = 30 \text{ K}$$
 $Q_{H_2O} = mC_P\Delta T = (100.0g)(4.184 \frac{J}{g \cdot K})(30 \text{ K}) = 12552 \text{ J}$
 $Q_{Cu} = mC_P\Delta T = (300.0g)(0.51 \frac{J}{g \cdot K})(30 \text{ K}) = 4590 \text{ J}$

q = 17142 J= 17000 J

B) (4 pt) What percentage of the heat is transferred to the copper kettle?

%q = 27 %

C) (4 pt) What was the initial temperature of the iron?

Ti = 93°C

- 29.) For the following questions, consider the following exothermic reaction taking place in a large sealed container at 298K where the equilibrium constant K = 25. 2 CH₄ (g) + S₈ (s) ↔ 2 CS₂ (l) + 4 H₂S (g)
- A) (4 pt) What is the expression for Q for the reaction? [HW 9.5]

$$Q = \frac{P_{H_2S}^4}{P_{CH_4}^2} = \frac{[H_2S]^4}{[CH_4]^2}$$

either

B) (15 pt) Complete the following table that describes the effect of various changes on an equilibrium mixture of the reaction initially at 298K. K_i is the equilibrium constant before the change occurs. [HW 9.72, 9.73, 9.75, 9.109, CQ 30.1, 30.2, 30.31

Change	Q vs. K _i	Shift toward	Change in K
	(Circle one)		
Increase pressure of H ₂ S	$Q > K_i$	Products	Increase
	$Q = K_i$	Reactants	Decrease
	$Q \leq K_i$	No Change	No Change
Reduce volume	$Q > K_i$	Products	Increase
	$Q = K_i$	Reactants	Decrease
	$Q \leq K_i$	No Change	No Change
Increase total pressure by	$Q > K_i$	Products	Increase
adding Ar (g)	$Q = K_i$	Reactants	Decrease
	$Q \le K_i$	No Change	No Change
Add S ₈ (s)	$Q > K_i$	Products	Increase
	$Q = K_i$	Reactants	Decrease
	$Q \leq K_i$	No Change	No Change
Increase temperature	$Q > K_i$	Products	Increase
	$Q = K_i$	Reactants	Decrease
	$Q \le K_i$	No Change	No Change

C) (6 pt) What is the equilibrium pressure of H₂S at 298 K if at equilibrium the pressure of CH₄ is 5.43 atm and 10 g of S₈ and 15 ml of CS₂ are present? [HW 9.29]

$$\frac{P_{H_2S}^4}{P_{CH_0}^2} = 25$$
 $P_{H_2S}^4 = 25(5.43 \text{ atm})^2 = 5.21 \text{ atm}$ $P = 5.21 \text{ atm}$

Quantum:

$$E = hv$$

$$\lambda v = c$$

$$\lambda_{deBroglie} = h / p = h / mv$$

$$E_{kin}$$
 (e-) = $hv - \Phi = hv - hv_0$

$$E_n = -\frac{Z^2}{n^2} R_{\infty}$$

$$\Delta x \Delta p \sim h$$

$$p = mv$$

Particle in a box (1-D Quantum):

$$E_n = h^2 n^2 / 8mL^2$$
; $n = 1, 2, 3...$

Vibrational:

$$E_v = (v + \frac{1}{2}) hA/2\pi; A = (k/m)^{\frac{1}{2}}$$

Rotational:

$$E_n = n(n + 1) hB$$
; $B = h/8\pi^2 I$; $I = 2mr^2$

$$m = m_A m_B / (m_A + m_B)$$

Ideal Gas:

$$PV = nRT$$

$$E_{\rm kin} = \frac{3}{2} \, RT$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Constants:

$$N_0 = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$R_{\infty} = 2.179874 \times 10^{-18} J$$

$$R_{\infty} = 3.28984 \times 10^{15} \text{ Hz}$$

$$k = 1.38066 \times 10^{-23} \text{ J K}^{-1}$$

$$h = 6.62608 \times 10^{-34} \text{ J s}$$

$$m_e = 9.101939 \times 10^{-31} \text{ kg}$$

$$c = 2.99792 \times 10^8 \text{ m s}^{-1}$$

$$T(K) = T(C) + 273.15$$

$$1 V = 1 J / C$$

Gas Constant:

$$R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$R = 8.20578 \times 10^{-2} L atm K^{-1} mol^{-1}$$

$$1 \text{ nm} = 10^{-9} \text{ m}$$

$$1 \text{ kJ} = 1000 \text{ J}$$

1 atm = 760 mm Hg = 760 torr
$$\approx$$
 1 bar

$$1 L atm \approx 100 J$$

Thermodynamics:

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

$$\Delta H^{\circ} = \sum \Delta H^{\circ}_{f} (products) - \sum \Delta H^{\circ}_{f} (reactants)$$

$$\Delta S^{\circ} = \sum S^{\circ} \text{ (products)} - \sum S^{\circ} \text{ (reactants)}$$

$$\Delta G^{\circ} = \sum \Delta G^{\circ}_{f} (products) - \sum \Delta G^{\circ}_{f} (reactants)$$

$$S = k_B ln W$$

$$\Delta S = q_{rev}/T$$

$$\Delta E = q + w$$

$$w = -P_{ext}\Delta V$$

$$Q = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$
 At equilibrium, $Q = K$

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$G = G^{\circ} + RTln(a)$$
; $a = activity = \gamma P/P^{\circ} \text{ or } \gamma[A]/[A]^{\circ}$

$$\Delta G^{\circ} = - RT \ln K$$

$$\Delta G^{\circ} = - nF\Delta C^{\circ}$$

$$\Delta \varepsilon = \Delta \varepsilon^{\circ} - (RT/nF) \ln Q$$

$$\ln K = -\frac{\Delta H^{\circ}}{R} \frac{1}{T} + \frac{\Delta S^{\circ}}{R}$$

$$\Delta T = ik_{b,f}m$$

$$\Pi = iMRT$$

$$P_{total} = P_A + P_B = X_A P_A^{\circ} + X_B P_B^{\circ}$$

Acid Base:

$$pH = -\log[H_3O^+]$$

$$pX = - \log X$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Kinetics:

$$[A]_t = [A]_0 e^{-kt}$$

$$ln[A]_t = ln[A]_0 - kt$$

$$t_{1/2} = \ln 2/k$$

$$1/[A]_t = 1/[A]_0 + kt$$

$$k = A e^{(-Ea/RT)}$$

$$ln(k_1/k_2) = E_a/R (1/T_2 - 1/T_1)$$

$$t_{1/2} = 1/[A]_0 k$$

$$t_{1/2} = [A]_0/kt$$