

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

Chemistry C2407x
Third Exam
December 2, 1999

Total Points: 150

1999
George Flynn
75 Minutes

Answer Key

All questions are NOT weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided and sign where indicated. Tear off this sheet and pass it to the right for the proctors to pick up.

Print your last name:

Print your first name:

Signature: _____

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Do not write anything else on this page. Answer the questions in the spaces provided on the following pages.

1a

3a

1b

3b

1c

3c

1d

3d

1e

4a

2a

4b

2b

4c

2c

4d

2d

4e

2e

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Problem 1: (35 points) [Oxtoby problem 8.17] 4.00 moles of hydrogen gas, H_2 , ($C_p = 28.8 \text{ J/K-mole}$) is expanded reversibly and isothermally at 400 K from an initial volume of 12.0 L to a final volume of 30.0 L.

a) (5 points) Calculate the change in energy E for the gas. Show all reasoning clearly.

Treat hydrogen as an ideal gas.

Change is carried out isothermally, $T = \text{constant}$

E for an ideal gas depends only on temperature

Therefore, $\Delta E = 0$, since T does not change

b) (5 points) Calculate the change in enthalpy H for the gas. Show all reasoning clearly.

$$\Delta H = \Delta E + \Delta(PV)$$

But $PV = nRT$, with n , R , and T constant

Therefore, $\Delta(PV) = \Delta(nRT) = 0$

$\Delta E = 0$ (part a).

$$\Delta H = 0 + 0 = 0$$

c) (10 points) Calculate w , the work done on the gas for this process. Show all reasoning clearly.

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

However, process is carried out reversibly, so

$$p_{\text{ext}} = p = nRT/V$$

$$w = - \int p dV = - \int (nRT/V) dV$$

Since n , R , T are constant, $w = - nRT \int (dV/V)$

$$w = -nRT \ln(V_f/V_i)$$

$n = 4$ moles, $R = 8.314 \text{ Joules/mole-deg}$, $T = 400 \text{ deg}$,

$$V_f = 30 \text{ L}, V_i = 12 \text{ L}$$

$$w = -(4)(8.314)(400) \ln(30/12)$$

$$w = - 12,189 \text{ Joules}$$

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d) (5 points) Calculate q , the heat absorbed by the gas for this process. Show all reasoning clearly.

$$\Delta E = q + w$$

However, $\Delta E = 0$ (part a)

Thus, $q = -w$

From part c, $-w = 12,189$ Joules

$q = 12,189$ Joules

e) (10 points) Calculate the change in entropy ΔS for the gas. Show all reasoning clearly.

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

But process is isothermal, $T = \text{constant}$, so

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

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

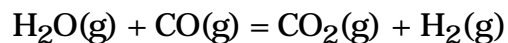
From part d, $q_{\text{rev}} = 12,189$ Joules and $T = 400$ K is given

$$\Delta S = (12,189 \text{ Joules}/400 \text{ deg})$$

$$\Delta S = 30.47 \text{ Joules/deg}$$

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Problem 2: (35 points) Consider the very important chemical transformation (one at the heart of the alternate fuels industry):



and the data:

	$\Delta H_f^\circ(25^\circ\text{C})$ (kJ/mole)	$S^\circ(25^\circ\text{C})$ (J/K $^\circ$ mole)	$\Delta G_f^\circ(25^\circ\text{C})$ (kJ/mole)	$C_p(25^\circ\text{C})$ (J/K $^\circ$ mole)
CO(g)	-110.5	197.6	-137.2	29.14
CO ₂ (g)	-393.5	213.6	-394.4	37.11
H ₂ O(g)	-241.8		-228.6	35.58
H ₂ (g)		130.6		28.82

a) (5 points) Calculate H°_{298} for this reaction. Show all reasoning clearly.

$$\Delta H^\circ_{298} = \Delta H_f^\circ(\text{CO}_2) + \Delta H_f^\circ(\text{H}_2) - \Delta H_f^\circ(\text{CO}) - \Delta H_f^\circ(\text{H}_2\text{O})$$

$$\Delta H_f^\circ(\text{H}_2) = 0 \text{ by definition}$$

$$\Delta H^\circ_{298} = (-393.5) + (0) - (-110.5) - (-241.8) \text{ kJ}$$

$$\Delta H^\circ_{298} = -41.2 \text{ kJoules}$$

b) (5 points) Calculate G°_{298} for this reaction. Show all reasoning clearly.

$$\Delta G^\circ_{298} = \Delta G_f^\circ(\text{CO}_2) + \Delta G_f^\circ(\text{H}_2) - \Delta G_f^\circ(\text{CO}) - \Delta G_f^\circ(\text{H}_2\text{O})$$

$$\Delta G_f^\circ(\text{H}_2) = 0 \text{ by definition}$$

$$\Delta G^\circ_{298} = (-394.4) + (0) - (-137.2) - (-228.6) \text{ kJ}$$

$$\Delta G^\circ_{298} = -28.6 \text{ kJoules}$$

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c) (5 points) Calculate S°_{298} for this reaction. Show all reasoning clearly.

$$\Delta G^{\circ}_{298} = \Delta H^{\circ}_{298} - T\Delta S^{\circ}_{298}$$

$$(\Delta G^{\circ}_{298} - \Delta H^{\circ}_{298})/T = -\Delta S^{\circ}_{298}$$

$$\Delta S^{\circ}_{298} = (\Delta H^{\circ}_{298} - \Delta G^{\circ}_{298})/T$$

ΔH°_{298} from part a and ΔG°_{298} from part b

$$\Delta S^{\circ}_{298} = [-41.2 - (-28.6)]/298 \text{ kJoules/deg}$$

$$\Delta S^{\circ}_{298} = -42.3 \text{ Joules/deg}$$

d) (10 points) Assuming all the gases involved in this reaction are ideal gases, calculate E°_{298} for this reaction. Show all reasoning clearly.

$$\Delta H^{\circ}_{298} = \Delta E^{\circ}_{298} + \Delta(PV)$$

But, $\Delta(PV) = \Delta(nRT)$, with R const and T = 298 K also const.

So $\Delta(PV) = RT\Delta(n)$, where Δn is the change in the number of moles of gas resulting from reaction.

$$\Delta n = 1+1-1-1 = 0$$

So $\Delta(PV) = 0$ and

$$\Delta H^{\circ}_{298} = \Delta E^{\circ}_{298}$$

$$\Delta E^{\circ}_{298} = \Delta H^{\circ}_{298} = -41.2 \text{ kJoules (from part a)}$$

e) (10 points) Compute the absolute entropy [S°_{298}] for $H_2O(g)$ at 298 K. Show all reasoning clearly.

$\Delta S^{\circ} = -42.3 \text{ Joules/deg}$ from part c

$$\text{But, } \Delta S^{\circ} = S^{\circ}_{298}(CO_2) + S^{\circ}_{298}(H_2) - S^{\circ}_{298}(CO) - S^{\circ}_{298}(H_2O)$$

All S°_{298} given except for $S^{\circ}_{298}(H_2O)$

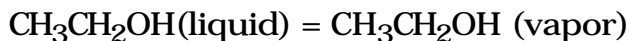
$$-42.3 \text{ Joules/deg} = 213.6 + 130.6 - 197.6 - S^{\circ}_{298}(H_2O)$$

$$42.3 \text{ Joules/deg} + 213.6 + 130.6 - 197.6 = S^{\circ}_{298}(H_2O)$$

$$S^{\circ}_{298}(H_2O) = 188.9 \text{ Joules/deg}$$

Print your name here:

Problem 3: (30 Points) The conversion of liquid ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, to ethanol vapor may be thought of as a chemical reaction carried out at a specific temperature T :



The following thermodynamic data for liquid and gaseous ethanol may be useful in answering the following questions:

	$\Delta H_f^\circ(25^\circ\text{C})$ (kJ/mole)	$S^\circ(25^\circ\text{C})$ (J/K $^\circ$ mole)	$\Delta G_f^\circ(25^\circ\text{C})$ (kJ/mole)	$C_p(25^\circ\text{C})$ (J/K $^\circ$ mole)
$\text{CH}_3\text{CH}_2\text{OH}(\text{g})$	-235.10	282.59	-168.57	65.44
$\text{CH}_3\text{CH}_2\text{OH}(\text{l})$	-277.69	160.7	-174.89	111.46

- a) (5 points) Calculate ΔH for the conversion of one mole of ethanol liquid to ethanol vapor at a pressure of one atmosphere and $T=25^\circ\text{C}$. Show all reasoning clearly.

$$\Delta H = \Delta H^\circ = \Delta H_f^\circ(\text{CH}_3\text{CH}_2\text{OH}(\text{g})) - \Delta H_f^\circ(\text{CH}_3\text{CH}_2\text{OH}(\text{l}))$$

$$\Delta H = -235.10 - (-277.69) \text{ kJoules}$$

$$\Delta H = 42.59 \text{ kJoules}$$

- b) (5 points) Calculate ΔS for the conversion of one mole of ethanol liquid to ethanol vapor at a pressure of one atmosphere and $T=25^\circ\text{C}$. Show all reasoning clearly.

$$\Delta S = \Delta S^\circ = S_{298}^\circ(\text{CH}_3\text{CH}_2\text{OH}(\text{g})) - S_{298}^\circ(\text{CH}_3\text{CH}_2\text{OH}(\text{l}))$$

$$\Delta S = 282.59 - 160.7 \text{ Joules/deg}$$

$$\Delta S = 121.89 \text{ Joules/deg}$$

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c) (5 points) Assuming that both S and H are independent of temperature, calculate the normal boiling point temperature for ethanol. Show all reasoning clearly.

$$\text{At } T_{\text{boiling}}, \Delta G^\circ = \Delta H^\circ - T_B \Delta S^\circ = 0$$

$$\Delta H^\circ = T_B \Delta S^\circ$$

$$T_B = \Delta H^\circ / \Delta S^\circ$$

ΔH° from part a and ΔS° from part b

$$T_B = 42,590 \text{ Joules} / (121.89 \text{ Joules/deg})$$

$$T_B = 349.4 \text{ K}$$

d) (15 points) If the chemical potential (Free Energy per mole) of liquid ethanol is independent of pressure, [$\mu_{\text{liq}}(T,p) = \mu_{\text{liq}}^\circ(T)$, all pressures] and the chemical potential of ethanol vapor is that of an ideal gas, [$\mu_{\text{vap}}(T,p) = \mu_{\text{vap}}^\circ(T) + RT \ln(p_{\text{vap}})$, where p_{vap} is the pressure of the gaseous ethanol], what is the pressure of ethanol vapor when ethanol vapor is in equilibrium with ethanol liquid at 298 K? Show all reasoning clearly.

ΔG for this process is the same as $\Delta\mu$ since μ is simply G for one mole of substance.

$$\Delta G = \mu_{\text{vap}}(T,p) - \mu_{\text{liq}}(T,p)$$

$$\mu_{\text{vap}}(T,p) - \mu_{\text{liq}}(T,p) = \mu_{\text{vap}}^\circ(T) + RT \ln(p_{\text{vap}}) - \mu_{\text{liq}}^\circ(T)$$

$$\Delta G = \mu_{\text{vap}}^\circ(T) - \mu_{\text{liq}}^\circ(T) + RT \ln(p_{\text{vap}})$$

$$\mu_{\text{vap}}^\circ(T=298) - \mu_{\text{liq}}^\circ(T=298) = \Delta G_{298}^\circ$$

$$\Delta G = \Delta G_{298}^\circ + RT \ln(p_{\text{vap}})$$

But, at equilibrium, $\Delta G = 0$ and $p_{\text{vap}} = p_{\text{eq}}$

$$\text{So } \Delta G_{298}^\circ = -RT \ln(p_{\text{eq}})$$

$$\Delta G_{298}^\circ = -168.57 - (-174.89) \text{ kJoules}$$

$$\Delta G_{298}^\circ = +6.32 \text{ kJoules}$$

$$\ln(p_{\text{eq}}) = -6320 / (8.314) (298)$$

$$p_{\text{eq}} = 0.078 \text{ atm (59.3 Torr)}$$

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Problem 4: (50 points) [A sibling of Oxtoby, 8.19] Water can be supercooled reversibly below its freezing point of 0° C to -10° C.

Supercooled water can also be warmed reversibly from -10° C to 0° C. Once supercooled, however, a slight mechanical shock is sufficient to convert supercooled liquid water to solid ice **irreversibly** and **isothermally** at -10° C. The molar enthalpy of fusion for converting solid ice to liquid water at -10° C is 5649 joules/mole while the molar enthalpy of fusion for converting solid ice to liquid water at 0° C is 6025 joules/mole. The molar heat capacity of ice (constant pressure, C_p , independent of temperature) is 37.7 joules/mole-deg while the molar heat capacity of water (constant pressure, C_p , independent of temperature) is 75.3 joules/mole-deg. All of the following manipulations are carried out at a constant pressure of 1 atm.

a) (10 points) Calculate the entropy change when one mole of liquid water, initially at -10° C, is warmed reversibly to 0° C. Show all reasoning clearly.

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

$$dq_{\text{rev}} = C_p dT$$

$$\Delta S = \int (C_p/T) dT$$

C_p = constant pressure heat capacity of liquid water

C_p = constant independent of T (given)

$$\Delta S = C_p \int (dT/T)$$

$$\Delta S = C_p \ln(T_f/T_i)$$

$C_p = 75.3$ joules/mole-deg, $T_f = 273$, $T_i = 263$ (given)

$$\Delta S = [75.3 \text{ joules/mole-deg}] \ln(273/263)$$

$$\Delta S = [75.3 \text{ joules/mole-deg}] (3.73) 10^{\circ}$$

$$\Delta S = 2.81 \text{ joules/mole-deg}$$

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b) (10 points) Calculate the entropy change when one mole of liquid water initially at 0° C is converted isothermally to ice at 0° C. (In case you have forgotten (!!), 0° C is the melting point of ice, defined to be the temperature at which water and ice are in equilibrium with each other.) Show all reasoning clearly.

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

Isothermal process, T = constant

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

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

Here $q_{\text{rev}} = -\Delta H_{\text{fusion}}$

T = 273 (Normal melting point of ice) (given)

$$\Delta H_{\text{fusion}} = 6025 \text{ joules/mole}$$

$$\Delta S = [-6025 \text{ joules/mole}]/273 \text{ deg}$$

$$\Delta S = -22.07 \text{ joules/mole-deg}$$

c) (10 points) Calculate the entropy change when one mole of ice initially at 0° C is cooled reversibly to -10° C. Show all reasoning clearly.

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

$$dq_{\text{rev}} = C_p dT$$

$$\Delta S = \int (C_p/T) dT$$

C_p = constant pressure heat capacity of solid water (ice)

C_p = constant independent of T (given)

$$\Delta S = C_p \int (dT/T)$$

$$\Delta S = C_p \ln(T_f/T_i)$$

$C_p = 37.7 \text{ joules/mole-deg}$, $T_f = 263$, $T_i = 273$ (given)

$$\Delta S = [37.7 \text{ joules/mole-deg}] \ln(263/273)$$

$$\Delta S = [37.7 \text{ joules/mole-deg}] (-3.73) 10^{-2}$$

$$\Delta S = -1.41 \text{ joules/mole-deg}$$

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d) (10 points) Calculate the entropy change when one mole of liquid water at -10°C is converted isothermally and irreversibly to ice at -10°C . Show all reasoning clearly.

The irreversible path $\text{H}_2\text{O}(\text{liq}, -10^{\circ}) \rightarrow \text{H}_2\text{O}(\text{solid}, -10^{\circ})$
has the same initial and final states as the reversible path
 $\text{H}_2\text{O}(\text{liq}, -10^{\circ}) \rightarrow \text{H}_2\text{O}(\text{liq}, 0^{\circ}) \rightarrow$
 $\text{H}_2\text{O}(\text{solid}, 0^{\circ}) \rightarrow \text{H}_2\text{O}(\text{solid}, -10^{\circ})$

Thus, these two paths must have the same ΔS since S is a state function.

ΔS for the reversible path is the sum of the three ΔS values calculated in parts (a), (b), and (c) above.

$$\Delta S = [2.81 + (-22.07) + (-1.41)] \text{ joules/mole-deg}$$

$$\Delta S = (-20.67) \text{ joules/mole-deg}$$

e) (10 points) Calculate the change in free energy (ΔG) when one mole of liquid water at -10°C is converted isothermally and irreversibly to ice at -10°C . Show all reasoning clearly.

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

Isothermal process has $T = \text{constant}$, so

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

$$T = 263, \Delta H_{\text{fusion}} = 5649 \text{ joules (given)}$$

$\Delta H = -5649 \text{ joules}$ (liquid to solid is opposite direction from fusion)

$$\Delta G = -5649 \text{ joules/mole} - (263 \text{ deg})(-20.67 \text{ joules/mole-deg})$$

$$\Delta G = -5649 \text{ joules/mole} + (5436 \text{ joules/mole})$$

$$\Delta G = -212 \text{ joules/mole}$$

The End