

CH353 – Physical Chemistry I
Spring 2013, Unique 52575

Exam 2 – February 15, 2013

Name: Kay

Always assume ideal gas unless directed otherwise.

You may use any material that does not have a heartbeat and does not connect to the internet or cellular network.

Honor Code:

“The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.”

I certify that the work on this exam is entirely my own.

Signature

Date

Chemistry Reference Sheet

		1A		2A		3-10										11B		12		13A		14A		15A		16A		17A		18																																																									
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71																	
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H Hydrogen 1.01	He Helium 4.00	Li Lithium 6.94	Be Beryllium 9.01	B Boron 10.81	C Carbon 12.01	N Nitrogen 14.01	O Oxygen 16.00	F Fluorine 18.00	Ne Neon 20.18	Na Sodium 22.99	Mg Magnesium 24.31	Al Aluminum 26.98	Si Silicon 28.09	P Phosphorus 30.97	S Sulfur 32.07	Cl Chlorine 35.45	Ar Argon 39.95	K Potassium 39.10	Ca Calcium 40.08	Sc Scandium 44.96	Ti Titanium 47.87	V Vanadium 50.94	Cr Chromium 52.00	Mn Manganese 54.94	Fe Iron 55.85	Co Cobalt 58.93	Ni Nickel 58.69	Cu Copper 63.55	Zn Zinc 65.39	Ga Gallium 69.72	Ge Germanium 72.61	As Arsenic 74.92	Se Selenium 78.96	Br Bromine 79.90	Kr Krypton 83.80	Rb Rubidium 85.47	Sr Strontium 87.62	Y Yttrium 88.91	Zr Zirconium 91.22	Nb Niobium 92.91	Mo Molybdenum 95.94	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 102.91	Pd Palladium 106.42	Ag Silver 107.87	Cd Cadmium 112.41	In Indium 114.82	Sn Tin 118.71	Sb Antimony 121.76	Te Tellurium 127.60	I Iodine 126.90	Xe Xenon 131.29	Cs Cesium 132.91	Ba Barium 137.33	La Lanthanum 138.91	Hf Hafnium 178.49	Ta Tantalum 180.95	W Tungsten 183.84	Re Rhenium 186.21	Os Osmium 190.23	Pt Platinum 195.08	Au Gold 196.97	Hg Mercury 200.59	Tl Thallium 204.38	Pb Lead 207.2	Bi Bismuth 208.98	Po Polonium (209)	At Astatine (210)	Rn Radon (222)	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Th Thorium 232.04	Pa Protactinium 231.04	U Uranium 238.03	Np Neptunium (237)	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (262)

Key

11 — Atomic number
 Na — Element symbol
 Sodium — Element name
 22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

1. (15 points) Determine if the following statements are true or false.

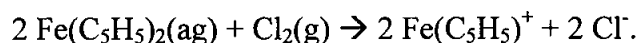
a. True ~~False~~ When comparing two possible paths for isothermal expansion, the system will do more work on the surroundings (i.e. greater negative value of w) along the path that has the lowest amount of heat is transferred between system and surroundings.

b. True ~~False~~ All adiabatic processes result in $\Delta S_{tot} = 0$.

c. True ~~False~~ A system will progress spontaneously to a state with a greater number of indistinguishable experimental configurations if $\Delta T = 0$.

d. True ~~False~~ Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) undergoes a phase transition from solid to vapor at 0.14 atm and 300 K. Under these conditions, $S_m(\text{g}) > S_m(\text{s})$.

e. True ~~False~~ When ferrocene is dissolved in water maintained at 300 K that has been saturated with chlorine gas, the following reaction occurs spontaneously:



It must be true that $S_m(\text{products}) > S_m(\text{reactants})$.

2. (20 points) In class, we derived an expression for the relationship between initial and final pressures and volumes in a system that expands adiabatically:

$$P_i V_i^\gamma = P_f V_f^\gamma \quad \text{where} \quad \gamma = \frac{C_{P,m}}{C_{V,m}}$$

for monatomic: $C_{V,m} = \frac{3}{2} R$
 $C_{P,m} = \frac{5}{2} R$
 $\gamma = \frac{5}{3}$

Compare this to Boyle's law, which describes the relationship between initial and final pressures and volumes in a system that expands isothermally, and explain the significance of the γ term.

Boyle's law: $P_i V_i = P_f V_f$, $P \propto \frac{1}{V}$
 Adiabatic: $P_i V_i^\gamma = P_f V_f^\gamma$, $P \propto \frac{1}{V^\gamma}$, $\gamma > 1$

In isothermal expansion, energy flows into the system as heat to maintain a constant temperature despite the fact that energy is being lost as work. In the adiabatic case, since no heat can enter the system, the temperature of the system must fall as work is done. This means that pressure must fall faster for an adiabatic process than for an isothermal process. This is expressed mathematically as $\gamma > 1$.

3. (25 points) For each of the following, circle which response correctly describes each requested property. Except when indicated, all questions refer to the system.

a. Irreversible adiabatic compression of an ideal gas.

T	<u>increases</u>	decreases	remains the same
V	increases	<u>decreases</u>	remains the same
P	<u>increases</u>	decreases	remains the same
U	<u>increases</u>	decreases	remains the same
H	<u>increases</u>	decreases	remains the same
S_{sys}	<u>increases</u>	decreases	remains the same
S_{surr}	increases	decreases	<u>remains the same</u>
S_{tot}	<u>increases</u>	decreases	remains the same

$q_{surr} = 0$ ($\Delta S_{surr} = 0$)
 $V_f < V_i$, $T_f > T_i$
 $\Delta S_{tot} > 0$
 so $\Delta S_{sys} > 0$
 because $\Delta T > 0$

b. An ideal gas escapes through a hole in a rigid container at constant temperature.

T	increases	decreases	<u>remains the same</u>
V	increases	decreases	<u>remains the same</u>
P	increases	<u>decreases</u>	remains the same
n	increases	<u>decreases</u>	remains the same
U	increases	decreases	<u>remains the same</u>
H	increases	decreases	<u>remains the same</u>
S_{sys}	increases	<u>decreases</u>	remains the same
S_{surr}	<u>increases</u>	decreases	remains the same
S_{tot}	increases	decreases	<u>remains the same</u>

$\Delta U = 0$
 $\Delta T = 0$
 $P \downarrow$ as $n \downarrow$
 because $\Delta T = 0$
 Assume reversible.

3 continued.

c. An ideal gas is heated at constant pressure.

$$\Delta P = 0 \quad \therefore U_f > U_L$$

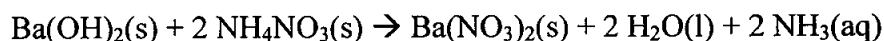
$$T_f > T_L$$

T	increases	decreases	remains the same
V	increases	decreases	remains the same
P	increases	decreases	remains the same
U	increases	decreases	remains the same
H	increases	decreases	remains the same
S_{sys}	increases	decreases	remains the same
S_{surr}	increases	decreases	remains the same
S_{tot}	increases	decreases	remains the same

Because $T_f > T_L$

Assume reversible

4. (20 points) In class, we saw that when solid barium hydroxide and ammonium nitrate are mixed, the resulting reaction is endothermic but proceeds spontaneously (the cold pack):



Given the following information, determine ΔH_{rxn} and ΔS_{rxn} of this reaction.

	ΔH_f° (kJ mol ⁻¹)	S_m° (J K ⁻¹ mol ⁻¹)	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)
Ba(OH) ₂ (s)	-812.1	70.2	47.8
NH ₄ NO ₃ (s)	-365.6	151.1	84.1
Ba(NO ₃) ₂ (s)	-800.2	84.2	49.1
H ₂ O(l)	-285.8	69.9	75.3
NH ₃ (aq)	-80.3	111.3	35.1

$$\Delta H_{rxn} = \sum_i \nu_i \Delta_f H(\text{product}) - \sum_i \nu_i \Delta_f H(\text{reactants})$$

$$\Delta H_{rxn} = 2(-80.3 \frac{\text{kJ}}{\text{mol}}) + 2(-285.8 \frac{\text{kJ}}{\text{mol}}) + (-800.2 \frac{\text{kJ}}{\text{mol}}) - [2(-365.6 \frac{\text{kJ}}{\text{mol}}) + (-812.1 \frac{\text{kJ}}{\text{mol}})]$$

$$\boxed{\Delta H_{rxn} = 10.9 \frac{\text{kJ}}{\text{mol}}}$$

$$\Delta S_{rxn} = \sum_i \nu_i S_m^\circ(\text{products}) - \sum_i \nu_i S_m^\circ(\text{reactants})$$

$$\Delta S_{rxn} = 2(111.3 \frac{\text{J}}{\text{mol K}}) + 2(69.9 \frac{\text{J}}{\text{mol K}}) + (84.2 \frac{\text{J}}{\text{mol K}}) - [2(151.1 \frac{\text{J}}{\text{mol K}}) + (70.2 \frac{\text{J}}{\text{mol K}})]$$

$$\boxed{\Delta S_{rxn} = 74.2 \frac{\text{J}}{\text{mol K}}}$$

★ Furthermore, $\Delta G = \Delta H - T\Delta S = 10.9 \frac{\text{kJ}}{\text{mol}} - (298\text{K})(0.0742 \frac{\text{kJ}}{\text{mol K}}) = -11.2 \frac{\text{kJ}}{\text{mol}}$
 $\Delta G < 0 \Rightarrow$ spontaneous @ room temp.

5. (20 points) Surprisingly, acetylene (HCCH) has a lower standard molar entropy at 298 K than hydrogen cyanide (HCN):

call these

	S_m° (J K ⁻¹ mol ⁻¹)	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)
A HCCH	200.9	43.9
B HCN	201.8	35.9

$$@ \Delta P = 0, S_f = S_c + C_p \ln\left(\frac{T_f}{T_c}\right)$$

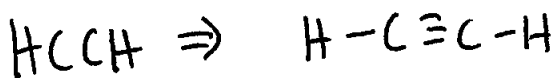
$$S_c = S_m^\circ \text{ for each species}$$

$S_f = \text{new entropy}$

a. Find the temperature at which both HCCH and HCN gasses have the same standard molar entropy.

$$\begin{aligned} \text{A} \quad S_f(A) &= S_m(A) + C_p(A) \ln\left(\frac{T_f}{T_c}\right) & \text{B} \quad S_f(B) &= S_m(B) + C_p(B) \ln\left(\frac{T_f}{T_c}\right) \\ T_f = T_c, \quad S_f(A) &= S_f(B), \Rightarrow S_m(A) + C_p(A) \ln\left(\frac{T_f}{T_c}\right) &= S_m(B) + C_p(B) \ln\left(\frac{T_f}{T_c}\right) \\ \text{Solve for } T_f: & C_p(A) \ln\left(\frac{T_f}{T_c}\right) - C_p(B) \ln\left(\frac{T_f}{T_c}\right) = S_m(B) - S_m(A) \\ \ln\left(\frac{T_f}{T_c}\right) &= \frac{S_m(B) - S_m(A)}{C_p(A) - C_p(B)} & \rightarrow T_f &= (298 \text{ K}) \exp\left[\frac{201.8 \text{ J/kmol} - 200.9 \text{ J/kmol}}{43.9 \text{ J/kmol} - 35.9 \text{ J/kmol}}\right] \\ T_f &= T_c \exp\left[\frac{S_m(B) - S_m(A)}{C_p(A) - C_p(B)}\right] & \boxed{T_f = 333 \text{ K}} & \end{aligned}$$

b. Suggest a possible explanation for why the standard molar entropy of HCCH gas is lower than that of HCN gas at 298 K.



HCCH + HCN are just 1 mass unit different, so this really is not an issue of size or shape (linear). The only intermolecular forces that HCCH is capable of are van der Waals forces, while HCN can actually form strong hydrogen bonds (the lone pair on the N is a great H-bond acceptor). In the solid + liquid phases, these H-bonds will be fulfilled, but then largely disappear in the gas phase. That means $w(s, l) \text{ HCN} \ll w(s, l) \text{ HCCH}$, while $w(g) \text{ HCN} \approx w(g) \text{ HCCH}$. That will give a large increase in entropy going into the gas phase.