

CH353 – Physical Chemistry I
Spring 2015, Unique 51170

Exam 4 – April 28, 2015

Name: Key

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. Calculators may be used for computing arithmetic only.

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

Periodic Table of the Elements California Standards Test

Chemistry Reference Sheet

1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18											
1A		2A		3A		4A		5A		6A		7A		8A		9A		10A		11A		12A		13A		14A		15A		16A		17A		18A											
1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18											
H Hydrogen 1.01		Li Lithium 6.94		Na Sodium 22.99		K Potassium 39.10		Rb Rubidium 85.47		Cs Cesium 132.91		Fr Francium (223)		Be Beryllium 9.01		Mg Magnesium 24.31		Ca Calcium 40.08		Sr Strontium 87.62		Ba Barium 137.33		Ra Radium (226)		B Boron 10.81		Al Aluminum 26.98		Ga Gallium 74.92		In Indium 114.82		Tl Thallium 204.38		Pb Lead 207.2		Bi Bismuth 208.98		Po Polonium (209)		At Astatine (210)		Rn Radon (222)	
He Helium 4.00		Be Beryllium 9.01		Mg Magnesium 24.31		Ca Calcium 40.08		Sr Strontium 87.62		Ba Barium 137.33		Ra Radium (226)		Li Lithium 6.94		Na Sodium 22.99		K Potassium 39.10		Rb Rubidium 85.47		Cs Cesium 132.91		Fr Francium (223)		He Helium 4.00		Ne Neon 20.18		Ar Argon 39.95		Kr Krypton 83.80		Xe Xenon 131.29		Rn Radon (222)									
		B Boron 10.81		Al Aluminum 26.98		Ga Gallium 74.92		In Indium 114.82		Tl Thallium 204.38		Pb Lead 207.2		Bi Bismuth 208.98		Po Polonium (209)		At Astatine (210)		Rn Radon (222)						C Carbon 12.01		Si Silicon 28.09		Ge Germanium 72.61		Sn Tin 118.71		Pb Lead 207.2											
		C Carbon 12.01		Si Silicon 28.09		Ge Germanium 72.61		Sn Tin 118.71		Pb Lead 207.2																N Nitrogen 14.01		P Phosphorus 30.97		As Arsenic 74.92		Sb Antimony 121.76		Bi Bismuth 208.98											
		N Nitrogen 14.01		P Phosphorus 30.97		As Arsenic 74.92		Sb Antimony 121.76		Bi Bismuth 208.98																O Oxygen 16.00		S Sulfur 32.07		Se Selenium 78.96		Te Tellurium 127.60		Po Polonium (209)											
		O Oxygen 16.00		S Sulfur 32.07		Se Selenium 78.96		Te Tellurium 127.60		Po Polonium (209)																F Fluorine 19.00		Cl Chlorine 35.45		Br Bromine 79.90		I Iodine 126.90		At Astatine (210)											
		F Fluorine 19.00		Cl Chlorine 35.45		Br Bromine 79.90		I Iodine 126.90		At Astatine (210)																Ne Neon 20.18		Ar Argon 39.95		Kr Krypton 83.80		Xe Xenon 131.29		Rn Radon (222)											
		Ne Neon 20.18		Ar Argon 39.95		Kr Krypton 83.80		Xe Xenon 131.29		Rn Radon (222)																He Helium 4.00		Ne Neon 20.18		Ar Argon 39.95		Kr Krypton 83.80		Xe Xenon 131.29		Rn Radon (222)									

Key

11	Average atomic mass*
Na	Element symbol
22.99	Element name

* 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~~ Increasing the temperature of a reaction always increases the equilibrium constant.
- b. ~~True~~ False When a reaction reaches equilibrium, the rate of the forward and backwards reactions are equal.
- c. ~~True~~ False If $Q < K_p$, a reaction proceeds further to products.
- d. True ~~False~~ The molar entropy of water at 100°C is greater than the molar entropy of $\text{H}_2(\text{g})$ at 100°C .
- e. ~~True~~ False n moles of $\text{N}_2(\text{g})$ react with $\text{H}_2(\text{g})$ to form $\text{NH}_3(\text{g})$. At equilibrium, there will be $2nz_{eq}$ moles of $\text{NH}_3(\text{g})$.

2. (20 points) Molecule A decomposes into molecules B and C. 10 moles of A is enclosed in a container with rigid walls and maintained at 298 K. At equilibrium, half of the original amount of A remains. What is the equilibrium constant of this reaction?



$$\text{I} \quad n \quad 0 \quad 0$$

$$\text{C} \quad -\frac{1}{2}n \quad +\frac{1}{2}n \quad +\frac{1}{2}n$$

$$\text{E} \quad n(1-\frac{1}{2}) \quad \frac{1}{2}n \quad \frac{1}{2}n$$

$$n_{\text{tot}} = \frac{1}{2}n + \frac{1}{2}n + \frac{1}{2}n = \frac{3}{2}n$$

$$x_i = \frac{\frac{1}{2}n}{\frac{3}{2}n} \quad \frac{\frac{1}{2}n}{\frac{3}{2}n} \quad \frac{\frac{1}{2}n}{\frac{3}{2}n}$$

$$x_i = \frac{1}{3} \quad \frac{1}{3} \quad \frac{1}{3}$$

$$P_i = \frac{1}{3}P_{\text{tot}} \quad \frac{1}{3}P_{\text{tot}} \quad \frac{1}{3}P_{\text{tot}}$$

$$K_p = \frac{P_B P_C}{P_A}$$

$$K_p = \frac{\frac{1}{3}P_{\text{tot}} \frac{1}{3}P_{\text{tot}}}{\frac{1}{3}P_{\text{tot}}}$$

$$K_p = \frac{1}{3}P_{\text{tot}}$$

3. (25 points) We have not talked much this semester about how important thermodynamic properties such as entropy and enthalpy are measured, but in general, measuring how *much* of something you have is significantly easier than measuring the *energy* of what you have. This in turn means that equilibrium constants are generally easier to measure than free energies for many molecules.

a) Set up a graph of $\ln K_p$ versus $1/T$ (i.e. $1/T$ is on the x-axis and $\ln K_p$ is on the y-axis). Draw a figure representing a reaction in which both ΔH°_{rxn} and ΔS°_{rxn} are greater than zero.

$$K_p = \exp\left(\frac{-\Delta G}{RT}\right)$$

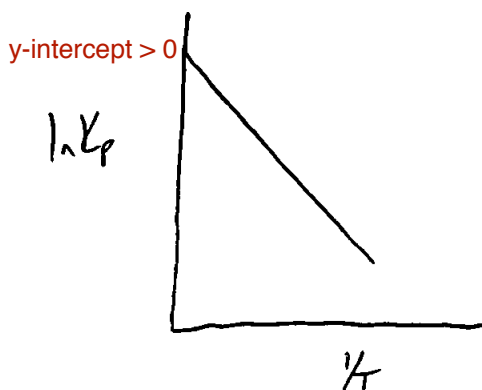
$$\ln K_p = \frac{-\Delta G}{RT} = \frac{-\Delta H + T\Delta S}{RT}$$

$$\ln K_p = \frac{-\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R}$$

$$y = mx + b$$

$$m = \frac{-\Delta H}{R} \quad b = \frac{\Delta S}{R}$$

$$\Delta H, \Delta S > 0$$



b) Using all of the information in this problem, describe an experiment in which you determine ΔG°_{rxn} of the formation of water from $H_2(g)$ and $O_2(g)$. You may assume that you can both control and measure the partial pressure and temperature of all reaction components at any time in your experiment.

1) Calculate K_p from P_i of rxn $K_p = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}}$ at 298 K

$$K_p = \exp\left(\frac{-\Delta G}{RT}\right) \Rightarrow \Delta G^\circ_{rxn} = -RT \ln K_p \quad w/ \quad T = 298 K$$

OR 2) Calculate K_p from P_i of rxn for a range of different temperatures and construct a plot similar to part a). The slope of the line will be equal to $\frac{-\Delta H_{rxn}}{R}$ and the y-axis intercept is equal to $\frac{\Delta S_{rxn}}{R}$. Using the calculated values of ΔH and ΔS , use $\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$ w/ $T = 298 K$ to get ΔG_{rxn} .

4. (20 points) How many collisions per second does a molecule of $N_2(g)$ have in air at 1 atm and 298 K? Assume the bond length of N_2 is 2.2 Å.

$$Z_{\text{coll}} = \frac{P N_A C_{\text{rel}} \sigma}{RT} \quad C_{\text{rel}} = \sqrt{2} \left(\frac{3RT}{FW} \right)^{1/2} \quad \sigma = \pi d^2 \quad FW_{N_2} = 28 \text{ g/mol} = 0.028 \text{ kg/mol}$$

*Units!

$$P_a = \frac{N}{m^2} = \frac{kg}{ms^2}$$

$$J = \frac{kg m^2}{s^2}$$

$$C_{\text{rel}} = \sqrt{2} \left(\frac{3(8.314 \text{ J/mol})(298 \text{ K})}{(0.028 \text{ kg/mol})} \right)^{1/2} \quad \sigma = \pi (2.2 \times 10^{-10} \text{ m})^2$$

$$C_{\text{rel}} = 728.63 \text{ m/s}$$

$$\sigma = 1.52 \times 10^{-19} \text{ m}^2$$

$$Z_{\text{coll}} = \frac{(101325 \text{ Pa})(6.022 \times 10^{23} \text{ particles/mol})(728.63 \text{ m/s})(1.52 \times 10^{-19} \text{ m}^2)}{(8.314 \text{ J/mol})(298 \text{ K})}$$

$$Z_{\text{coll}} = 2.73 \times 10^9 \text{ collisions/sec}$$

5. (20 points) Explain, in clear comprehensible English using any equations and figures you may need, i) why reactions in which K_p is very small (i.e. $< 10^{-10}$) still proceed along the reaction coordinate to some extent; and ii) why reactions in which K_p is very large (i.e. $> 10^{10}$) rarely go to 100% products.

Mathematically: $K_p = \frac{P_{\text{products}}}{P_{\text{reactants}}}$ and for $K_p < 10^{-10}$ or $K_p > 10^{10}$, either case, $K_p \neq 0$ therefore $P_{\text{products}}, P_{\text{reactants}} \neq 0$.

~~Also, at equilibrium, the rate of formation~~

Also, at low K_p , ~~entropy~~ favorable entropy of mixing drives the formation of products. At high K_p , the entropy penalty of "unmixing" prevents the reaction from going to 100% products.