Chemistry 102 Spring 2019
Discussion #4
Chapters 11 and 12

Student name_____________________ TA name_________________ Section_________________

Things you should know when you finish the Discussion hand out:

- Average molar kinetic energy $= \overline{\mathrm{E}} = \frac{\mathrm{M}\cdot u_{\mathrm{rms}}^2}{2} = \frac{3}{2}\mathrm{R}\cdot\mathrm{T}$; $u_{\mathrm{rms}} = \sqrt{u_{\mathrm{avg}}^2} = \sqrt{\frac{3\cdot R\cdot T}{M}}$
- Rate $= \frac{\text{amount}}{\text{Time}}$; rate $\propto$ velocity
- Page 438 in the text book "Summary of Intermolecular Forces" Table 11.15.
- $\left(\mathrm{P}_{obs} + a\left[\frac{n}{\mathrm{V}}\right]^2\right)(\mathrm{V}_{container} - b\cdot n) = n\cdot\mathrm{R}\cdot\mathrm{T}$

  Where $a\left[\frac{n}{\mathrm{V}}\right]^2$ accounts for intermolecular forces; units of $a = \left(\frac{\mathrm{L^2\cdot bar}}{\mathrm{mol^2}}\right) = \left(\frac{\mathrm{100kPa\cdot L^2}}{\mathrm{mol^2}}\right)$

  $b\cdot n$ Accounts for non-zero molecule volume; units of $b = \left(\frac{\mathrm{L}}{\mathrm{mol}}\right)$
- Phase diagram
  - Triple point
  - Critical point

1. Two identical containers, one red and one yellow, are inflated with different gases at the same volume and pressure. Both containers have an identically sized hole that allows the gas to leak out. It takes four times as long for the yellow container to leak out compared to the red container. If the red container is twice as hot as the yellow container, what is the ratio of the molar masses of the gases (M_{yellow} / M_{red})?

2. A container is filled with He at 18°C and 7.92 bar. It is found that the pressure of the container drops by 75.% in 35 minutes, due to a small hole. If the container had instead been filled with Ne at 18°C and 7.92 bar, what would be the pressure of the Ne after 35 minutes? Express your answer in bar, and in atm .

3. Which of the following combinations of conditions will a gas behave most ideally? Explain your choice.
   a. Low P and low T
   b. Low P and high T
   c. High P and high T
   d. High P and low T

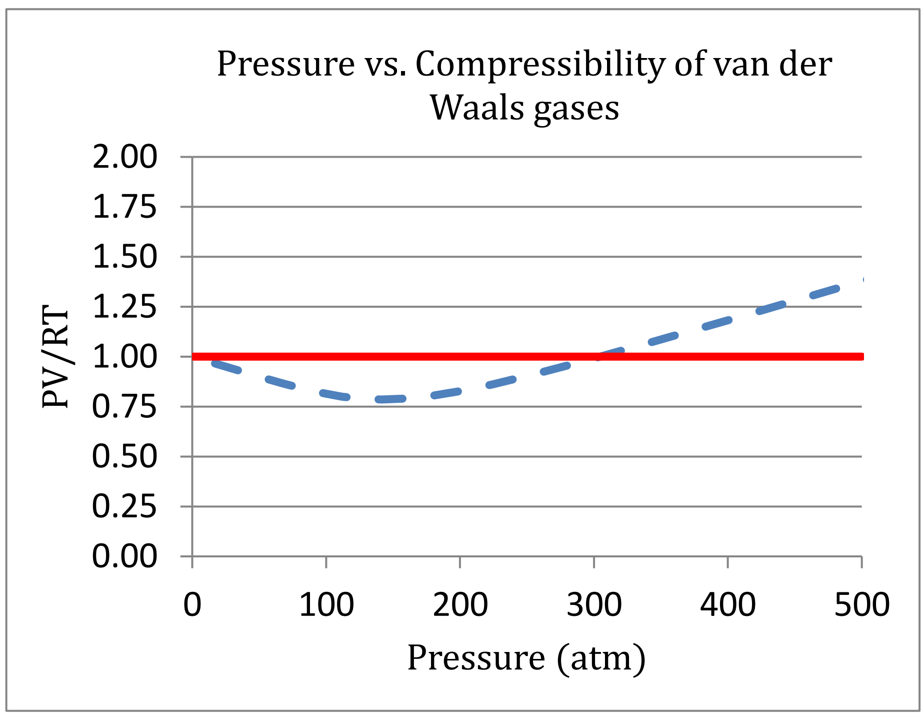
4. Solve the van der Waals real gas equation for the pressure.

a. To investigate how the *a* coefficient affects the pressure, set the *b* coefficient to zero. Does *a* increase or decrease the pressure compared to what you would expect for an ideal gas?

b. To investigate how the *b* coefficient affects the pressure, set the *a* coefficient to zero. Does *b* increase or decrease the pressure compared to what you would expect for an ideal gas?

c. Below is a plot of the compressibility (PV/RT) as a function of changing pressure for 1 mole of a real gas (dashed line) and an ideal gas (solid line). Using what you learned in parts (a) and (b), at what pressures is the *a* coefficient dominant and at what pressures is the *b* coefficient dominant.

(note: y-axis is $\frac{\left(\frac{PV}{RT}\right)_{real}}{\left(\frac{PV}{RT}\right)_{ideal}}$).



5. Put the following molecules in order of increasing Van der Waals constant, *b*: Cl_2, N_2, C_2H_6, C_3H_8.

6. For each of the pair of molecules below, which has the highest value of Van der Waals constant, *a*? Identify the dominant intermolecular forces.

H_2O vs CO_2

Ne vs F_2

C_6H_6 vs CH_3OH

7. Which of the following gases will behave least ideally under the same conditions? Explain your choice using the *a* and *b* Van der Waals coefficients.

CH_4 or SO_2

Cl_2 or N_2

8. Match the molecules below with their *a* and *b* van der Waals coefficients.

Molecules	$a\ \left(\frac{L^2 \cdot bar}{mol^2}\right)$	$b\ \left(\frac{L}{mol}\right)$
Water (H_2O)	0.2476	0.02661
Argon (Ar)	5.536	0.03029
Hydrogen (H_2)	1.363	0.03219
Benzene (C_6H_6)	18.24	0.1154

9. The boiling point of cyclohexane, C_6H_{12}, is 353.9 K, its molecular weight is 84.16, and its van der Waals coefficients are $a = 23.11$ bar L^2/mol^2 and $b = 0.1424$ L/mol. At 354.0 K the vapor pressure of cyclohexane is 1.0164 bar and the vapor density is 0.03453 mol/L. Calculate the vapor pressure (in bar) of cyclohexane at 354.0 K if it behaved as an ideal gas.

   a. Calculate the density of liquid cyclohexane, in g/mL.

10. O_2 and H_2O have similar values of van der Waals constant, *b,* but different van der Waals constant, *a*. Which one will have higher pressure at the same temperature and volume?

11. NO_2 and Trifluoromethane (CHF_3) have similar values of Van der Waals constant, *a,* but different van der Waals constant, *b*. Which one will have higher pressure at the same temperature and volume?

12. A 5.0mol sample of NH_3 gas is kept at 2.0 L container and 27°C. Calculate the pressure (in bar) of the gas assuming it does not behave ideally. (a =4.0 bar·L^2/mol^2 and b = 0.040 L/mol)

What is the percent error compared to an ideal gas?

13. Consider a container filled with $^{15}N_2$ gas and placed in larger container filled only with $^{14}N_2$. If a small hole is made in the smaller container, initially as the gases effuse, will the smaller container gain or lose mass? Assume the pressures inside the containers are the same. Explain your answer. It may help to draw a picture.

14. Two identical containers, one red and one yellow, are filled with different noble gases at the same temperature and pressure. Both containers have an identically sized hole in them allowing the gases to leak out. If it takes the red container 10.0 seconds to empty and the yellow container 57.3 seconds to empty, what are the noble gases contained in each container? *Hint: rate is proportional to amount/time.*

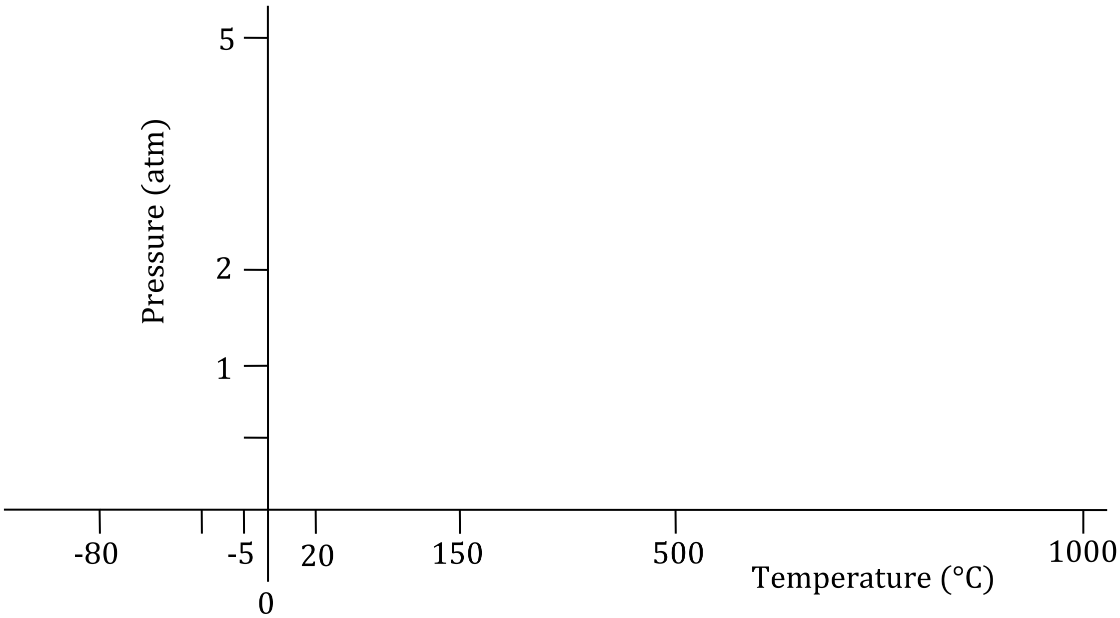
15. In 2.00 min, 29.7mL of helium effuses through a small hole. Under the same conditions (temperature and pressure), a 10.00 mL of a mixture of CO and CO_2 effuse through the same hole in the same amount of time. Calculate the percent composition by volume of the mixture.

16. Two identical containers filled with the same number of moles of gas at the same temperature. Container A contains a gas with a molar mass of 40. g/mol, and container B contains a gas with a molar mass of 160. g/mol. A hole of identical size made in each container. What is the ratio $time_A/time_B$ of the times necessary for the number of moles of gas to drop to half in each container?

17. Imagine a substance with the following points on the phase diagram: a triple point at 0.5 atm and -5°C; a normal melting point at 20°C; a normal boiling point at 150°C; and a critical point at 5 atm and 1000°C. For this, complete the following:

a. What does it mean to have a normal solid-liquid line?

b. Roughly, sketch the phase diagram, using units of pressure (atm) and temperature (°C).



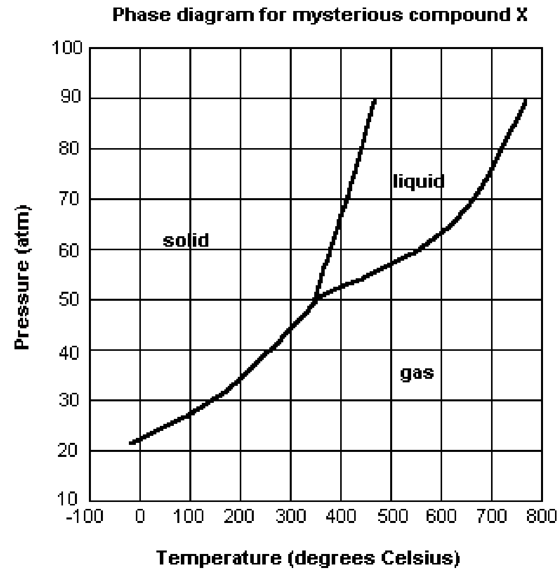
c. Rank the states with respect to increasing density:

d. Describe what one would see at pressures and temperatures above 5 atm and 1000°C:

e. Describe what will happen to the substance when it begins in a vacuum at -15°C and is slowly pressurized:

f. Describe the phase changes from -80°C to 500°C at 2 atm:

18. For each of the following questions refer to the phase diagram for mysterious compound.



   a. What is the critical temperature of compound X?
   b. If you were to have a bottle containing compound X in your closet, what phase would it most likely be in?
   c. At what temperature and pressure will all three phases coexist?
   d. If I have a bottle of compound X at a pressure of 45 atm and temperature of 100°C, what will happen if I raise the temperature to 400°C?
   e. Why can't compound X be boiled at a temperature of 200°C?
   f. If I wanted to, could I drink compound X?

19. At 70.0°C, liquid water is injected into a rigid, evacuated 1.000 L container. After the water has come to equilibrium with its vapor, the volume of the liquid phase is 137 mL. The vapor pressure at 70.0°C is 31.1760 kPa. Calculate the moles of water vapor present in the space above the liquid. Assume vapor behaves as an ideal gas at 70.0°C.

Handout Answers:

1. 8
2. 5.28bar
3. b
4. $P_{obs} = \frac{n \cdot R \cdot T}{V \cdot b \cdot n} - a\left[\frac{n}{V}\right]^2$
   a. '*a*' decreases P_{obs}
   b. '*b*' increases P_{obs}
   c. '*a*' dominates at low P; '*b*' dominates at higher P
5. $N_2 < Cl_2 < C_2H_6 < C_3H_8$
6. H_2O; F_2; C_6H_6
7. SO_2; Cl_2
8.
9. 1.04
   a. 0.5910
10. $P_{O2} > P_{H2O}$
11. $P_{CF3H} > P_{NO2}$
12. P_{obs} = 44 bar; P_{ideal} = 62 bar; 29%
13. Gain
14. Yellow—Xe; Red—He
15. X_{CO2} = 45.6%; X_{CO} = 54.4%
16. 0.5
17.
   a. Positive slope
   b.
   c. Gas < liquid < solid
   d. Only supercritical fluid
   e. Deposition (opposite of sublimation) gas → solid
   f. Solid → liquid → gas
18.
   a. > 750°C
   b. Gas
   c. ≈350°C; ≈50 atm
   d. Sublime; solid → gas
   e. No liquid phase present
   f. NO…
19. $9.43*10^{-3}$

In preparation for next week lecture and discussion sections:

1. Using your own words define lattice enthalpy ($\Delta_{lattice}H$):
2. Is the lattice enthalpy ($\Delta_{lattice}H$) (choose one):

   always positive never positive sometimes positive

   Write the chemical equation representing lattice enthalpy ($\Delta_{lattice}H$) of $MgCl_2$:

   Draw the energy diagram representing lattice enthalpy ($\Delta_{lattice}H$):

3. Using your own words define enthalpy of aquation ($\Delta_{aq}H$):
4. Is the enthalpy of aquation ($\Delta_{aq}H$) (choose one):

   always positive never positive sometimes positive

   Write the chemical equation representing enthalpy of aquation ($\Delta_{aq}H$) of $MgCl_2$:

   Draw the energy diagram representing enthalpy of aquation ($\Delta_{aq}H$):

   Draw the picture of hydrated $MgCl_2$ ions by water:

5. What do you need to know to find enthalpy of solution ($\Delta_{soln}H$):
6. Using your own words define enthalpy of solution ($\Delta_{soln}H$):
7. Is the enthalpy of solution ($\Delta_{soln}H$) (choose one):

   always positive never positive sometimes positive

   Write the chemical equation representing enthalpy of solution ($\Delta_{soln}H$) of solid $MgCl_2$:

8. Can enthalpy of solution ($\Delta_{soln}H$) predict solubility?

Useful information:

- Units of concentrations
  - Molality, $m\left(\frac{\text{mol}}{\text{kg}}\right) = \frac{\text{moles}_{\text{solute}}}{\text{mass}_{\text{solvent}}\ (\text{kg})}$
- Colligative property where *i* is a *van't Hoff factor*
  - Osmotic Pressure: $\Pi = MRT \cdot i$; where $M\left(\frac{mol}{L}\right)$ is Molarity
  - Freezing Point Lowering: $\Delta T_{fp} = -|k_{fp}| \cdot m \cdot i$

    $\Delta T_{fp} = T_{fp_{solution}} - T_{fp_{solvent}} < 0$
  - Boiling Point Elevation: $\Delta T_{fp} = +|k_{bp}| \cdot m \cdot i$

    $\Delta T_{bp} = T_{bp_{solution}} - T_{bp_{solvent}} > 0$
  - Vapor Pressure Lowering: $p_{solvent} = \chi_{solvent} \cdot p°_{pure\ solv}$

    $\Delta p_{solvent} = \chi_{solute} \cdot p°_{pure\ solv}$
- Refer to Page 466-478 in the text book Mahaffy

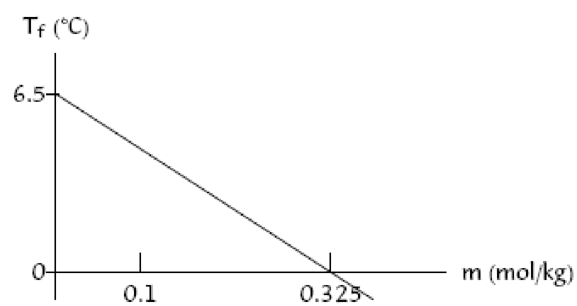
9. The freezing temperature of the solution is always ____________ compared to the freezing temperature of the pure solvent.

   greater lower same

10. The boiling temperature of the solution is always ___________ compared to the boiling temperature of the pure solvent.

    greater lower same

11. The figure to the right is the experimental plot of freezing point temperature, T_f, versus molality, *m*, for the solution of an unknown solute in cyclohexane. Calculate to two significant figures the freezing point depression constant K_f for cyclohexane, in °C·kg/mol (use $i = 1$ for this problem).



12. What is the boiling point of a 0.100*m* sucrose/water solution? ($K_{b,water} = 0.500°C/m$)

13. Circle the solution below that has the lowest freezing point and <u>explain your answer</u>.

    a. 4mol NaCl(s) in 1L of water

    b. 3mol $CaCl_2$(s) in 1L of water

    c. 2mol $AlCl_3$(s) in 1L of water

    d. 4mol $C_6H_{12}O_6$(s) in 1L of water

14. The normal freezing point of cyclohexane is 6.6°C. A 0.20 g sample of an unknown solute is dissolved in 50. mL of cyclohexane (d = 0.80 g/mL, $K_f = 20.°C/m$). If the freezing point of the solution is 3.6°C, what is the molar mass of the solute?

15. At 25°C vapor pressure of pure water is 24 mmHg and that of seawater is 23.20 mmHg. Assuming that seawater contains only NaCl estimate its molal concentration.

16. The freezing point of benzene (C_6H_6) is 6°C at 1 atm. In a laboratory experiment, students synthesized a new compound and found that when 40. grams of the compound were dissolved in 2000 grams of benzene (K_f = 5.12 K·kg/mol), the solution froze at 4°C. The compound found to be nonvolatile and a non-electrolyte. Calculate the molar mass of the compound.

17. 29.0 g of NaCl(s) is mixed with 200. g of ice. Calculate the boiling point of the mixture. The boiling point elevation constant for water is K_b = 0.5°C/mol (use i=2 for this problem)

18. What mass of $CaCl_2$ (MW = 111 g/mol; i = 3) is required to lower the freezing point of 10.0 mL of water (K_f=1.86°C/m) by 1°C?

19. Benzene freezes at 5.51°C (K_f = 5.12°C/m). A benzene/acetic acid solution freezes at 2.01°C. How many moles of acetic acid were added to 500. g of benzene?

Numerical Answers:

Write the chemical equation representing lattice enthalpy ($\Delta_{lattice}H$) of $MgCl_2$: **$MgCl_2(s) \rightarrow Mg^{2+}(g) + 2Cl^-(g)$**
Write the chemical equation representing enthalpy of aquation ($\Delta_{aq}H$) of $MgCl_2$: **$Mg^{2+}(g) + 2Cl^-(g)$ $Mg^{2+}(aq) + 2Cl^-(aq)$**
Write the chemical equation representing enthalpy of solution ($\Delta_{soln}H$) of solid $MgCl_2$: **$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$**

9. lower
10. higher
11. 20
12. 100.05
13. B
14. 30.
15. 0.80
16. 50
17. 102.5
18. 0.199 g
19. 0.342 mol benzene