Exercises Topic 3: States of matter

1. Fill the following table concerning the solids.

Type of solid	Particles on lattice	Inter-molecular forces	Properties	Examples
Ionic				NaCl, Al_2O_3
		metallic		
Covalent			↑↑T_b, ↑↑T_m; ↑↑E; ↑↑Hardness	Diamond, CSi
Molecular (small molecules)	Molecules			CO_2, wax
Molecular (big molecules)			Moderate T_b, T_m	

Solution:

Type of solid	Particles on lattice	Inter-molecular forces	Properties	Examples
Ionic	anions cations	coulombic	$f(Z_1,Z_2,r_0)$ ↑T_b, T_m; ↑E; ↑Hardness	NaCl, Al_2O_3
Metallic	Cations	metallic	f(nº shared e^-) ↑T_b, T_m; ↑Ductility; ↑Conductivity	Ti, Cu, Fe
Covalent	Atoms	Covalent	↑↑T_b, ↑↑T_m; ↑↑E; ↑↑Hardness	Diamond, CSi
Molecular (small molecules)	Molecules	Dipole, London	↓ T_b, T_m	CO_2, wax
Molecular (big molecules)	Molecules	Dipole, London	Moderate T_b, T_m	Polyethylene, polyamide

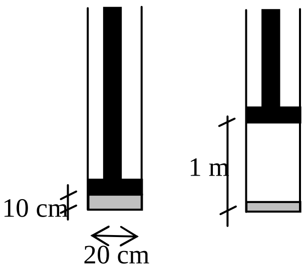
2. Consider two 3L-tanks, A and B, connected by a valve. While closed, the tank A has 0.2 moles of N_2 gas. The tank B is filled with as many litres of O_2 as those obtained from the thermal decomposition of 50 g of potassium chlorate at 20 °C ($KClO_3$ (s) → KCl (s) + O_2 (g)). a) What is the total pressure in each tank while the valve is closed? (**Hint**: balance the equation) (b) What are the partial pressures and total pressure long after opening the valve?
Solution: a) $P_{T(tank\ A)}$ = 1.22 atm; $P_{T(tank\ B)}$ = 4.98 atm . b) $P(N_2)$ = 0.61 atm; $P(O_2)$ = 1.66 atm; P_T = 2.27 atm.

3. You are provided with two samples of two different gases A and B. Molecular mass of A doubles the corresponding of B. The average velocity of A molecules also doubles that of B. If both samples contain the same number of molecules per liter and if the pressure of sample B is 4 atm: (a) Calculate the pressure on A. (b) Which is the ratio between the temperatures of both gases?
Solution: a) P_A = 32 atm. b) T_A/T_B = 8

4. A mixture of oxygen (16%) and nitrogen (84%) has a volume of 2400 cm^3 at 1 atm pressure and 23 ºC. It is bubbled through water at 23 ºC in such a way that the collected gas is

saturated in water and the pressure is 1 atm. Calculate (a) Final volume of the mixture. (b) Partial pressures of O_2 and N_2 in the wet mixture.
Data: P(H_2O, 23ºC) = 25 mmHg
Solution: a) 2.48 L. b) P(O_2) = 0.157 atm, P(N_2) = 0.823 atm.

5. Assume you have a vertical cylinder of radius 10 cm and height L m, equipped with a piston. The piston is separated from the bottom of the cylinder a distance of 10 cm and this cavity is completely filled with liquid water at 80ºC. The piston begins to move vertically very slowly and the whole ensemble is maintained at 80 ºC. The piston stops when reaches a distance of 1 m from the bottom. Look in the web for the equilibrium water vapor pressure at 80 ºC and 10 ºC and for the density at 80 ºC and answer the following questions: (a) What would be the pressure inside? (b) What would be the level of water and how many moles of water have passed to the gas phase? (c) What distance should the piston be displaced to completely evaporate all the water? (d) At the distance set in section c) the piston is fixed and temperature is decreased to 20 ºC. Would water condense? How much?
Solution:



a) As the piston moves a vacuum is created in the cavity the piston leaves below. Water evaporates to fill the vacuum until water vapor pressure equals the equilibrium value at 80 ºC. You can look in the web http://www.engineeringtoolbox.com/water-thermal-properties-d_162.html
finding P^0(H_2O, 80 ºC) = 47.5 kN/m^2 = 47.5·10^3 N/m^2 = 47.5·10^3 Pa

b) The amount of water in the gas phase can be calculated assuming ideal gas behavior, but for doing so you will need the gas constant in appropriate units. You can look in the web http://en.wikipedia.org/wiki/Gas_constant finding 8.314 m^{3}Pa K^{-1} mol^{-1}.

$$n = \frac{47.5 10^3 V_{gas}}{8.314 \times (273+80)} \frac{Pa}{Pa \cdot m^3 \cdot K^{-1} \cdot mol^{-1} \cdot K} = 0.0173 V_{gas} \qquad (1)$$

where V_{gas} is the volume of the gas cavity.

Now the problem is calculating the volume of the gas cavity since the evaporated water decreases the liquid water level. We can set out the problem in the following way:
Initially, before the piston begins to move, the water volume in the liquid phase is V_{liq} (init) = $\pi 0.1^2 \cdot (0.1)$ = 3.142·10^{-3} m^3. After the piston moves, the total cylinder volume is V_{cyl} = $\pi 0.1^2 \cdot (1)$ = V_{gas} + V_{liq}(after), where V_{gas} is the volume of the gas cavity and V_{liq}(after) is the volume of liquid water after evaporating n moles.

But V_{liq}(after) = V_{liq} (init) – V_n, that is to say, to calculate the liquid water volume after the evaporation we need to subtract the volume of evaporated water from the initial liquid volume. To calculate the volume of liquid water that has passed to the gas phase we need the density of water at 80 ºC. You can look for it in the web http://www.engineeringtoolbox.com/water-thermal-properties-d_162.html finding ρ = 0.972 g·cm^{-3}.

$$V_n = \frac{n \times M_{H_2O}}{\rho_{H_2O,80^\circ C}} = \frac{n \times 18 g \cdot mol^{-1}}{0.972 g \cdot cm^{-3}} = n \cdot 18.52 cm^3 = n \cdot 18.52 10^{-6} m^3 \qquad (2)$$

Therefore, the volume of the gas cavity is

$$\begin{aligned} V_{gas} &= V_{cyl} - V_{liq}(after) = V_{cyl} - V_{liq}(init) + V_n = 3.142 \cdot 10^{-2} - 3.142 \cdot 10^{-3} + n \cdot 18.52 \cdot 10^{-6} = \\ &= 0.028278 + 0.0173 \times 18.52 \cdot 10^{-6} V_{gas} \approx 0.028278 \ m^3 \end{aligned} \qquad (3)$$

Replacing this value in equation (1) we arrive to the number of moles of water in the gas phase:
n = 0.0173×0.028278 = 4.892·10^{-4} moles.
To calculate the level of water after evaporation we need the volume of liquid water V_{liq}(after) = V_{liq} (init) – V_n = V_{liq} (init) - n×18.52·10^{-6} = 3.142·10^{-3} - 4.892·10^{-4}×18.52·10^{-6} ~3.142·10^{-3}. This means that the volume variation is insignificant.

c) To completely evaporate all the water, the volume of the gas phase must accommodate all the water at a pressure equal to the vapor pressure of water at 80 ºC (= 47 500 Pa). The number of moles of water in the gas phase would be

$$n = \frac{V_{liq}(init)\rho_{H_2O,80°C}}{M_{H_2O}} = \frac{3.142 \cdot 10^{-3} m^3 \times 10^6 cm^3 \cdot m^{-3} \times 0.972 g \cdot cm^3}{18 g \cdot mol^{-1}} = 169.668\ moles \quad (4)$$

Therefore,

$$L = \frac{V}{\pi \cdot 10^{-2}} = \frac{nRT}{P\pi \cdot 10^{-2}} = \frac{169.668 \times 8.314 \times 353}{47{,}500 \times \pi \times 10^{-2}} = 333.7\ m \quad (5)$$

d) The pressure inside the cylinder is 47,500 N/m^2 which corresponds to the equilibrium vapor pressure of water at 80 ºC. If temperature is decreased to 20 ºC, water will condense up to the point at which vapor pressure equals the equilibrium value at 20 ºC, which is

$P^0(H_2O$, 20 ºC) = 2.3 kN/m^2 = 2.3·10^3 N/m^2 = 2.3·10^3 Pa

Now the question is how much water can be accommodated inside a cylinder of 333.7 m length at 22,300Pa?. The answer is easy assuming ideal gas behavior

$$n = \frac{PV}{RT} = RT = \frac{2.3 10^3 \pi \cdot 10^{-2} \cdot 333.7}{8.314 \times 293} = 9.898\ moles$$

The amount of condensed water will be the difference between the moles in gas phase at 80 ºC and a 20 ºC = 169.668 – 9.898 = 159.77 moles.

6. A 200 cm^3 chamber equipped with a piston contains a mixture of CO and C_2H_2 at 7.5 atm and 77ºC. 4.5 g of O_2 are injected in the chamber, being this amount more than needed for a complete combustion of the gas mixture. After combustion the system returns to the initial temperature and it is found 1042 cm^3 of a gas mixture over 0.5 cm^3 of liquid water. Calculate: (a) Percentage composition in volume of the gas mixture before adding oxygen. (b) Percentage composition in volume after combustion at the final temperature.
Data: ρ(H_2O(liq), 77ºC) = 0.978 g·cm^{-3}; P(H_2O, 77ºC) = 314.1 mmHg
Solution: a) 74.4% CO, 25.6% C_2H_2. b) 57.3% CO_2, 26% H_2O, 16.6% O_2.

7. Two containers with exactly the same volume V, are filled with 1 mol of nitrogen and 1 mol of H_2O(g) respectively, at the same temperature T. Assuming that both gases follow the Van der Waals equation, in which container the pressure is higher?
Data:

Gas	a (L^2·atm·mol^2)	b (L·mol^{-1})
N_2	1.35	0.0386
H_2O	5.47	0.0305

Solution: P(N_2) > P(H_2O)

8. An ideal gas is contained in an ampoule at 600 mmHg. A certain amount of gas is removed in such a way that the pressure inside the ampoule decreases to 520 mmHg. The removed gas occupies 1.52 cm^3 at 1 atm pressure. Assuming that all measurements have been done at the same temperature, calculate the ampoule's volume.
Solution: V = 14.4 cm^3

9. Estimate the molar heat of vaporization of a liquid whose vapour pressure doubles when the temperature is raised form 80 ºC to 90 ºC.

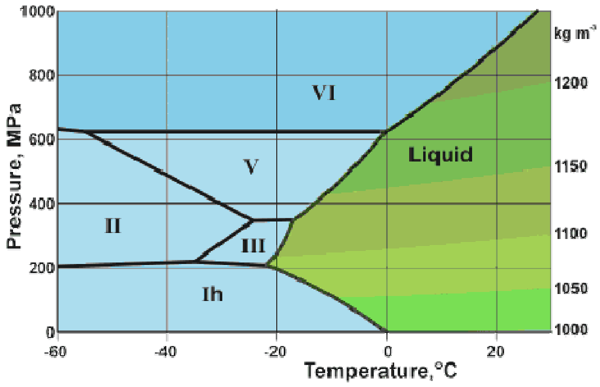
Solution: ΔH^o_v = 73.9 kJ/mol

10. Consider an osmosis apparatus in which both compartments are equipped with a glass tube of 1 mm internal diameter that stands vertically in contact with the liquids inside. One compartment is filled with water and the other with a solution of a substance of molecular mass M = 1200 $g\cdot mol^{-1}$ and concentration C = 0.6 $g\cdot L^{-1}$. Initially, the level of both liquids inside the tubes was the same. Calculate: (a) The osmotic pressure of the solution at 25 ºC. (b) The freezing point depression of the solution. (c) The difference in liquid heights of both glass tubes after equilibrium is reached.

Data: K_C=1.86 ºC kg/mol; consider as 1 $g\cdot cm^{-3}$ the density of the solution

Solution: a) $\pi_0 = 1.239\cdot 10^3$ Pa = 0.0122 atm. b) $\Delta T_C = 9.3\cdot 10^{-4}$ ºC. c) $h_{eq} - h_0$ = 12.4 cm.

11. A portion of the phase diagram of water is shown below. Indicate: a) How many triple points are there? What are their coordinates and which phases coexist? b) What would happen if at a constant temperature of -25 ºC, we raise the pressure from 100 MPa to 1000 MPa? C) And what if at a constant pressure of 500 MPa we lower the temperature from 20 ºC to -60 ºC?



http://www.lsbu.ac.uk/water/phase.html

Solution: a) I_h + III + Liquid; Ih + II + III; L + III + V; III + V + II; II + V + VI; L + V + VI; b) Ih→(0.2GPa) III→0.3(GPa) II→(0.9 GPa) V→1GPa) VI → (2GPa) VIII → (50GPa) VII. c) L→ (20ºC) V→(-10ºC) II →(-45 ºC)

12. A 0.250g sample of hemoglobin was dissolved in H_2O to prepare 50 mL of solution. At 25 °C the osmotic pressure of the solution was 1.35 mmHg, what is the approximate molecular weight of hemoglobin?

Solution: M_H = 68 800 $g\cdot mol^{-1}$

13. Vapor pressure of benzene and ethanol at 50ºC are: 271 and 220 Torr respectively. a) Calculate the vapor pressure of a mixture containing the same weights of both substances at 50ºC as well as, b) the molar fraction of ethanol in the vapor phase assuming ideal behavior. c) Vapor pressure of the mixture at 50 ºC was measured in an experiment and it was obtained a value of 300 torr. Compare with your result and and extract the sign of the enthalpy of mixing both substances. Will the mixture present an azeotropic composition?

Data: M(ethanol)=46 g/mol, M(benzene)=78g/mol.
Solution: a) P_v = 238.92 torr; b) $y_{ethanol}$ = 0.579; c) The mixture has a higher vapor pressure than ideal behavior so the mixing enthalpy will be positive and the mixture will present an azeotrope with minimum boiling temperature

14. The normal boiling point of acetone, an important laboratory and industrial solvent, is 56.2 ºC and its enthalpy of vaporization is 25.5 kJ/mol. At what temperature does acetone have a vapor pressure of 300 mmHg?
Solution: T = 298.8 K = 22.6 ºC

15. The minimum mass concentration of oxygen required for fish life is 4 $mg \cdot L^{-1}$. (a) What is the minimum partial pressure of O_2 over a lake at 15 ºC to support fish life? (b) Assuming that the temperature dependence of Henry's constant is given by the following equation $k_H(T) = 0.0013 \cdot \exp\{(1700) \cdot [(1/T) - 1/(298.15)]\}$, where T is the temperature in Kelvin, calculate the temperature at which solubility of oxygen is below 4 $mg \cdot L^{-1}$.
Data: Henry's constant for O_2 at 20 ºC is $k_H(15ºC) = 1.58 \cdot 10^{-3}$ $mol \cdot L^{-1} \cdot atm^{-1}$.
Solution: a) 0.14 atm; b) 342 K

16. The volume of blood in the body of a certain deep-sea diver is about 6.0L. Blood cells make up about 55% of the blood volume and the remaining 45 % is an aqueous solution called plasma. Diver provided with a simple air bottle dives to 40 m. Calculate: (a) The pressure at that depth (b) The maximum nitrogen mass that can be dissolved in the plasma at 37 ºC. (c) The volume that such amount of nitrogen would occupy if the diver ascends very quickly.
Data: Henry's constant of N_2 at 37 ºC $k_H(37) = 5.8 \cdot 10^{-4}$ $mol \cdot L^{-1} \cdot atm^{-1}$
Solution: a) ~ 4 atm; b)$6.264 \cdot 10^{-3}$ mol; c) 172 ml

17. A soft drink is made by dissolving CO_2 gas at 4.00 atm in a flavored solution and sealing the solution in aluminium cans at 20 ºC. (a) How many moles of CO_2 are contained in a 330 mL can of the soft drink?. (b) Assuming that the temperature dependence of Henry's constant is given by the following equation $k_H(T) = 0.035 \cdot \exp\{(2400) \cdot [(1/T) - 1/(298.15)]\}$, where T is the temperature in Kelvin, calculate the volume of CO_2 that will be transformed into gas phase when you drink the soft drink.
Data: Henry's constant of CO_2 at 20 ºC $k_H(20) = 2.3 \cdot 10^{-2}$ $mol \cdot L^{-1} \cdot atm^{-1}$
Solution: a) 0.0303 mol; b) At the beginning, all the moles of dissolved CO_2 will transform into gas in the stomach but s the partial pressure of CO_2 increases, replacing the air, solubility of CO_2 will increase. So we can not make an accurate calculation; we can only calculate the maximum amount, which is 841 cm^3.