

Chemistry 431  
Problem Set 1  
Fall 2023  
Solutions

1. It is known that 25.0 ml of liquid benzene ( $C_6H_6$ ) contains  $1.018 \times 10^{24}$  carbon atoms. Determine the density of liquid benzene.

**Answer:**

$$\left(\frac{1.018 \times 10^{24} \text{ atoms}}{25.0 \text{ ml}}\right) \left(\frac{\text{molecule}}{6 \text{ atoms}}\right) \left(\frac{\text{mol}}{6.022 \times 10^{23} \text{ molecules}}\right) \left(\frac{78.11 \text{ g}}{\text{mol}}\right)$$
$$= 0.880 \text{ g ml}^{-1}$$

2. (a) A 5.0 kg ball collides with a 10.0 kg ball initially at rest. The collision is elastic and the final velocity of the 5.0 kg ball is  $-0.333 \text{ m s}^{-1}$ . Determine the initial velocity of the 5.0 kg ball.

**Answer:**

$$m_1 v_{1,i} + m_2 v_{2,i} = m_1 v_{1,f} + m_2 v_{2,f}$$
$$\frac{1}{2} m_1 v_{1,i}^2 + \frac{1}{2} m_2 v_{2,i}^2 = \frac{1}{2} m_1 v_{1,f}^2 + \frac{1}{2} m_2 v_{2,f}^2$$

Let  $v = v_{1,i}$      $x = v_{2,f}$

Given  $v_{2,i} = 0$ , we have

$$5.0v = 5.0(-0.333) + 10.0x$$
$$\frac{1}{2}(5.0)v^2 = \frac{1}{2}(5.0)(-0.333)^2 + 5.0x^2$$
$$x = \frac{5.0v + 1.67}{10.0}$$
$$2.5v^2 = 0.28 + 5.0 \left(\frac{5.0v + 1.67}{10.0}\right)^2$$
$$1.25v^2 - 0.84v - 0.42 = 0$$

$$v = \frac{0.84 \pm \sqrt{0.84^2 + 4(0.42)(1.25)}}{2(1.25)}$$

$$= 1.0, -0.35$$

Only the positive solution is physical so that

$$v = 1.0 \text{ m s}^{-1}$$

- (b) The two balls having the same initial velocities as in part “a” collide and stick together. Use momentum conservation to find the final velocity of the two-ball unit. Show the kinetic energy is not conserved.

**Answer:**

$$(15 \text{ kg}) v_f = 5 \text{ kg m s}^{-1}$$

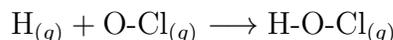
$$v_f = \frac{1}{3} \text{ m s}^{-1}$$

$$KE_f = \frac{1}{2}(15 \text{ kg})(1/3 \text{ m s}^{-1})^2 = 0.833 \text{ J}$$

$$KE_i = \frac{1}{2}(5.0 \text{ kg})(1.0 \text{ m s}^{-1})^2 = 2.5 \text{ J}$$

Then  $KE_i \neq KE_f$  and  $(2.5-0.833) \text{ J} = 1.67 \text{ J}$  goes into heat.

3. In this problem we apply the treatment of classical inelastic collisions to the gas-phase reaction



where the hydrogen atom collides head-on with the OCl molecule to form a bound, linear triatomic molecule. We assume the collision takes place in one dimension, and we assume initially the OCl molecule is at rest and the H atom has an initial velocity of  $+2730 \text{ m s}^{-1}$  (the average speed of a hydrogen atom at 298K). Calculate 1) the final velocity of the HOCl molecule after the collision, 2) the final kinetic energy of the HOCl molecule and 3) the change in the total energy in the bonds making up HOCl after the collision.

**Answer:**

$$p_i = p_f \quad m_H v_H + m_{\text{OCl}} v_{\text{OCl}} = m_{\text{HOCl}} v_{\text{HOCl}}$$

$$1(2730 \text{ ms}^{-1}) + 0 = 52.5 v_{\text{HOCl}} \quad v_{\text{HOCl}} = 52.0 \text{ ms}^{-1}$$

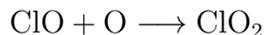
$$KE_f = \frac{1}{2} m_{\text{HOCl}} v_{\text{HOCl}}^2 = \frac{1}{2} \left( \frac{52.5}{6.022 \times 10^{26}} \text{ kg} \right) (52.0 \text{ ms}^{-1})^2 = 1.18 \times 10^{-22} \text{ J}$$

$$KE_i = \frac{1}{2} \left( \frac{1.00 \text{ kg}}{6.022 \times 10^{26}} \right) (2730. \text{ ms}^{-1})^2 = 6.19 \times 10^{-21} \text{ J}$$

$$KE_i + E_{\text{bonds},i} = KE_f + E_{\text{bonds},f}$$

$$\Delta E_{\text{bonds}} = E_{\text{bonds},f} - E_{\text{bonds},i} = KE_i - KE_f = 6.07 \times 10^{-21} \text{ J}$$

4. In a study of the elementary, molecular collision process



the ClO molecule is initially stationary (i.e.  $\vec{v} = 0$ ) and aligned along the  $x$  axis. The O atom moves in the positive  $x$  direction directly along the ClO bond. After the O and ClO species collide, the ClO<sub>2</sub> molecule forms, and the total internal vibrational energy of ClO<sub>2</sub> is found to be greater than the initial ClO vibrational energy by  $4.00 \times 10^{-21}$  J. Calculate the initial speed of the O atom before the collision.

**Answer:**

Let  $KE_1$  be the initial kinetic energy of the oxygen atom and  $KE_2$  be the final molecular kinetic energy. Let  $E_{v1}$  be the initial vibrational energy of ClO and  $E_{v2}$  be the final vibrational energy of ClO<sub>2</sub>. Then

$$KE_1 + E_{v1} = KE_2 + E_{v2}$$

or

$$KE_1 = KE_2 + E_{v2} - E_{v1} = KE_2 + 4.00 \times 10^{-21} \text{ J}$$

Using momentum conservation

$$m_O v_0 = m_{\text{ClO}_2} v_{\text{ClO}_2}$$

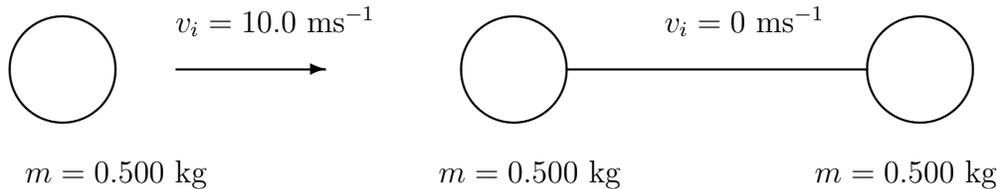
where  $m_O$  is the mass of the oxygen atom,  $m_{\text{ClO}_2}$  is the mass of ClO<sub>2</sub>,  $v_0$  is the initial velocity of the O atom along the  $x$  direction and  $v_{\text{ClO}_2}$  is the final molecular speed. Then

$$v_{\text{ClO}_2} = \frac{m_O}{m_{\text{ClO}_2}} v_0$$

and

$$\begin{aligned} \frac{1}{2} m_O v_0^2 &= \frac{1}{2} m_{\text{ClO}_2} v_{\text{ClO}_2}^2 + 4.00 \times 10^{-21} \text{ J} \\ \frac{1}{2} m_O v_0^2 &= \frac{1}{2} m_{\text{ClO}_2} \left( \frac{m_O v_0}{m_{\text{ClO}_2}} \right)^2 + 4.00 \times 10^{-21} \text{ J} \\ v_0^2 &= \frac{m_O}{m_{\text{ClO}_2}} v_0^2 + \frac{4.00 \times 10^{-21} \text{ J}}{m_O/2} \\ v_0^2 \left( 1 - \frac{16.0}{32.0 + 35.5} \right) &= \frac{8.00 \times 10^{-21} \text{ J}}{16.0 \text{ kg}/6.022 \times 10^{26}} \\ v_0 &= 628. \text{ ms}^{-1} \end{aligned}$$

5.



Three spherical balls each of mass  $0.500 \text{ kg}$  are placed on a one-dimensional, linear and frictionless track as pictured above. The two spheres on the right side are connected by a spring, and the spring is depicted by a horizontal line in the figure. Initially, the two connected spheres on the right both have velocity of  $0$ . The sphere on the left has an initial velocity of  $10.0 \text{ m s}^{-1}$ . On collision the sphere on the left sticks to the center sphere, and the entire three-sphere assembly continues to move on the frictionless track. Assuming no energy is dissipated into heat, calculate the energy of vibration of the spring after the collision.

**Answer:**

$$m_1 v_1 = m_2 v_2$$

$$(0.500 \text{ kg})(10.0 \text{ m s}^{-1}) = (1.500 \text{ kg})v_2 \quad v_2 = 3.33 \text{ m s}^{-1}$$

$$\begin{aligned} \Delta KE &= \Delta(1/2 mv^2) = \frac{1}{2}(0.500 \text{ kg})(10.0 \text{ m s}^{-1})^2 - \frac{1}{2}(1.500 \text{ kg})(3.33 \text{ m s}^{-1})^2 \\ &= 16.7 \text{ J} = \text{energy of vibration of the spring after the collision} \end{aligned}$$

6. A constant force of  $500$  Newtons is applied upwards to a  $20.0 \text{ kg}$  block over  $12.0$  meters. In addition to the force of gravity, a frictional force of  $-5.0$  Newtons also acts on the block.

(a) What is the change in the total energy of the block?

**Answer:**

$$\Delta E = (500 \text{ N})(12 \text{ m}) = 6000 \text{ J}$$

(b) What is the change in the kinetic energy of the block?

**Answer:**

$$F_{net} = 500 \text{ N} - (9.8 \text{ m s}^{-2})(20.0 \text{ kg}) - 5.0 \text{ N} = 299. \text{ N}$$

$$\Delta KE = (299 \text{ N})(12 \text{ m}) = 3588 \text{ J}$$

(c) What is the change in the potential energy of the block?

**Answer:**

$$\Delta PE = (20.0 \text{ kg})(9.8 \text{ m s}^{-2})(12.0 \text{ m}) = 2352 \text{ J}$$

(d) Calculate the amount of work that is dissipated into heat.

**Answer:**

$$q = (12.0 \text{ m})(5.0 \text{ N}) = 60.0 \text{ J}$$

7. At what temperature does neon gas have a density of  $0.80 \text{ g L}^{-1}$ , when the pressure is  $1.0 \text{ bar}$ ?

**Answer:**

$$pV = nRT$$
$$T = \frac{PV}{nR} = \frac{PV}{(m/M)R} = \frac{PM}{\rho R}$$

where  $M$  is the gram molecular mass and  $\rho$  is the density. Then

$$T = \frac{(1.0 \text{ bar})(20.18 \text{ g mol}^{-1})}{(0.80 \text{ g L}^{-1})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})} = 303\text{K}$$

8. An ideal gas at  $2.0 \text{ bar}$  pressure occupies a bulb of unknown volume. A syringe is inserted into the bulb and some of the gas is withdrawn at constant temperature. It is found that the volume of the gas in the syringe is  $1.0 \text{ cm}^3$  and the pressure is  $4.0 \text{ bar}$  while the pressure in the bulb is reduced to  $1.92 \text{ bar}$ . Find the volume of the bulb.

**Answer:**

$$P_1V_1 = P_2V_2$$
$$(2.00 - 1.92)V = (4.0)(1.0)\text{cm}^3$$
$$V = 50.\text{cm}^3$$

9. A  $10.0 \text{ liter}$  bulb is used to confine  $5.0 \text{ grams}$  of  $\text{CO}_2$  gas and  $3.0 \text{ grams}$  of  $\text{N}_2$  gas at  $25^\circ\text{C}$ . Find the mole fractions and partial pressures of each gas.

**Answer:**

$$(5.0 \text{ g}) \left( \frac{\text{mol}}{44.01 \text{ g}} \right) = 0.11 \text{ mol CO}_2$$
$$(3.0 \text{ g}) \left( \frac{\text{mol}}{28.02 \text{ g}} \right) = 0.11 \text{ mol N}_2$$
$$\chi_{\text{N}_2} = \chi_{\text{CO}_2} = 0.5$$
$$P = \frac{nRT}{V} = \frac{(0.22 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})}{10.0 \text{ L}}$$
$$= 0.54 \text{ bar}$$
$$P_{\text{N}_2} = P_{\text{CO}_2} = .5(0.54 \text{ bar}) = 0.27 \text{ bar}$$

10. Molecular iodine gas dissociates into iodine atoms according to the reaction



When 1.28 moles of pure gas phase molecular iodine are introduced into a 100. liter flask at a temperature of 1497K and allowed to come to equilibrium, the final total pressure is found to be 2.0 bar. Calculate the partial pressure of molecular iodine vapor in the equilibrium mixture.

**Answer:**

	$n_{\text{I}_2}$	$n_{\text{I}}$
initial	1.28 mol	0 mol
change	$-x$ mol	$2x$ mol
equilibrium	$(1.28 - x)$ mol	$2x$ mol

$$n_{\text{tot}} = n_{\text{I}_2} + n_{\text{I}} = (1.28 + x) \text{ mol}$$

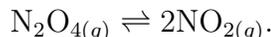
$$P = \frac{n_{\text{tot}}RT}{V}$$

$$2.0 \text{ bar} = \frac{((1.28 + x) \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(1497. \text{ K})}{100. \text{ L}}$$

$$x = 0.33 \text{ mol}$$

$$P_{\text{I}_2} = \frac{((1.28 - 0.33) \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(1497. \text{ K})}{100. \text{ L}} = 1.2 \text{ bar}$$

11. A sample of 20.0 grams of  $\text{N}_2\text{O}_4$  gas is introduced into a 5.0 liter flask at 298K and allowed to dissociate and come to equilibrium according to the reaction



Given that at equilibrium 85.6% of the initial quantity of  $\text{N}_2\text{O}_4$  gas has dissociated, calculate the equilibrium total pressure in the flask.

**Answer:**

$$n_{\text{N}_2\text{O}_4} = \frac{20.0 \text{ g}}{2(14. \text{ g mol}^{-1}) + 4(16. \text{ g mol}^{-1})} = 0.217 \text{ mol}$$

	$n_{\text{N}_2\text{O}_4}$	$n_{\text{NO}_2}$
initial	0.217 mol	0 mol
change	$-(0.856)(0.217) \text{ mol}$	$2(0.856)(0.217) \text{ mol}$
equilibrium	0.0313 mol	0.372 mol

$$n_{tot} = (0.0313 + 0.372) \text{ mol} = 0.403 \text{ mol}$$

$$P = \frac{n_{tot}RT}{V} = \frac{(0.403 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298. \text{ K})}{5.0 \text{ L}} = 2.0 \text{ bar}$$

12. A tank used in scuba diving contains 100. L of compressed air with an initial pressure of 100.0 bar. After a diver inhales three times at full lung capacity at constant temperature and with lung pressure of 0.976 bar, the final pressure in the tank is 99.8 bar. Calculate the volume of the diver's lungs.

**Answer**

$$P_1V_1 = P_2V_2$$

$$(100.0 - 99.8)(100. \text{ L}) = 0.976V_2$$

$$V_2 = 20.5 \text{ L}$$

$$V_{lung} = V_2/3 = 6.83 \text{ L}$$

13. Gas phase  $\text{PCl}_5$  dissociates according to the reaction



When pure  $\text{PCl}_{5(g)}$  is placed in a flask of fixed volume at  $250.^\circ\text{C}$ , the initial pressure of the pure  $\text{PCl}_{5(g)}$  is 43.48 bar. After equilibrium is reached, the final total pressure is 78.27 bar. Calculate the mole fraction of  $\text{Cl}_{2(g)}$  in the flask containing the equilibrium mixture.

**Answer:**

	$n_{\text{PCl}_5}$	$n_{\text{PCl}_3}$	$n_{\text{Cl}_2}$
initial	$n_0$	0	0
change	$-\alpha n_0$	$\alpha n_0$	$\alpha n_0$
equilibrium	$(1 - \alpha)n_0$	$\alpha n_0$	$\alpha n_0$

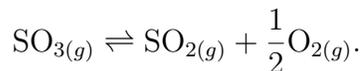
$$n_{tot} = n_{\text{PCl}_3} + n_{\text{Cl}_2} + n_{\text{PCl}_5} = n_0(1 + \alpha)$$

$$P = \frac{n_{tot}RT}{V} = \frac{(1 + \alpha)n_0RT}{V} = (1 + \alpha)P_0$$

$$78.27 = (1 + \alpha)43.48 \quad \alpha = 0.800$$

$$\chi_{\text{Cl}_2} = \frac{n_{\text{Cl}_2}}{n_{tot}} = \frac{n_0\alpha}{n_0(1 + \alpha)} = \frac{\alpha}{1 + \alpha} = 0.44$$

14. Sulfur trioxide in the gas phase dissociates into sulfur dioxide gas and oxygen gas according to the reaction



When pure sulfur trioxide gas is placed in an enclosed container of fixed volume at 1100. K, the initial pressure is measured to be 2.548 bar. The system is allowed to come to equilibrium at a fixed temperature of 1100 K, and the final total pressure is 3.000 bar. Calculate the fraction,  $\alpha$  (i.e. the degree of dissociation), of the original sulfur trioxide that dissociates when equilibrium is reached.

**Answer:**

Let  $n_0$  be the initial number of moles of sulfur trioxide.

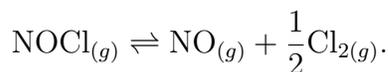
	$n_{\text{SO}_3}$	$n_{\text{SO}_2}$	$n_{\text{O}_2}$
initial	$n_0$	0	0
change	$-\alpha n_0$	$\alpha n_0$	$\alpha n_0/2$
equilibrium	$(1 - \alpha)n_0$	$\alpha n_0$	$\alpha n_0/2$

$$n_{\text{tot}} = n_{\text{SO}_3} + n_{\text{SO}_2} + n_{\text{O}_2} = n_0(1 + \alpha/2)$$

$$P_{\text{tot}} = \frac{n_{\text{tot}}RT}{V} = \frac{n_0RT}{V}(1 + \alpha/2) = P_0(1 + \alpha/2)$$

$$3.000 = 2.548(1 + \alpha/2) \quad \alpha = 0.3548$$

15. A sample of pure NOCl gas is placed in a container of fixed volume at a temperature of 500. K and allowed to dissociate according to the reaction



When equilibrium is reached, the degree of dissociation of NOCl is found to be  $\alpha = 0.265$ , and the total pressure is measured to be 2.00 bar. Calculate the initial pressure of the NOCl gas before the dissociate reaction commences.

**Answer:**

Let  $n_0$  be the initial number of moles of NOCl.

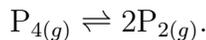
	$n_{\text{NOCl}}$	$n_{\text{NO}}$	$n_{\text{Cl}_2}$
initial	$n_0$	0	0
change	$-\alpha n_0$	$\alpha n_0$	$\alpha n_0/2$
equilibrium	$(1 - \alpha)n_0$	$\alpha n_0$	$\alpha n_0/2$

$$n_{\text{tot}} = n_{\text{NOCl}} + n_{\text{NO}} + n_{\text{Cl}_2} = n_0(1 + \alpha/2)$$

$$P_{\text{tot}} = \frac{n_{\text{tot}}RT}{V} = P_0(1 + \alpha/2)$$

$$2.00 \text{ bar} = P_0(1 + 0.265/2) \quad P_0 = 1.77 \text{ bar}$$

16. Consider the gas-phase reaction



At 1325 K, pure  $\text{P}_{4(g)}$  is placed in a container of fixed volume and temperature, and the initial pressure is found to be 1.80 bar. After equilibrium between  $\text{P}_{4(g)}$  and  $\text{P}_{2(g)}$  is attained, the total pressure is measured to be 2.00 bar. Calculate the mole fractions of  $\text{P}_{4(g)}$  and  $\text{P}_{2(g)}$  in the equilibrium mixture.

**Answer:**

	$n_{\text{P}_4}$	$n_{\text{P}_2}$
initial	$n_0$	0
change	$-\alpha n_0$	$2\alpha n_0$
equilibrium	$(1 - \alpha)n_0$	$2\alpha n_0$

$$n_{tot} = n_0(1 + \alpha)$$

$$P_{tot} = \frac{n_{tot}RT}{V} = \frac{n_0(1 + \alpha)RT}{V} = P_0(1 + \alpha)$$

$$2.00 = 1.80(1 + \alpha) \quad \alpha = 0.111$$

$$\chi_{\text{P}_4} = \frac{n_0(1 - \alpha)}{n_0(1 + \alpha)} = 0.800 \quad \chi_{\text{P}_2} = 1 - \chi_{\text{P}_4} = 0.200$$

17. Gas-phase phosgene dissociates into carbon monoxide gas and chlorine gas according to the reaction



When pure phosgene is introduced into a closed flask at 500.°C the initial pressure is found to be 1.82 bar and the total pressure when equilibrium is reached is found to be 3.50 bar. Calculate the mole fraction and partial pressure of phosgene gas in the equilibrium mixture.

**Answer:**

	$n_{\text{COCl}_2}$	$n_{\text{CO}}$	$n_{\text{Cl}_2}$
initial	$n_0$	0	0
change	$-\alpha n_0$	$\alpha n_0$	$\alpha n_0$
equilibrium	$n_0(1 - \alpha)$	$\alpha n_0$	$\alpha n_0$

$$n_{tot} = n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2} = n_0(1 + \alpha)$$

$$P_{tot} = \frac{n_{tot}RT}{V} = \frac{(1 + \alpha)n_0RT}{V} = (1 + \alpha)P_0$$

$$\alpha = \frac{P_{tot}}{P_0} - 1 = \frac{3.50}{1.82} - 1 = 0.923$$
$$\chi_{COCl_2} = \frac{n_{COCl_2}}{n_{tot}} = \frac{1 - \alpha}{1 + \alpha} = 4.00 \times 10^{-2}$$
$$P_{COCl_2} = \chi_{COCl_2} P_{tot} = 0.140 \text{ bar}$$