CHEM1612 Worksheet 3: Free Energy and the Gas Laws

Model 1: Enthalpy ($\Delta_{rxn}H$) and Entropy ($\Delta_{rxn}S$) of Reaction

In week 2, you developed a way of working out the value of enthalpy change for any reaction from the values of the enthalpies of formation of the reactants and products:

$$\Delta_{rxn}H° = \Delta_f H° \text{ (products)} - \Delta_f H° \text{ (reactants)} \qquad (1)$$

The change in entropy in a reaction can similarly be calculated as the difference in the entropies of the reactants and products:

$$\Delta_{rxn}S° = S° \text{ (products)} - S° \text{ (reactants)} \qquad (2)$$

Nitrogen dioxide, NO_2, is a prominent air pollutant. At low temperatures, it is in equilibrium with its dimer, N_2O_4. Starting from NO_2, the formation of the dimer can be studied using one of the two equations below:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad (A)$$

$$NO_2(g) \rightleftharpoons \tfrac{1}{2} N_2O_4(g) \qquad (B)$$

Starting from the dimer, the formation of NO_2 can be studied using one of the two equations below:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad (C)$$

$$\tfrac{1}{2} N_2O_4(g) \rightleftharpoons NO_2(g) \qquad (D)$$

Critical thinking questions

1. Using the data below, calculate $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction A.

   $\Delta_f H°$: $NO_2(g)$, 33 kJ mol^{-1}, $N_2O_4(g)$ 9 kJ mol^{-1}. $S°$: $NO_2(g)$, 240 J K^{-1} mol^{-1}, $N_2O_4(g)$ 304 J K^{-1} mol^{-1}

2. Explain in *words* the origin of the *sign* of $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ in terms of the chemical changes in the reaction.

3. Calculate $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction B. How are these values related to your answer to Q1?

4. Calculate $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction C and explain in *words* the origin of the *sign* of $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ in terms of the chemical changes in the reaction.

5. What are the values of $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction D?

Model 2: Free Energy of Reaction ($\Delta_{rxn}G$)

Reactions can be favoured if the products are more stable than the reactants. This occurs when the *enthalpy decreases*: $\Delta_{rxn}H < 0$. Reactions can also be favoured if the *entropy increases*: $\Delta_{rxn}S > 0$. Depending on the reaction, these factors can work together or in opposition. They are combined in the definition of the change in the *free energy*, $\Delta_{rxn}G$:

$$\Delta_{rxn}G° = \Delta_{rxn}H° - T\Delta_{rxn}S° \quad (3)$$

Because a favourable reaction may have $\Delta_{rxn}H < 0$ and / or $\Delta_{rxn}S > 0$, a favourable reaction will have $\Delta_{rxn}G < 0$.

Critical thinking questions

1. Is reaction A in Model 1 favourable or unfavourable with respect to the *enthalpy* factor?

2. Is reaction A in Model 1 favourable or unfavourable with respect to the *entropy* factor?

3. Is reaction C in Model 1 favourable or unfavourable with respect to the *enthalpy* factor?

4. Is reaction C in Model 1 favourable or unfavourable with respect to the *entropy* factor?

5. Given your answers to Q1 – 4 and the equation for $\Delta_{rxn}G°$ above, what additional factor needs to be considered to predict whether reaction A or C is favourable?

6. Calculate $\Delta_{rxn}G°$ for reaction A at the two temperatures below and predict whether the reaction is favourable.

   (a) $T = 298$ K

   (b) $T = 398$ K

7. Calculate $\Delta_{rxn}G°$ for reaction C at the two temperatures below and predict whether the reaction is favourable.

   (a) $T = 298$ K

   (b) $T = 398$ K

8. Using your answer to Q6, predict what happens to an *exothermic* reaction as the temperature is increased.

9. Using your answer to Q7, predict what happens to an *endothermic* reaction as the temperature is increased.

10. What combination of signs for $\Delta_{rxn}H$ and $\Delta_{rxn}S$ lead to a reaction that is *never* favourable?

Model 3: The Gas Laws

- Boyle's Law (1660). The volume of a gas varies inversely with pressure:

  $V = k_B \times \frac{1}{P}$ k_B is Boyle's constant

- Charles' Law (1787). The volume of a gas varies linearly with temperture:

  $V = k_C \times T$ k_C is Charles' constant

- Avogadros' Hypothesis (1812). The volume of a gas varies linearly with the number of moles:

  $V = k_A \times n$ k_C is Avogadro's gas constant

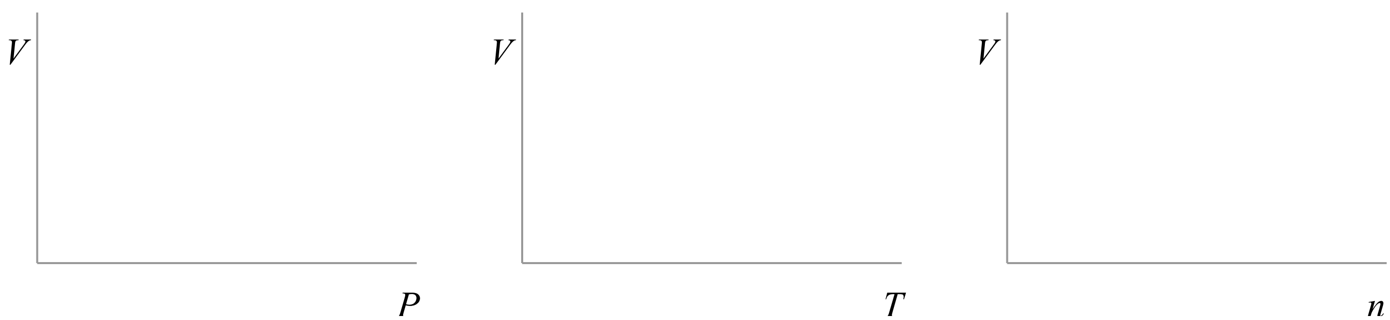
- These are unified in the ideal gas law:

  $PV = nRT$ R is the universal gas constant

Critical thinking questions

1. *Sketch* on the graph below how the volume of a gas changes as:

   (i) P is increased (ii) T is increased (iii) n is increased



2. One mole of gas occupies 22.414 L at a pressure of 1.000 atm and a temperature of 0 °C (273.15 K). This is known as standard temperature and pressure or STP.

   Use the ideal gas law to work out the value of the universal gas constant, R, and its units using this data.

3. The S.I. unit for volume is m^3 and for pressure is Pa where 1 m^3 = 1000 L and 1 atm = 1.01325×10^5 Pa.

   (a) What is the volume occupied by one mole of gas at STP in m^3?

   (b) Use the ideal gas law to work out the value of the universal gas constant, R, and its units when volume and pressure are given in S.I. units.

Model 4: Partial Pressures

In a mixture of gases, the *partial pressure* of a gas is the pressure it would have if it alone occupied the volume. The total pressure of a gas mixture is the sum of the partial pressures of each individual gas in the mixture:

$$P = P_A + P_B + P_C + P_D + ... = \sum_i P_i$$

Critical thinking questions

These exercises are based on those used in the theory parts of scuba diving courses.

The density of salt water is 1.03 g mL^{-1} which translates to an increase in pressure of 1.00 atm for every 10.0 m of depth below the surface. If the pressure at the surface is 1.00 atm, it will be 2.00 atm at 10.0 m, 3.00 atm at 20.0 m, 4.00 atm at 30.0 m etc. Scuba equipment controls the air flow to the lungs so that their *volume* is the same at depth as at the surface. It does this by providing air at a *pressure* equal to that of the water at that depth.

1. The density of air at 1.000 atm and 25°C is 1.186 g L^{-1}. Assuming that air is 80% nitrogen and 20% oxygen by volume, what are the partial pressures of the two gases?

2. A balloon is inflated at the surface to 6.0 L, the approximate volume of the lungs. What volume would the balloon have at a depth of 15.0 m?

3. At a depth of 30.0 m, the balloon is filled from a cylinder to a volume of 5.0 L and sealed. What volume will the balloon be at the surface?

4. A 'reverse block' is a painful effect that occurs when air is trapped inside a cavity (such as in the ears or inside a tooth) during a diver's ascent. Discuss with your group the cause of the pain.

5. A 12 L air cylinder is filled to a pressure of 200. atm in an air conditioned diving shop at 22 °C. What will be the pressure inside the tank once it has been left in the sun at 35 °C?

6. What happens to the *density* of the air in a diver's lungs during descent?

7. What is the partial pressure of O_2 in a diver's lungs at a depth of 10.0 m?

8. Oxygen toxicity occurs when its partial pressure reaches around 1.6 atm*. What depth of water does this correspond to?

---

* This figure is dependent on the time spent and the individual physiology and is used here for illustrative purposes only