

1) Does reaction with a decrease in enthalpy ($\Delta H < 0$) always proceed spontaneously?

NO, spontaneity depends on ΔG which is a function of BOTH ΔH and ΔS

2) When a substance converts from gas \rightarrow liquid, what is the change in entropy?

This state change leads to a decrease in entropy, the liquid state is MORE ordered (LESS random) than the gaseous state.

3) If a reaction is third-order with respect to reactant A, what effect will doubling the concentration of A do to the reaction rate?

The rate will be EIGHT times larger.

4) Is the molar entropy of water vapor (g) greater or less than that of hydrogen gas?

Greater, more atoms equals more microstates.

5) Which combinations of ΔH and ΔS lead to ΔG values which are NOT dependent on temperature?

$\Delta H > 0$ paired with $\Delta S < 0$

$\Delta H < 0$ paired with $\Delta S > 0$

6) List several examples of changes which INCREASE entropy, we went over 4 cases at the start of Ch 18.

State change from solid to liquid or liquid to gas

Dissolving and ionic solid to form an aqueous solution

Raising the temperature of a substance

Reactions which produce larger numbers of moles

7) What is MOLAR ENTROPY and how do we know if one molecule has a greater molar entropy than another?

The value of entropy for 1 mole of a substance at standard conditions. This value depends on the state of the substance (s, l, g) as well as the number of atom/particles that the substance consists of.

8) What is the SECOND law of thermodynamics and what does it tell us about spontaneity?

The entropy of the universe increases in a spontaneous process ($\Delta S_{\text{univ}} > 0$) and is unchanged during equilibrium ($\Delta S_{\text{univ}} = 0$).

9) Predict the signs of ΔH , ΔS , and ΔG for the condensation of water vapor on your bathroom mirror at 32 °C.

$\Delta H < 0$, this is an EXOTHERMIC process

$\Delta S < 0$, the liquid state is lower entropy than the gaseous state

$\Delta G < 0$, at ANY temperature that is less than the boiling point of water (100 °C), this will occur spontaneously

10) For a reaction, $\Delta H^\circ = 80.9 \text{ kJ}$ and $\Delta S^\circ = -80.7 \text{ J/K}$, calculate ΔG° . Is this reaction spontaneous at 25 °C?

$$\Delta G = \Delta H - T\Delta S$$

$$\begin{aligned}\Delta G &= (80.9 \text{ kJ}) - (298 \text{ K})(0.0807 \text{ kJ/K}) \\ &= 56.85 \text{ kJ}\end{aligned}$$

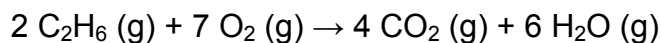
It is non-spontaneous at this temperature. That is what the positive value tells you!

11) If a reaction is non-spontaneous at a given temperature, how would you determine when the reaction becomes spontaneous?

Solve the free-energy equation for temperature.

$T = \Delta H / \Delta S$, This temperature will be the point at which the reaction switches from being non-spontaneous to spontaneous.

12) Write the rate expressions for all reactants and products:



$$-\frac{1}{2} \frac{\Delta[\text{C}_2\text{H}_6]}{\Delta t} \quad -\frac{1}{7} \frac{\Delta[\text{O}_2]}{\Delta t} \quad +\frac{1}{4} \frac{\Delta[\text{CO}_2]}{\Delta t} \quad +\frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

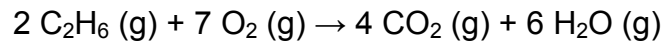
13) A reaction has the following rate law: $\text{Rate} = k[\text{A}]^2[\text{B}]^3$. If the concentration of **A** is **doubled** and the concentration of **B** is **tripled**, by what factor will the rate increase?

The new rate is 108 times larger.

14) For a second-order reaction, how can you graphically determine the rate constant (k)?

Plot $\frac{1}{[\text{A}]}$ vs t, the slope of the line will be equal to the rate constant.

15) For the following reaction, the rate of O₂ loss was measured to be 0.352 M/s.



Determine the rate of CO₂ production over the same period of time.

$$\frac{1}{7} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{7} \frac{0.352 \text{M}}{\text{s}}$$

$$\frac{1}{4} \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{7} \frac{0.352 \text{M}}{\text{s}}$$

$$\frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{4}{7} \frac{0.352 \text{M}}{\text{s}} = 0.201 \text{ M/s}$$

16) A given reaction is determined to be first-order with a rate constant of 0.025 min⁻¹. If the reaction is started with an initial concentration of reactant A of 0.500 M, what will be the concentration of A after 7.5 minutes?

$$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$$

$$\ln[\text{A}]_t = -(0.025 \text{ min}^{-1})(7.5 \text{ min}) + \ln(0.500 \text{ M})$$

$$\ln[\text{A}]_t = -0.8806$$

$$[\text{A}]_t = e^{(-0.8806)} = 0.4145 \text{ M}$$

17) A certain first-order reaction starts with an initial concentration of 0.50 M. 75% of this reactant is used up in 10 minutes. What is the half-life (t_{1/2}) of the reaction?

You need to calculate k before you can do anything with half-life.

$$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$$

$$\ln(0.125) = -k(10 \text{ min}) + \ln(0.50) \quad \text{SOLVE for } k$$

$$k = 0.2772 \text{ min}^{-1}$$

$$t_{1/2} = 0.693/k$$

$$= (0.693)/(0.2772 \text{ min}^{-1})$$

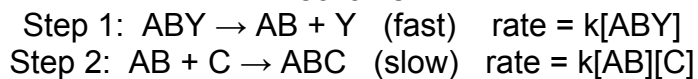
$$= 4.99 \text{ min}$$

18) Explain why all collisions between reactant molecules do not lead to product formation.

- may not have total energy which exceeds E_a
- may not collide in proper orientation

19) The following reaction has the mechanism shown below. $ABY + C \rightarrow ABC + Y$

Mechanism

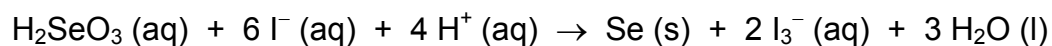


Write the rate law for this reaction.

The rate law for the overall reaction is determined by the SLOWEST step in the reaction, in this case it is step 2.

Rate Law: rate = $k[AB][C]$

20) Determine the order of each reactant and write the RATE LAW for this reaction.



$[H_2SeO_3]$	$[H^+]$	$[I^-]$	Initial Rate (M/s)
$1.0 \times 10^{-4} M$	$1.0 \times 10^{-2} M$	$1.0 \times 10^{-2} M$	1.66×10^{-7}
$3.0 \times 10^{-4} M$	$1.0 \times 10^{-2} M$	$1.0 \times 10^{-2} M$	4.98×10^{-7}
$1.0 \times 10^{-4} M$	$3.0 \times 10^{-2} M$	$1.0 \times 10^{-2} M$	14.94×10^{-7}
$1.0 \times 10^{-4} M$	$1.0 \times 10^{-2} M$	$2.0 \times 10^{-2} M$	6.64×10^{-7}

rate = $k[H_2SeO_3][H^+]^2[I^-]^2$