JANUARY 2024 Canadian Chemistry Olympiad Problem Set

Kinetics Problem Set

1. Determination of rate laws from experimental data:

$$BrO_3^-{}_{(aq)} + 5\ Br^-{}_{(aq)} + 6\ H^+{}_{(aq)} \rightarrow 3\ Br_{2(aq)} + 3\ H_2O_{(l)}$$

Experimental data	Initial concentration (in M)			Initial rate (in M s^{-1})
	$[BrO_3^-]$	$[Br^-]^I$	$[H^+]$	
1		0.10	0.10	$v_1 = 1.2 \cdot 10^{-3}$
2	0.20	0.10	0.10	$v_2 = 2.4 \cdot 10^{-3}$
3	0.10	0.30	0.10	$v_3 = 3.6 \cdot 10^{-3}$
4	0.20	0.10	0.15	v4 = $5.4 \cdot 10^{-3}$

2. Given that all the data above satisfy a rate equation of the form: rate = k $[BrO_3^-]^a[Br^-]^b[H^+]^c$
Determine the value of *a*.

3. Given that all the data above satisfy a rate equation of the form: rate = k $[BrO_3^-]^a[Br^-]^b[H^+]^c$
Determine the value of *b*.

4. Given that all the data above satisfy a rate equation of the form: rate = k $[BrO_3^-]^a[Br^-]^b[H^+]^c$
Determine the value of *c*.

5. Determine the rate constant *k* (round to the closest integer)

6. Determine the unit of *k*.
A) $M^{-1}\ s^{-1}$
B) $M^{-2}\ s^{-1}$
C) M^2 s
D) s^{-1}
E) $M^{-3}\ s^{-1}$

7. The highly toxic gas carbonyl chloride (phosgene) is used to synthesize many organic compounds.

$$CO_{(g)} + Cl_{2\,(g)} \rightarrow COCl_{2\,(g)}$$

Experimental data:

	Initial concentration [X] in M		
Experiment	[CO]	$[Cl_2]$	Initial rate in M s^{-1}
1	0.12	0.20	0.121
2	0.24	0.20	0.241
3	0.24	0.40	0.682

Given that all the data above satisfy a rate equation of the form: rate = k $[CO]^a[Cl_2]^b$, determine the value of *a*.

8. Given that all the data above satisfy a rate equation of the form: rate = k $[CO]^a[Cl_2]^b$, determine the value of *b*.

9. Determine the rate constant *k* with 2 decimal places.

10. What is the unit of *k*?
A) $M^{-1}\ s^{-1}$
B) $M^{-0.5}\ s^{-1}$
C) $M^{-2.5}\ s^{-1}$
D) s^{-1}
E) $M^{-1.5}\ s^{-1}$

11. For the reaction: $2\ A + B + C \rightarrow \text{Products}$
the following data were obtained with a fixed initial concentration of B:

Run	$[A]_0$ (M)	$[C]_0$ (M)	Initial Rate (M/min)
I	0.1	0.1	0.1
II	0.1	0.2	0.2
III	0.2	0.4	0.4

In an entirely different experiment in which $[A]_0$= 10 M; $[B]_0$ = 0.02 M, and $[C]_0$ = 0.02 M, the following results were found:

Time (min)	0	5	15	75
[B] (M)	0.02	0.01	0.005	0.00125

Given that all the data above satisfy a rate equation of the equation of the form: rate = $k\,[A]^a[B]^b[C]^c$
Determine the value of *k* with no unit (round to the closest integer).

12. Given that all the data above satisfy a rate equation of the form: rate = $k\,[A]^a[B]^b[C]^c$. What is the unit of *k*?
A) $M^{-1}\ min^{-1}$
B) $M^{-1}\ min$
C) $M^{-2}\ min^{-1}$
D) min^{-1}
E) $M\ min^{-1}$

13. Given that all the data above satisfy a rate equation of the form: rate = $k\,[A]^a[B]^b[C]^c$
Enter the value of *a* below.

14. Given that all the data above satisfy a rate equation of the form: rate = $k\,[A]^a[B]^b[C]^c$
Enter the value of *b* below.

15. Given that all the data above satisfy a rate equation of the form: rate = $k\,[A]^a[B]^b[C]^c$
Enter the value of *c* below.

16. Iodine 131 has e half-life of 8 days and decays by a first order process (as is always the case for radioactive decay). How much of a 8.0 grams sample of iodine 131 will remain after 15.0 days?
Report your answer in grams with 3 decimal places.

17. Mercury(II) is eliminated from the body by a 1^{st} order process that has a $t_{1/2}$ of 6 days. A farming family accidentally ingested mercury(II) by eating contaminated grain. What percentage of the mercury(II) would remain in their bodies after 30 days if therapeutic measures were not taken?
Provide your answer with 3 decimal places.

18. After the earthquake and tsunami disaster, the soil, the air, and the water near the Fukushima Daiichi Nuclear Power Plant in Japan was found to be contaminated with radioactive ^{137}Cs which has a half-life of 30.1 years. How many years must pass before the radioactivity drops to 10% of its initial value?
Round your answer to the closest integer.

19. The first-order rate constant for the gas fase decomposition of dimethyl ether is $3.2\ \cdot 10^{-4}\ s^{-1}$ at 450 °C. The reaction is carried out in a constant volume container. Initially only the reactant, dimethyl ether, is present and the pressure is 0.387 atm.

a. What is the pressure (in atm) of the reactant after 210.0 seconds? Assume ideal-gas behaviour.

Provide your answer with 4 decimal places.

20. The first-order rate constant for the gas fase decomposition of dimethyl ether is $3.2\ \cdot 10^{-4}\ s^{-1}$ at 450 °C. The reaction is carried out in a constant volume container. Initially only the reactant, dimethyl ether, is present and the pressure is 0.387 atm.

b. What is the total pressure (in atm) after 211.0 seconds if the reaction is: $C_2H_6O \rightarrow CH_4 + CO + H_2$

Provide your answer with 4 decimal places.

21. 1. In aqueous solution, the inversion of sucrose to form glucose and fructose is catalyzed by H^+.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H+} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(ftuctose)}}{C_6H_{12}O_6}$$

The kinetics of this reaction follows the rate equation: $-\dfrac{d[sucrose]}{dt} = k\,[H_2O][H^+][\text{sucrose}]$.

a. In a dilute acqueous solution of pH 5 at T = 300 K, it was found that 10% of the sucrose had inverted in 1 minute. What is the value of k?
Provide your answer to 2 decimal places with no units.

22. b. What is the unit of k?

A) $M^{-2}\ min^{-1}$
B) $M\ min^{-1}$
C) $M^{-1}\ min^{-1}$
D) $M^{-1}\ min^{-2}$
E) $M^{-1}\ min$

23. c. A solution of 10^{-2} mol/L in each of sucrose, H_2O and HCl in the organic solvent dioxane was prepared. If k is independent of solvent, how long (in minutes) would it take at 300 K to invert 87.5% of the sucrose? Provide your answer to one decimal place.

24. 2. The rate of a certain chemical reaction is found to increase by the factor 3.0 from 87.1 to 145.9 °C What is the activation energy (in kJ/mol) for this reaction?
Round your answer to the first decimal place.

25. 1. The following reaction of methane with molecular chlorine

$$CH_{4\,(g)} + Cl_{2\,(g)} \rightarrow CH_3Cl_{\,(g)} + HCl_{\,(g)}$$

has the following mechanism in terms of elementary reactions with rate constant k_a, k_b, k_c, and k_d

step l ....$Cl_2 \rightarrow 2\ Cl\cdot$	k_a
step 2....$CH_4 + Cl\cdot \rightarrow \cdot CH_3 + HCl$	k_b
step 3. ..$\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$	k_c
step 4....$Cl\cdot + Cl\cdot \rightarrow Cl_2$	k_d

a. Choose any intermediate(s) below.

A) CH_4
B) Cl_2
C) CH_3Cl
D) HCl
E) $\cdot CH_3$
F) $Cl\cdot$

26. b. Deriving the rate law for the overall reaction gives a rate law of the form:

$$v = k_{observed}\,[CH_4]^a[Cl_2]^b[CH_3Cl]^c[HCl]^d$$

Which of the following expression is equal to $k_{observed}$?

A) $k_{obs} = \sqrt{\dfrac{k_a^{\,2}k_b}{k_d}}$ B) $k_{obs} = \sqrt{\dfrac{k_a k_b^{\,2}}{k_d}}$ C) $k_{obs} = \dfrac{k_a k_b}{k_d}$ D) $k_{obs} = \sqrt{k_a k_b k_c}$

E) $k_{obs} = \dfrac{1}{2}\sqrt{\dfrac{k_a k_b^{\,2}}{k_d}}$

27. c. Give the value of b

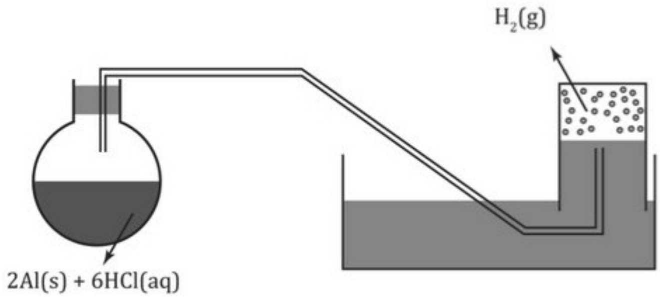
28. d. Give the value of c

Thermodynamic Problem Set

1. 1. Use the ideal gas law to calculate the pressure, in atm, exerted by 1.00 mol of $Cl_{2\,(g)}$ confined to a volume of 2.00 L at 273 K.
Provide your answer with 1 decimal place.

2. 2. The reaction of aluminum with HCl produces hydrogen gas. 35.5 mL of H_2 is collected in a sealed container over water at 26 °C and the pressure is measured to be 755 mmHg. How many moles of H_2 were produced? (The vapour pressure of water at 26 °C is 25.2 mmHg)

$$2\,Al_{(s)} + 6\,HCl_{(aq)} \rightarrow 2\,AlCl_{3\,(aq)} + 3\,H_{2\,(g)}$$



Provide your answer with 3 significant figures.

3. Aerospace engineers sometimes write the gas law in terms of the mass of the gas rather than the number of moles.

$$PV = mR_{specific}T$$

In such a formulation, the molar mass of the gas must be incorporated into the value of the gas constant (the gas constant will change for different gases, represented by $R_{specific}$ in the above equation).

3. Assume the mole fractions of O_2 and N_2 in air are 0.21 and 0.79, respectively. Calculate the average molar mass of air (the mass of one mole of air) and use this number to calculate $R_{specific}$ for air in $m^2\,s^{-2}\,K^{-1}$.
Provide your answer of $R_{specific}$ with 1 decimal place.

4. 1. A quantity of 0.850 moles of an ideal gas initially at a pressure of 15.0 atm and 300 K is allowed to expand isothermally until its final pressure is 1.00 atm. Calculate the work (w), in kJ, when the expansion is done against a constant external pressure.
Provide your answer with 2 decimal places.

5. 2. Work may be done by a system or on the system during phase changes. Calculate the work for:
a. The complete conversion of 1 mol of ice to water at 273 K and 1 atm. The molar volumes of ice and water al 273 K are 0.0196 L mol^{-1} and 0.0180 L mol^{-1}, respectively, (in J with 3 decimal places)

6. b. The complete conversion of 1 mol of water to steam at 373 K and 1 atm. The molar volume of water 373 K is 0.0188 L mol^{-1}. (in J rounded to the nearest integer)

7. 3. One mole of carbon and 0.5 mol of oxygen undergo the reaction

$$C_{(s)} + {}^{1}/_{2}\,O_{2\,(g)} \rightarrow CO_{(g)}$$

in an enclosed container with a freely moveable piston exposed to a constant external pressure of 1 atm and immersed in a heat bath at 298 K. The heat evolved for the reaction as written is determined to be 213.21 kJ.
a. Determine the volume change for the reaction, in L.
Provide your answer with 2 decimal places.

8. b. For the production of 1 mol of $CO_{(g)}$, determine the work (*w* in kJ).
Provide your answer with 2 decimal places.

9. c. Using the above, determine ΔU for the reaction (in kJ).
Provide your answer with 2 decimal places.

10. 1. When 1 mol of glycine (NH_2CH_2COOH) undergoes a combustion reaction al constant atmospheric pressure (1 atm), 981.0 kJ of heat are released. Calculate *q*, *w*, ΔU and ΔH when 5.0 g of glycine are burned at a constant pressure of 1.00 atm and T= 298 K. Assume that the combustion is complete and that two of the combustion products are nitrogen gas and liquid water.
Enter *q* in kJ with 1 decimal place.

11. Enter *w* in kJ with 4 decimal places.

12. Enter ΔU in kJ with 1 decimal place.

13. Enter ΔH in kJ with 1 decimal place.

14. 2. Consider the combustion of methanol:

$$2\ CH_3OH_{(l)} + 3\ O_{2\ (g)} \rightarrow 4\ H_2O_{(l)} + 2\ CO_{2\ (g)} \qquad \Delta H^\circ = -1453.0\ kJ$$

What is the value of ΔH° under each of the following conditions, in kJ, do not round your answer:

a. 3 moles of methanol are reacted:

15. b. The direction of the reaction is reversed

16. c. Water vapor is produced during the reaction instead of liquid water (ΔH°_{vap} = 44.0 kJ mol^{-1})

17. 3. Lithium oxide is used to lower the melting point of ceramic precursors. Use the enthalpies below to determine ΔH° (in kJ with l decimal place) for the reaction:

$$2\ LiH_{(s)} + O_{2\ (g)} \rightarrow Li_2O_{(s)} + H_2O_{(l)}$$

$$2\ LiOH_{(s)} \rightarrow Li_2O_{(s)} + H_2O_{(l)} \qquad \Delta H^\circ = 379.1\ kJ$$
$$LiOH_{(s)} + H_{2\ (g)} \rightarrow LiH_{(s)} + H_2O_{(l)} \qquad \Delta H^\circ = 111.0\ kJ$$
$$2\ H_2O_{(l)} \rightarrow 2\ H_{2\ (g)} + O_{2\ (g)} \qquad \Delta H^\circ = 285.9\ kJ$$

18. 4. Use the following heat of combustion data to determine the enthalpy of formation of methanol (CH_3OH) in kJ mol^{-1} with 1 decimal place.

$$CH_3OH_{(l)} + {}^3/_2\ O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2\ H_2O_{(l)} \qquad \Delta H^\circ = -726.4\ kJ$$
$$C_{(graphite)} + O_{2\ (g)} \rightarrow CO_{2\ (g)} \qquad \Delta H^\circ = -393.5\ kJ$$
$$H_{2\ (g)} + {}^1/_2\ O_{2\ (g)} \rightarrow H_2O_{(l)} \qquad \Delta H^\circ = -285.8\ kJ$$

19. 5. ΔH°_{vap} for the evaporation of liquid oxygen: $O_{2\ (l)} \rightarrow O_{2\ (g)}$ is 6.82 kJ mol^{-1}. Determine ΔH°_f for $O_{2\ (l)}$ in kJ mol^{-1} with 2 decimal places.

20. 1. Hydrazine (H_2NNH_2) was used as a rocket fuel in World War II. Hydrazine acts as a base as described by the reaction below:

$$H_2NNH_{2\ (aq)} + H_2O_{(l)} \rightarrow H_2NNH_3{}^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K_b = 3.0 \cdot 10^{-6}$$

a. Calculate ΔG°, in kJ, for the reaction at 298 K (round your answer to the closest integer).

21. b. What is the value of ΔG_{rxn} at equilibrium?

22. c. What is the value of ΔG_{rxn}, in kJ, at 298 K when [OH^-] = 2.37 ·10^{-5} M; [$H_2NNH_3{}^+$] = 7.89 ·10^{-3} M; [H_2O] = 55.5 M, and [H_2NNH_2] = 0.061 M?
Provide your answer with 2 decimal places.

23. 2. Glucose and fructose phosphates are found at equilibrium ($Glu_{(aq)} \rightarrow Fru_{(aq)}$) in metabolic pathways. ΔG° at 298 K is 1.67 kJ for this reaction.

a. Determine the equilibrium constant for the reaction as written at 298 K.

Provide your answer with 2 decimal places.

24. b. What is the composition (%Glu and %Fru) at equilibrium at 298K?
Enter %Glu below (round to the closest integer).

25. 3. Consider the equilibrium below:

$$N_2O_{4\,(g)} \rightarrow 2\ NO_{2\,(g)}$$

and the thermodynamic data in the table.

	$N_2O_{4\,(g)}$	$NO_{2\,(g)}$
$\Delta H_f°$ (kJ mol^{-1})	9.66	33.84
$\Delta G_f°$ (kJ mol^{-1})	98.28	51.84
$S_m°$ (J mol^{-1} K^{-1})	304.3	240.45

a. At what temperature (in K) will an equilibrium mixture contain one bar pressure EACH of $N_2O_{4\,(g)}$ and $NO_{2\,(g)}$?
Provide your answer with 1 decimal place.

26. b. At what temperature (in K) will an equilibrium mixture at a total pressure of 1.00 bar contain twice as much NO_2 as N_2O_4?
Round your answer to the closest integer.

27. c. To what temperature (in K) must the system be raised to make the equilibrium constant equal to 1000?
Round your answer to the closest integer.