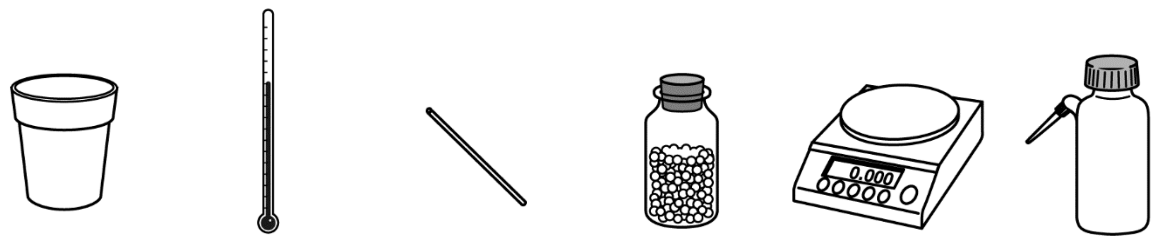
(c) Calculate the concentration of urea, in mol/L, in the saturated solution at 20.°C.

(d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 *M*. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.



Polystyrene Cup | Thermometer | Stirring Rod | Bottle of Urea | Balance | Distilled Water

(e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

	$S°$ (J/(mol·K))
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	?

(f) The entropy change for the dissolution of urea, ΔS°_{soln}, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, $S°$, of aqueous urea.

(g) Using particle-level reasoning, explain why ΔS°_{soln} is positive for the dissolution of urea in water.

(h) The student claims that $\Delta S°$ for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

The student decides to determine the molarity of the same Na_2CO_3 solution using a second method. When Na_2CO_3 is dissolved in water, $CO_3^{2-}(aq)$ hydrolyzes to form $HCO_3^-(aq)$, as shown by the following equation.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows HCO_3^-(aq) + OH^-(aq) \qquad K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 2.1 \times 10^{-4}$$

(f) The student decides to first determine $[OH^-]$ in the solution, then use that result to calculate the initial concentration of $CO_3^{2-}(aq)$.

(i) Identify a laboratory method (not titration) that the student could use to collect data to determine $[OH^-]$ in the solution.

(ii) Explain how the student could use the measured value in part (f)(i) to calculate the <u>initial</u> concentration of $CO_3^{2-}(aq)$. (Do not do any numerical calculations.)

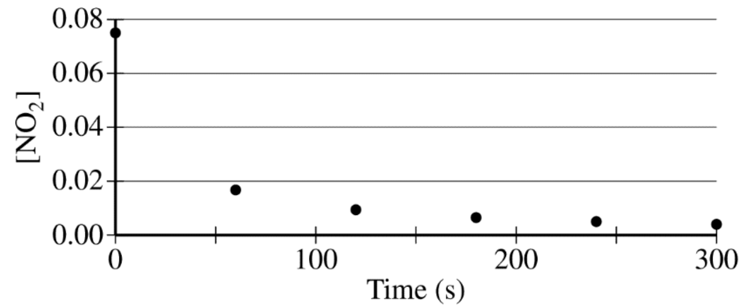
(g) In the original Na_2CO_3 solution at equilibrium, is the concentration of $HCO_3^-(aq)$ greater than, less than, or equal to the concentration of $CO_3^{2-}(aq)$? Justify your answer.

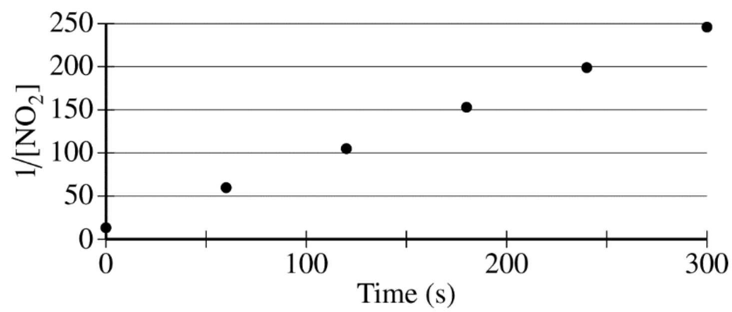
(h) The student needs to make a CO_3^{2-}/HCO_3^- buffer. Is the Na_2CO_3 solution suitable for making a buffer with a pH of 6? Explain why or why not.

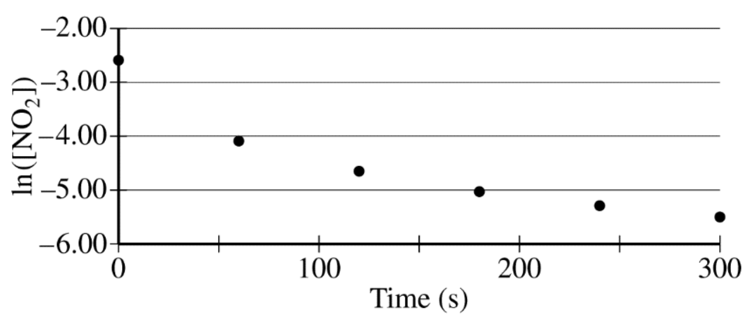
6. Nitrogen dioxide, $NO_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

(b) Write the rate law for the decomposition of $NO_2(g)$.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism I

Step 1:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step 2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b) ? Justify your answer.

Mechanism II

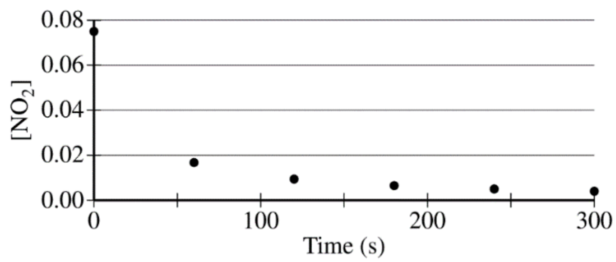
Step 1:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$	*slow*

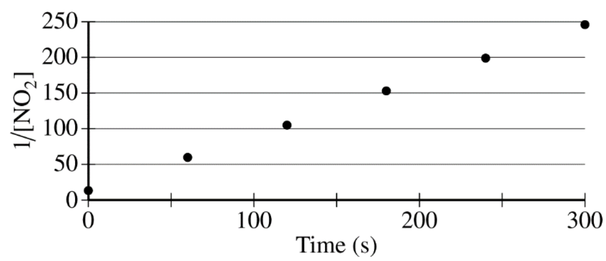
Question 6

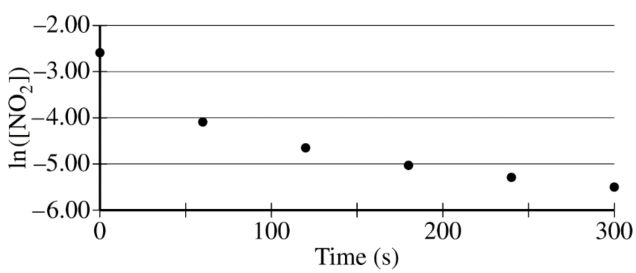
Nitrogen dioxide, $NO_2(g)$, is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $NO_2(g)$ decomposes according to the equation below.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

The concentration of a sample of $NO_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.







(a) Explain how the graphs indicate that the reaction is second order.

The linear graph of $\frac{1}{[NO_2]}$ vs. time indicates a second-order reaction.	1 point is earned for the correct answer.

Question 6 (continued)

(b) Write the rate law for the decomposition of $NO_2(g)$.

rate = $k[NO_2]^2$	1 point is earned for the correct answer.

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I

Step 1:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step 2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

Yes. Step 1 is slow, therefore it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[NO_2][NO_2] = k[NO_2]^2$, which is consistent with the second-order rate law in part (b).	1 point is earned for the correct answer with justification.

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism II

Step 1:	$NO_2(g) + NO_2(g) \rightleftarrows N_2O_4(g)$	*fast equilibrium*
Step 2:	$N_2O_4(g) \rightarrow 2\ NO(g) + O_2(g)$	*slow*

Yes. Step 2 is slow; therefore, it is the rate-determining step of this mechanism. The rate law of this elementary reaction is rate = $k[N_2O_4]$. Because N_2O_4 is an intermediate, it cannot appear in the rate law of the overall reaction. Because $K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$ in step 1, $[N_2O_4] = K_{eq}[NO_2]^2$. Then, substituting $K_{eq}[NO_2]^2$ for $[N_2O_4]$ in the rate law of step 2 gives rate = $(k\ K_{eq})[NO_2]^2$, which is consistent with the rate law in part (b).	1 point is earned for the correct answer with justification.