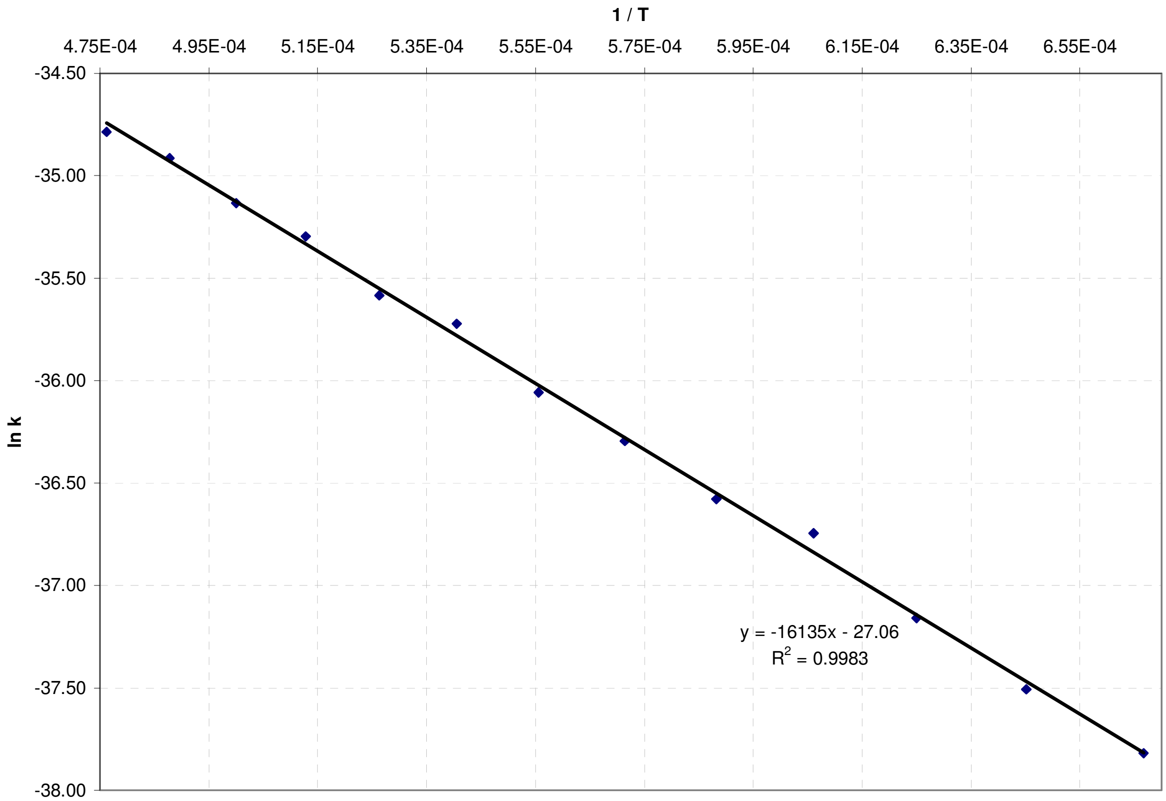
CHM 106
Exam I

1. Kinetic studies on the reaction $CS_2(g) + O_2(g) \rightarrow CS(g) + SO_2(g)$ were conducted at a variety of temperatures. A plot of the natural log of the rate constant versus the reciprocal of the temperature is shown below.



Calculate the value of the activation energy for this reaction.

2. The species triphenylmethyl, $(C_6H_5)_3C$, is an unusual organic compound because it is stable, despite the fact that it has an unpaired electron. This species is in equilibrium with its dimer ($C_{38}H_{30}$) as shown below:

$$2\,(C_6H_5)_3C \Leftrightarrow C_{38}H_{30}$$

The equilibrium constant for this reaction is $K = 2.51 \times 10^3$.

a) If the initial concentration of triphenylmethyl and its dimer are both 0.100 M, what direction must the system shift in order to reach equilibrium?

b) Calculate the equilibrium concentration of triphenylmethyl.

3. Suppose the following reaction is at equilibrium:

$$UO_2(s) + 4\ HF(g) \Leftrightarrow UF_4(g) + 2\ H_2O(g)$$

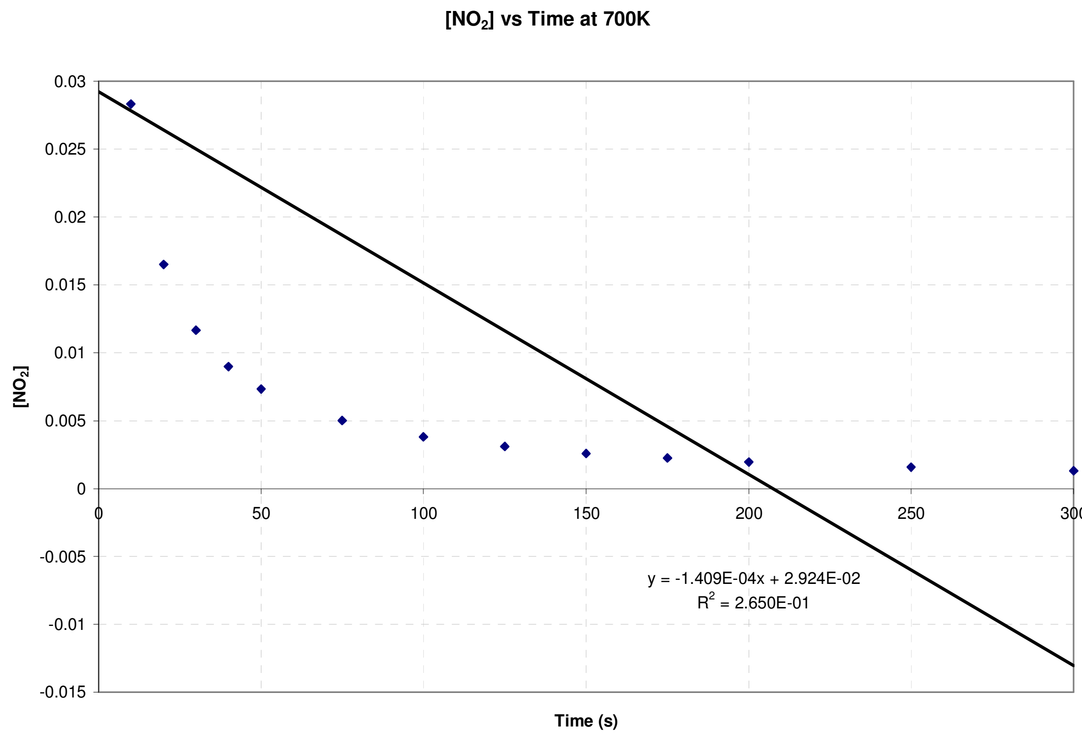
Predict the effect that each of the following changes has on the equilibrium, and explain your answer.

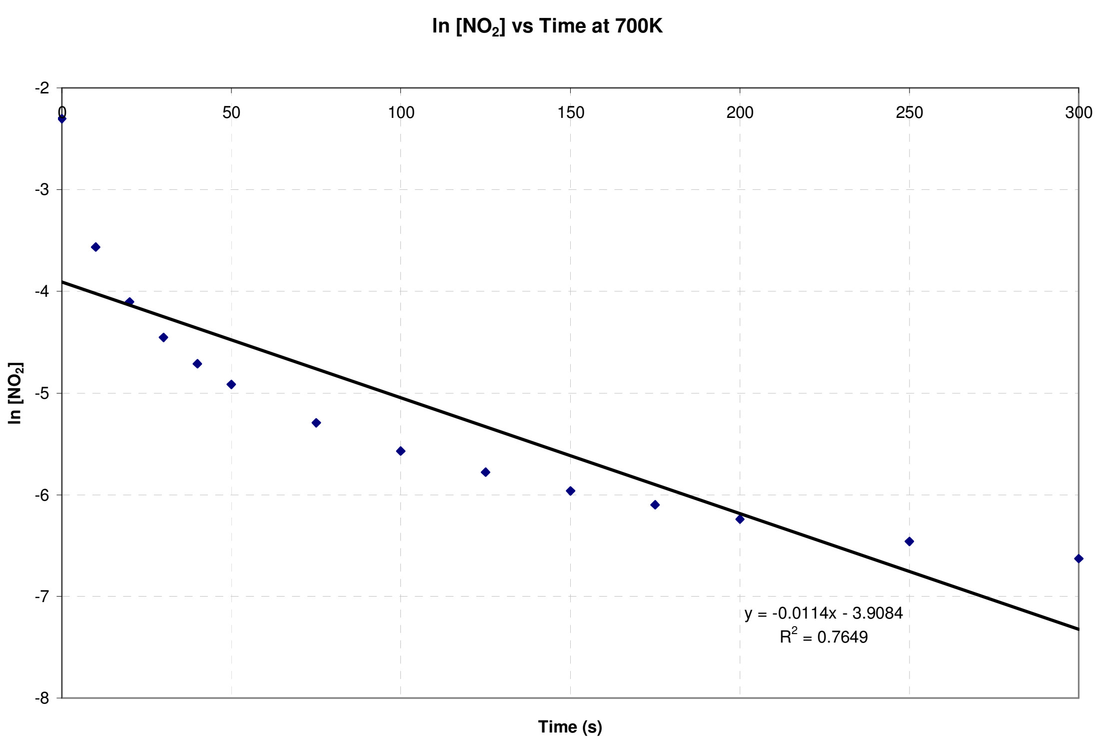
a) Additional $UO_2(s)$ is added to the reaction vessel.

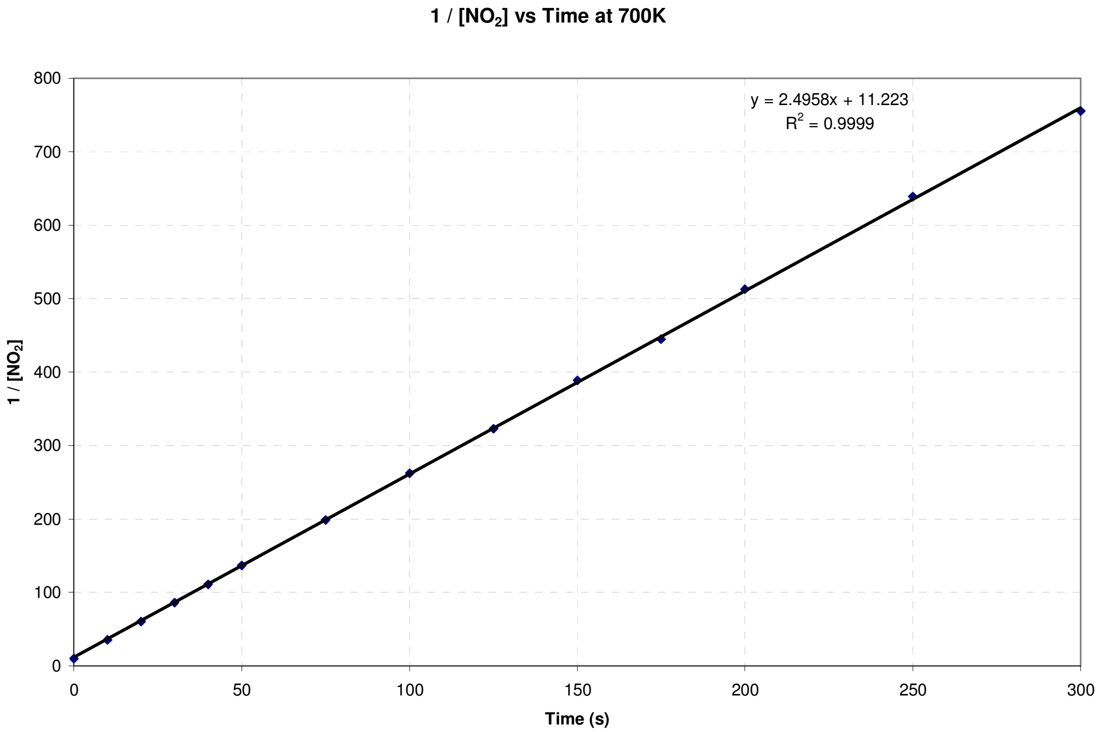
b) The reaction is performed in a glass vessel and the HF(*g*) reacts with the glass.

c) Water vapor is removed from the reaction vessel.

4. The reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ was studied in several different kinetic experiments. In the first group of experiments, (conducted at a temperature of 700K) the concentration of $[NO_2]$ was observed over time. Three plots were prepared, of $[NO_2]$ versus time, ln $[NO_2]$ versus time, and 1 / $[NO_2]$ versus time. The plots are presented below.



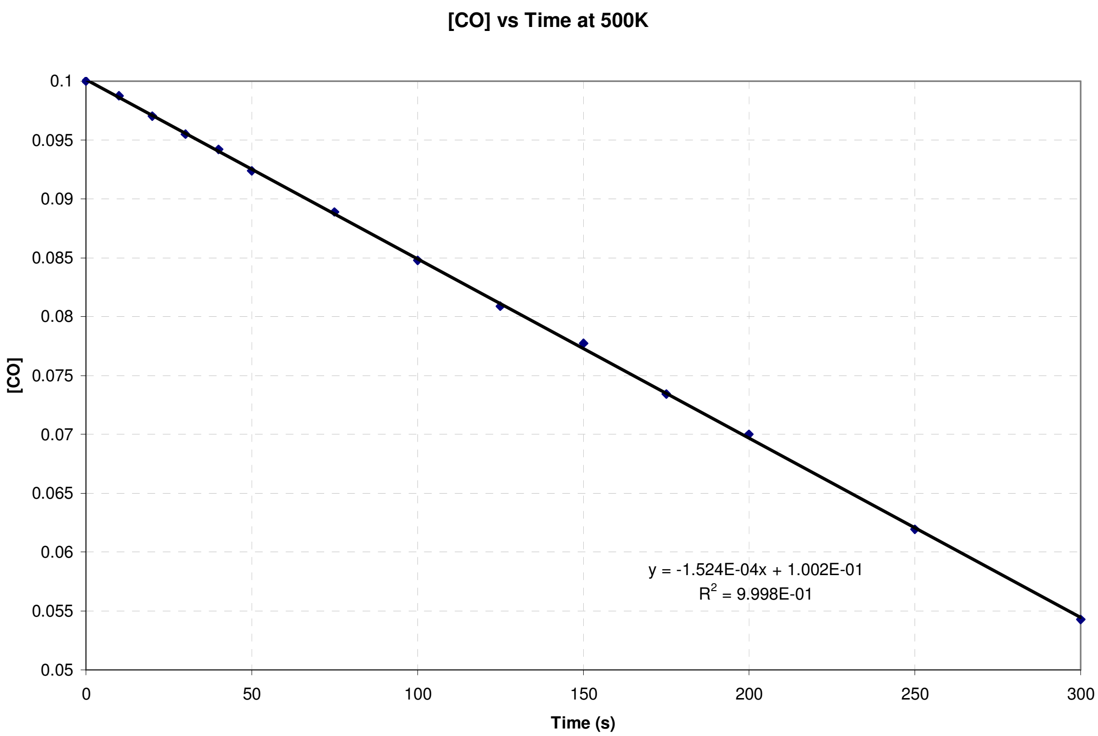


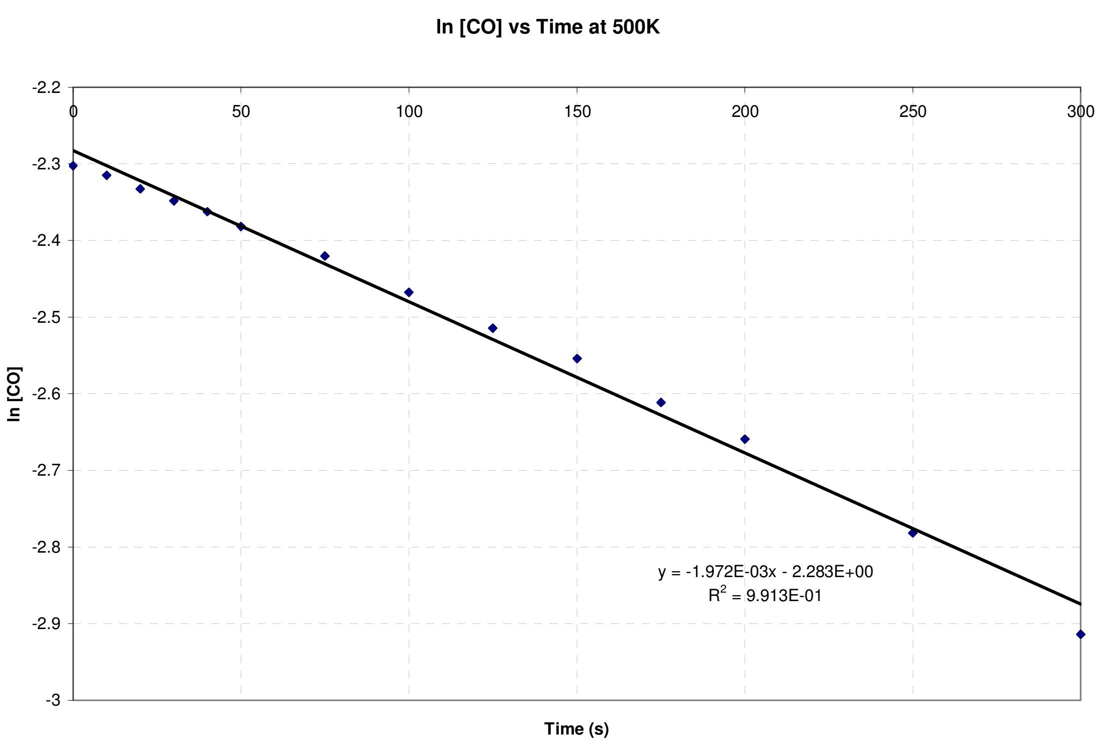


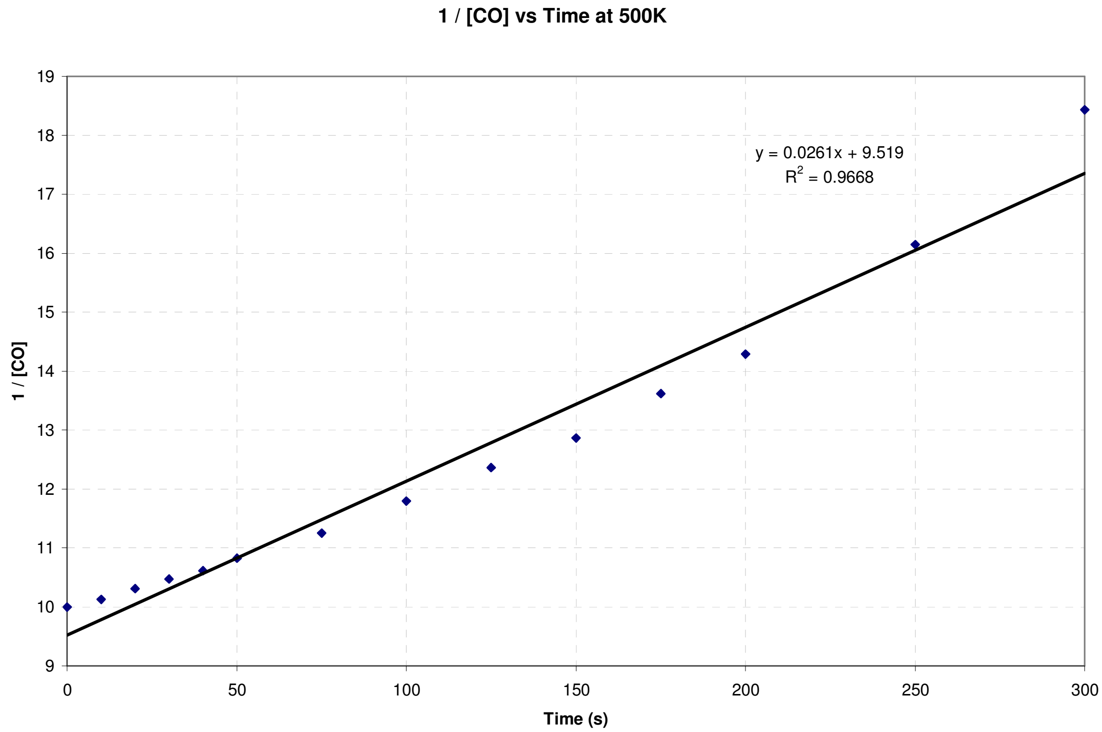
a) Based on these three plots, what is the order of the reaction with respect to NO_2? Recall that the closer the R^2 value is to 1, the better the data fits to the regression line.

b) What is the value of the rate constant at 700K?

Another series of experiments were performed (at 500K), this time observing the concentration of [CO] over time. A similar set of plots was prepared and are presented below.







c) Based on these three plots, what is the order of the reaction with respect to CO?

d) What is the value of the rate constant at 500K?

e) What is the (differential) rate law for this reaction?

5. At 25 °C, $K_p = 2.9 \times 10^{-3}$ for the following reaction:

$$NH_4OCONH_2(s) \Leftrightarrow 2\ NH_3(g) + CO_2(g)$$

A large quantity of NH_4OCONH_2(*s*) is placed in a rigid container under vacuum at 25 °C and the system is allowed to reach equilibrium.

a) What is the equilibrium expression for this reaction?

b) What is the equilibrium partial pressure (in atm) of NH_3 in this reaction?

c) What is the total pressure (in atm) inside the flask at equilibrium?

6. The reaction $4\,HBr(g) + O_2(g) \rightarrow 2\,H_2O(g) + 2\,Br_2(g)$ the following initial rate data were collected:

$[HBr]_0$ (mol / L)	$[O_2]_0$ (mol / L)	Initial rate (mol / L · s)
0.010	0.010	2.41×10^{-3}
0.010	0.030	7.23×10^{-3}
0.020	0.030	4.82×10^{-3}

a) What is the (differential) rate law?

b) What is the value of the rate constant?

c) For this reaction, the following mechanism has been proposed:

$HBr + O_2 \rightarrow HOOBr$	slow
$HOOBr + HBr \rightarrow 2\,HOBr$	fast
$HOBr + HBr \rightarrow H_2O + Br_2$	fast
$HOBr + HBr \rightarrow H_2O + Br_2$	fast

Is this mechanism consistent with the kinetics data? Explain.

Equations and Constants

$$PV = nRT$$

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

$$\ln [A] = -kt + \ln [A]_0$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$ax^2 + bx + c = 0$$

$$[A] = -kt + [A]_0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$K_p = K(RT)^{\Delta n}$$

R = 8.314 J / mol · K = 0.0821 L · atm / mol · K