#1. (2011)

In an experiment, all the air in a rigid 2.0 L flask is pumped out. Then some liquid ethanol is injected into the sealed flask, which is held at 35°C. The amount of liquid ethanol initially decreases, but after five minutes the amount of liquid ethanol in the flask remains constant. Ethanol has a boiling point of 78.5°C and an equilibrium vapor pressure of 100 torr at 35°C.

(a) When the amount of liquid ethanol in the flask is constant, is the pressure in the flask greater than, less than, or equal to 100 torr? Justify your answer.

Since the amount of liquid ethanol remains constant, the amount of ethanol vapor must also be constant, so the liquid/vapor must be at equilibrium. so the vapor pressure is equal to 100 torr.

(b) The flask is then heated to 45°C, and the pressure in the flask increases. In terms of kinetic molecular theory, provide TWO reasons that the pressure in the flask is greater at 45°C than at 35°C.

① As temp increases, a larger number of the liquid molecules will have enough kinetic energy to vaporize, so more ethanol molecules will enter the gas phase. gas pressure is proportional to the number of molecules, so pressure will increase.

② Since the vapor molecules are at a higher temperature, they have a higher kinetic energy and faster speed. So the ethanol (gas) molecules will hit a given surface more times per second, and, since they are faster, they will exert more force with a given collision.

In a second experiment, which is performed at a much higher temperature, a sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 M. The ethanol begins to decompose according to the chemical reaction represented below.

$$CH_3CH_2OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$
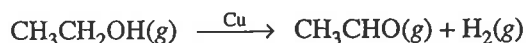
The concentration of ethanol gas over time is used to create the three graphs below.
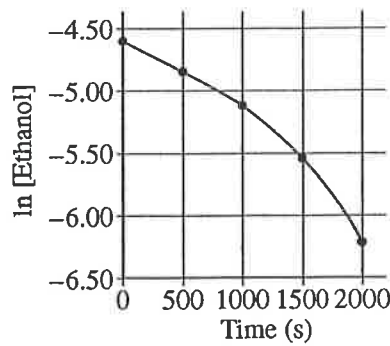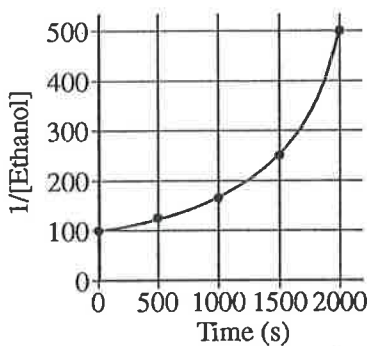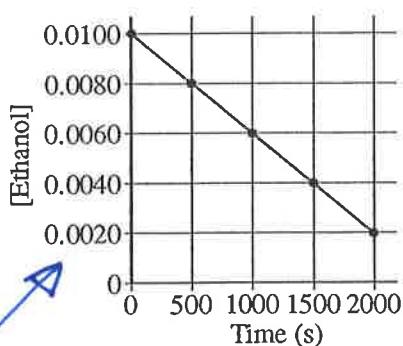
(c) Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.

(i) Determine the order of the reaction with respect to ethanol. Justify your answer.

The reaction must be ~~zeroeth~~ Zero order. The graph shows that the concentration of ethanol is decreasing at a constant rate, which means that the rate of reaction is not dependent on the concentration of ethanol.

(Also, if first order, ln[eth] vs t would be linear, and it isn't. if 2nd order, 1/[eth] vs t would be linear, and it isn't)
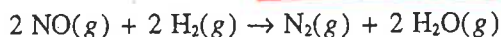
(#1 Cont'd)

(ii) Write the rate law for the reaction. $r = k[ethanol]^0$ or $\boxed{r = k}$

(iii) Determine the rate constant for the reaction, including units.

The slope of [ethanol] vs time would show use the rate of change of ethanol. Using the 1st two points of (0 seconds 0.0100 M) and (500 s, 0.0080 M), so slope $= \left(\dfrac{.0080 \, M - .0100 \, M}{500s - 0s}\right) = -.0000040 \dfrac{M}{s}$

So $r = k = .0000040 \, M/s$ or $\boxed{4.0 \times 10^{-6} \, M/s}$

(#2)

$$2 \, NO(g) + 2 \, H_2(g) \rightarrow N_2(g) + 2 \, H_2O(g)$$

Experiments were conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L)		Initial Rate of Formation of N_2 (mol/L·min)
	[NO]	[H$_2$]	
1	0.0060	0.0010	1.8 × 10⁻⁴
2	0.0060	0.0020	3.6 × 10⁻⁴
3	0.0010	0.0060	0.30 × 10⁻⁴
4	0.0020	0.0060	1.2 × 10⁻⁴

(annotations: [H$_2$] column expts 1,2 marked ×2; [NO] column expts 3,4 marked ×2; rate column expts 1,2 marked ×2; rate column expts 3,4 marked ×4)

(a) (i) Determine the order for each of the reactants, NO and H$_2$, from the data given and show your reasoning.
(ii) Write the overall rate law for the reaction.

In expts 1 and 2, doubling [H$_2$] while [NO] is constant causes the rate of rxn to double. ∴ Rxn is first order with respect to H$_2$

In expts 3 and 4, doubling [NO] while [H$_2$] is constant causes the rate to increase by a factor of 4, or 2^2. So the rxn is 2nd order with respect to NO.

So $\boxed{r = k[NO]^2[H_2]^1}$

(b) Calculate the value of the rate constant, k, for the reaction. Include units.

expt 1: $r = k[NO]^2[H_2]$

$1.8 \times 10^{-4} \, M/min = k(.0060 \, M)^2 (.0010 \, M)$ ∴ $k = 5000 \, M^{-2} min^{-1}$

expt 4: $1.2 \times 10^{-4} \, M/min = k(.0020 \, M)^2 (.0060 \, M)$ ∴ $k = 5000 \, M^{-2} min^{-1}$ (just checking!)

$\boxed{k = 5.0 \times 10^3 \, M^{-2} min^{-1}}$ or $\dfrac{l^2}{mol^2 \, min}$

(#2 Cont'd)

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.
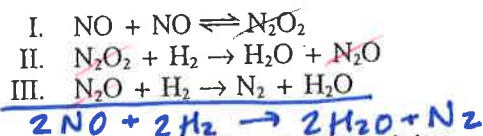
Expt 2 started with $[NO] = .0060 M$ and $[H_2] = .0020 M$
so when half of the H_2 has been consumed, $\frac{1}{2}(.0020)$ or $.0010 M$ has reacted.

$.0060 \text{ M NO} - \left(\dfrac{.0010 \text{ mole } H_2}{L}\right)\left(\dfrac{2 \text{ mole NO}}{2 \text{ mole } H_2}\right) = \boxed{.0050 \text{ M NO remains}}$

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

from last page:

$r = k[NO]^2[H_2]$

I. $NO + NO \rightleftharpoons N_2O_2$
II. $N_2O_2 + H_2 \rightarrow H_2O + N_2O$
III. $N_2O + H_2 \rightarrow N_2 + H_2O$

$2NO + 2H_2 \rightarrow 2H_2O + N_2$

It adds up to the original rxn given, so it is consistent w/ overall stoichiometry.

Based on the data presented, which of the above is the rate-determining step? Show that the mechanism is consistent with

(i) the observed rate law for the reaction, and
(ii) the overall stoichiometry of the reaction.

(i) step II must be the rate-determining (slow) step,
and steps I, III must be relatively fast.

If step II is the rate determining step, then the rate law would be $r = k_2[N_2O_2][H_2]$. but N_2O_2 is an intermediate, so it can't be in the overall rate law.

but • if step I is fast, it will reestablish equilibrium quickly as N_2O_2 is used up. at equilibrium, $r_{forward} = r_{reverse}$,
so $k_f[NO]^2 = k_r[N_2O_2]$

so $[N_2O_2] = \dfrac{k_f}{k_r}[NO]^2$

This matches our rate law from part (a)!

we can substitute this into our rate law for step 2:
$r = \dfrac{k_2 k_f}{k_r}[NO]^2[H_2]$ or $r = k[NO]^2[H_2]$ ✓

where $k = \dfrac{k_2 k_f}{k_r}$

(e) Explain why an increase in temperature increases the rate constant, k.

As temperature increases, a larger fraction of molecules will have enough kinetic energy to meet the activation requirement. (more of the collisions will be energetic enough to break bonds!) so the rate, and k, will increase. (molecules will also collide slightly more frequently)
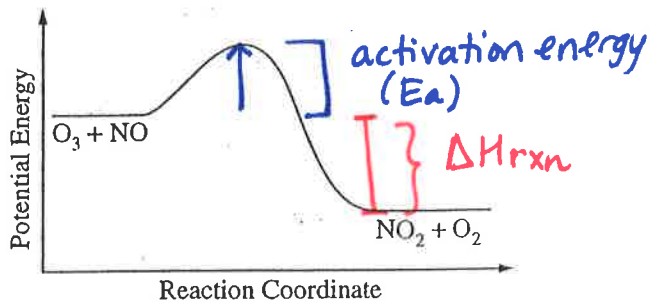
3 Answer the following questions regarding the kinetics of chemical reactions.

(a) The diagram below at right shows the energy pathway for the reaction $O_3 + NO \rightarrow NO_2 + O_2$.

Clearly label the following directly on the diagram.
   (i) The activation energy (E_a) for the forward reaction
   (ii) The enthalpy change (ΔH) for the reaction

[handwritten on diagram:] activation energy (E_A)] ; ΔH_{rxn} ; $O_3 + NO$; $NO_2 + O_2$

Potential Energy (y-axis) ; Reaction Coordinate (x-axis)

(b) The reaction $2 N_2O_5 \rightarrow 4 NO_2 + O_2$ is (first order with respect to N_2O_5.) *[handwritten:]* ← so, $r = k[N_2O_5]^1$

   (i) Using the axes at right, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.

   [graph axes: Initial $[N_2O_5]$ (y-axis), Time (x-axis), with decaying curve]

   (ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, t.

   [handwritten:] Draw a tangent line at that time, t. Find the slope of the tangent line. The absolute value of the slope is equal to the rate of disappearance of N_2O_5.
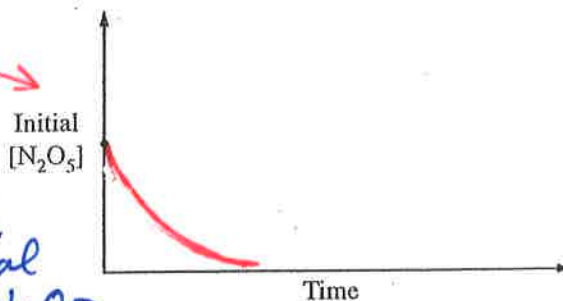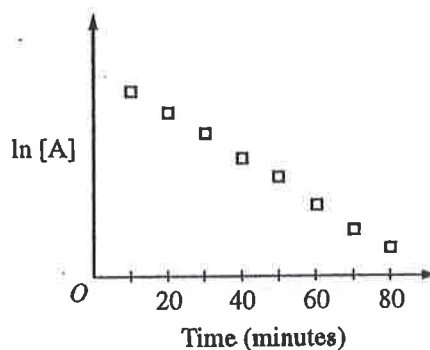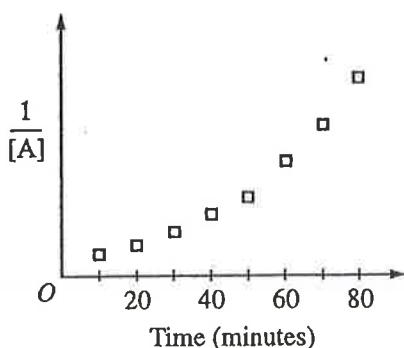
   (iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, k, could be determined. *[handwritten:]* We are told that the rxn is first order, so $r = k[N_2O_5]^1$. Use the concentration of N_2O_5 at the point used to calculate the rate in (ii). plug in: rate $= k[N_2O_5]$ and solve for k.

   (iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, k? Explain.

   [handwritten:] no effect. the rate constant is not dependent on concentration.

(c) Data for the chemical reaction $2 A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of the data.

[graph 1: $\frac{1}{[A]}$ (y-axis) vs Time (minutes) with points rising, x-axis 20 40 60 80]

[graph 2: ln [A] (y-axis) vs Time (minutes) with points descending, x-axis 20 40 60 80]

Use the information in the graphs above to answer the following.

   (i) Write the rate-law expression for the reaction. Justify your answer.

   [handwritten:] $r = k[A]^1$; since ln[A] vs time is linear, the rxn must be 1st order.

   (ii) Describe how to determine the value of the rate constant for the reaction.

   [handwritten:] Calculate the slope of the graph of ln[A] vs time. The absolute value of the slope is equal to k.

(#4)

$$2A + B \rightarrow C + D$$
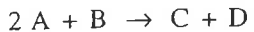
The following results were obtained when the reaction represented above was studied at 25°C.

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C (mol L^{-1} min^{-1})
1	0.25	0.75	4.3×10^{-4}
2	0.75	0.75	1.3×10^{-3}
3	1.50	1.50	5.3×10^{-3}
4	1.75	?	8.0×10^{-3}

×3 (1→2 for [A]); ×2 (2→3 for [A]); ×2 (2→3 for [B]); × 3.02 (rate 1→2); × 4.08 (rate 2→3)

(a) Determine the order of the reaction with respect to A and to B. Justify your answer.

It is first order with respect to [A]. In expts 1 and 2, [B] is constant, and when [A] triples, the rate increases by a factor of 3.02, so the rate approximately triples. Since [A] and the rate increase by ≈ the same factor, it is first order for A.

In expts 2 and 3, [A] and [B] both double, and the rate increases by a factor of about 4 (4.08). We already know it is first order with respect to [A], so that means that when [A] doubles, this alone would cause the rate to double. therefore, the remaining factor of two increase in rate must be caused by [B] doubling. Since doubling [B] causes the rate to double, it must be first order with respect to [B].

OR:
$$\frac{rate(3)}{rate(2)} = \frac{5.3 \times 10^{-3}\ M/min}{1.3 \times 10^{-3}\ M/min} = \frac{k\ [1.50M]^1\ [1.50\ m]^x}{k\ [.75\ m]^1\ [.75\ m]^x}$$

(A) (B) / (A) (B)

$$4.08 = 2\ (2)^x$$
$$2.04 = (2)^x$$
$$x = \frac{\ln(2.04)}{\ln(2)} = 1.03$$
$$1.03 \approx 1\ !$$

(b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.

$$r = k\ [A]^1\ [B]^1$$

using trial 1: $4.3 \times 10^{-4}\frac{M}{min} = k\ (.25M)(.75M)$

$$\boxed{k = .0023\ M^{-1}\ min^{-1}}$$

↑
(or .0023 for trial 2
or .0024 for trial 3)

(c) Determine the initial rate of change of [A] in Experiment 3.

$$\left(\frac{5.3 \times 10^{-3}\ mole\ C}{L \cdot min}\right)\left(\frac{2\ mole\ A}{1mole\ C}\right)(-1) = \boxed{-.011\ \frac{M}{Min}}$$

or $\boxed{\dfrac{-.011\ moles\ A}{L \cdot min}}$

(d) Determine the initial value of [B] in Experiment 4.

$$r = k[A]^1[B]^1$$
$$8.0 \times 10^{-3}\frac{M}{Min} = (.0023\ M^{-1}\ min^{-1})(1.75M)[B]$$

$$[B] = 1.988 \rightarrow \boxed{2.0\ M}$$
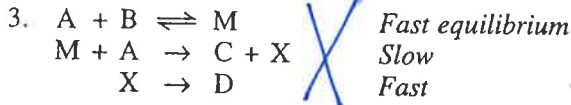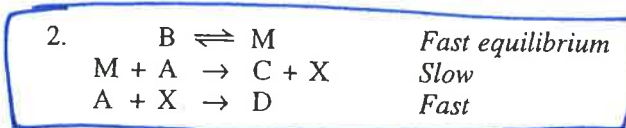
(#4, Cont'd)

In part (b), we got $r = k[A]'[B]'$

(e) Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.
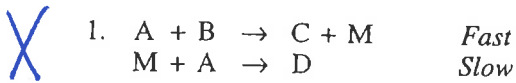
~~1.~~   A + B → C + M   *Fast*
      M + A → D   *Slow* ← would give $r = k[M][A]$ ~~and~~ and there is no way to substitute for M, since there is no fast equilibrium before the slow step. So this doesn't work.

2.   B ⇌ M   *Fast equilibrium*
   M + A → C + X   *Slow*
   A + X → D   *Fast*

3.   A + B ⇌ M   *Fast equilibrium*
   M + A → C + X   *Slow*
       X → D   *Fast*

this one works!

based on the slow step, $r = k_{slow}[M][A]'$

but the preceding step is fast; the first rxn must establish equilibrium quickly as M reacts in step 2.

at Equilibrium, fwd rate = reverse rate

$$k_{forward}[B] = k_{reverse}[M]$$

so $[M] = \left(\dfrac{k_f}{k_r}[B]\right)$ ← we can substitute into the "original" rate law!

$$r = k_{slow}[M][A]' = k_{slow}\left(\dfrac{k_f}{k_r}\right)[B][A]$$

$$r = k[B][A]$$

where $k = \dfrac{k_{slow}\,k_f}{k_r}$

this matches the rate law we found!

(3) doesn't work.

$r_{slow} = k_{slow}[M][A]$

@ equilibrium,
  $r_f = r_r$
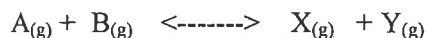$$k_f[A][B] = k_r[M]$$
$$[M] = \dfrac{k_f}{k_r}[A][B]$$

so $r_{slow} = \dfrac{k_{slow}\,k_f}{k_r}[A][B][A] = k[A]^2[B]$, which doesn't match.

Problem "R"

$A_{(g)} + B_{(g)} \longleftrightarrow X_{(g)} + Y_{(g)}$

$\Delta H_{rxn} = -10.0$ kJ/mole $E_a = 50.0$ kJ/mole

In the above reversible reaction, the forward reaction involves a collision of an "A" with a "B", and the reverse reaction involves a collision of an "X" with a "Y".   (Both the forward and reverse reactions occur in a single elementary step).
Therefore, the forward reaction has the rate law, $r_{fwd} = k_{fwd}[A]^1[B]^1$
          and the reverse reaction has the rate law, $r_{rev} = k_{rev}[X]^1[Y]^1$

potential energy

Rxn progress

1a.   Use the ΔH_{rxn} and E_a of the forward reaction to sketch the energy profile for this reaction on the graph. Use a scale of 1 square = 5 kJ

b.   What is the value of ΔH_{rxn} for the reverse reaction? +10.0 kJ/mole
c.   What is the value of Ea for the reverse reaction? 60.0 kJ/mole

2. At 20.°C, this rxn has a forward rate constant of 0.0185 $M^{-1}s^{-1}$ and a reverse rate constant of 0.000350 $M^{-1}s^{-1}$.
a.   Write an expression for Kc, in terms of the appropriate concentrations.

$$K_c = \frac{[x][y]}{[A][B]}$$

——— no catalyst
——— with Pt catalyst

b.   Use the rate constants for the forward and reverse reactions to calculate Kc at 20. °C

$$Keq = \frac{k\,(forward)}{k\,(reverse)} = \frac{.0185\ M^{-1}s^{-1}}{.000350\ M^{-1}s^{-1}} = 52.857 \rightarrow \boxed{52.9}$$

3. Now we will raise the temperature from 20°C to 40°C!!!!
At 40.°C, this rxn has a forward rate constant of 0.0688 $M^{-1}s^{-1}$, and a reverse rate constant of 0.00169 $M^{-1}s^{-1}$.
a.   Use the rate constants for the forward and reverse reactions to calculate Kc at 40. °C

$$Keq = \frac{k_f}{k_r} = \frac{.0688}{.00169} = \boxed{40.7}$$

b. How did increasing temperature affect the value of the forward rate constant (and, therefore, the forward rate of reaction)? (did r(forward) and k(forward) increase or decrease? it increased
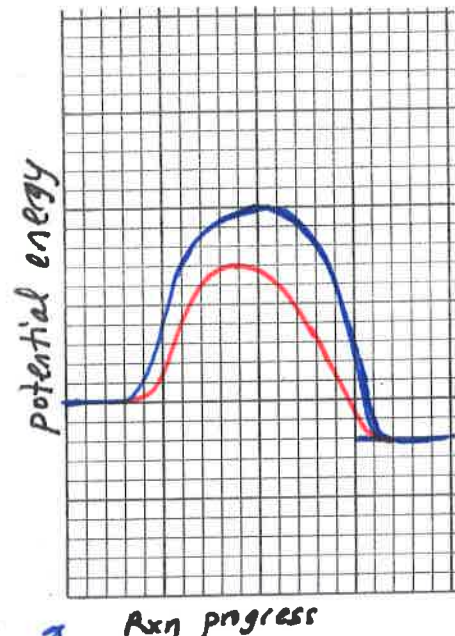
c. How did increasing temperature affect the value of the reverse rate constant (and, therefore, the rate of the reverse reaction)?   it increased

d. How did increasing temperature affect the value for Keq? it decreased.
e. To explain why Keq was affected this way; which rate constant increased/decreased by a larger factor: the forward or the reverse rate constant? The reverse rate constant increased by a larger factor.
(The kf increased by x 3.72 and kr increased by x4.83)
f. Does the effect on Keq seem consistent with the fact that the reaction is exothermic? Explain.

yes. Exothermic rxns are favored by low temp; Keq increases as temp decreases.

g. Explain, using collision theory, why the rates and rate constants increased as temp increased.

As temp increases, the reactant molecules increase in speed (so also increase in kinetic energy). So the collisions between reactant molecules will occur more frequently. And, more importantly, the reactants will collide with more force and energy ("harder" collisions.), so a larger fraction of the collisions will have enough kinetic energy to meet the activation energy requirements; a larger fraction of collisions we be hard enough to break reactant bonds.

5. Now we will go back to 20. °C, but we will add a platinum catalyst, which changes the activation energy for the forward reaction from 50 kJ/mole to 35 kJ/mole! When catalyzed with Pt at 20.°C, the forward rate constant is 8.73 $M^{-1}s^{-1}$, and the reverse rate constant is 0.165 $M^{-1}s^{-1}$.

a. Show the energy diagram for the catalyzed rxn. (use the same graph that you used for the uncatalyzed rxn).
b. What is the activation energy for the reverse reaction, when catalyzed with Platinum? **45 kJ/mole**
c. Use the rate constants to calculate Keq for the catalyzed rxn at 20.°C.

$$Keq = \frac{k_f}{k_r} = \frac{(8.73 M^{-1}s^{-1})}{(0.165 M^{-1}s^{-1})} = 52.909 \rightarrow \boxed{52.9}$$

d. How did adding a catalyst affect the value of the forward rate constant? **k_f increased**

e. How did adding at catalyst affect the value of the reverse rate constant? **k_r increased**

f. How did adding a catalyst affect the value for Keq? **It stayed the same!!!**

g. Explain, using collision theory, how/why a catalyst increases/decreases the rate of reaction.

A catalyst lowers the activation energy required. So, even though the kinetic energy of the reactants hasn't changed (since temp is the same), a larger fraction of the collisions will have enough kinetic energy to meet the Ea required / a larger fraction of collisions will involve KE ≥ Ea. So a larger number of collisions will be successful!

h. Why did the catalyst affect/not affect the Keq?

It increases the forward and reverse rates (and rate constants) by the same factor, since the fwd and reverse Ea are lowered by the same # of kilojoules. So Keq, the ratio of k_f/k_r, stays the same.
(For example, in this rxn, the fwd k and reverse k each increased by a factor of 471!)