EQUILIBRIUM PROBLEMS
RICE FALL 2018

1. A flask containing 1.00 atm of NO_2 and 1.50 atm of N_2O_4 is allowed to proceed to equilibrium at a given temperature.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

When equilibrium is established the partial pressure of NO_2 is 0.500 atm.

a) Calculate the magnitude of the equilibrium constant for this reaction at this temperature.

ICE table with Initial Conditions

	$2NO_2(g)$	**$\rightleftharpoons$**	**$N_2O_4(g)$**
Initial	**1.00 atm**		**1.50 atm**
Change			
Equilibrium	**0.500 atm**		

ICE Table with Change row

	$2NO_2(g)$	**$\rightleftharpoons$**	**$N_2O_4(g)$**
Initial	**1.00 atm**		**1.50 atm**
Change	**-0.500 atm**		**+0.250 atm**
Equilibrium	**0.500 atm**		

ICE Table with all equilibrium amounts

	$2NO_2(g)$	**$\rightleftharpoons$**	**$N_2O_4(g)$**
Initial	**1.00 atm**		**1.50 atm**
Change	**-0.500 atm**		**+0.250 atm**
Equilibrium	**0.500 atm**		**1.75 atm**

$$K_p = \frac{P_{N_2O_4}}{P^2_{NO_2}} = \frac{1.75}{0.500^2} = 7.00$$

b) After the reaction mixture has established equilibrium, 0.250 atm of N_2O_4 are added to the reaction flask. Which direction (left to right; right to left; or no change) will the reaction proceed to re-establish equilibrium? Explain in terms of Q and Kp.

	$2NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
Initial (@ Equilibrium)	**0.500 atm**		**1.75 atm**
Add			**+0.250 atm**
New Initial	**0.500 atm**		**2.00 atm**

Adding 0.250 atm of N_2O_4 places a stress on the equilibrium.

$$Q = \frac{P_{N_2O_4}}{P^2_{NO_2}} = \frac{2.00}{0.500^2} = 8.00$$

Q is greater than K_p. To re-establish equilibrium the reaction quotient must decrease, to do that means the product amounts must decrease and the reactant amounts must increase. The reaction will shift from right to left to re-establish equilibrium.

c) Does the position of equilibrium favor the products side or the reactants side? Explain.

The position of equilibrium favors the products because K_p is greater than 1. The equilibrium expression is;

$$K_p = \frac{P_{N_2O_4}}{P^2_{NO_2}}$$

If this quotient is greater than 1, the amount of products must is greater than the amount of reactants.

2. The equilibrium constant for the reaction

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

At a certain temperature is 1.48 x 10^4. The equilibrium constant for the reaction

$$NO_2(g) \rightleftharpoons \frac{1}{2} O_2(g) + NO(g)$$

What is the equilibrium constant for this reaction at the same temperature?

The new chemical equation is the reverse of the first chemical equation and all of the coefficients have been divided by 2.

For the reaction

$$\mathbf{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)}$$

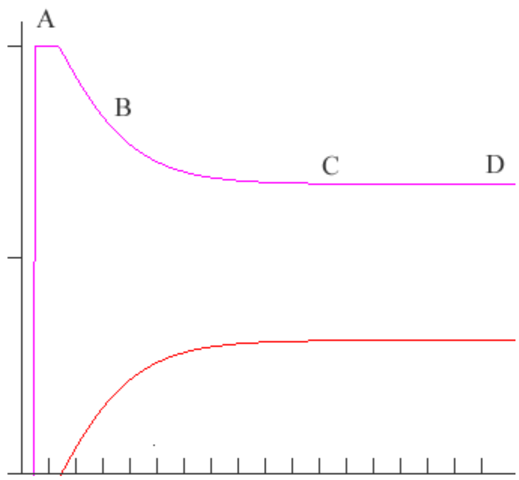
$$\mathbf{K_p = \frac{P^2_{NO_2}}{P^2_{NO} \cdot P_{O_2}} = 1.48 \text{ x } 10^4}$$

For the reaction

$$\mathbf{NO_2(g) \rightleftharpoons \frac{1}{2} O_2(g) + NO(g)}$$

$$\mathbf{K_p' = \frac{P_{NO} \cdot P^{1/2}_{O_2}}{P_{NO_2}} = \frac{1}{(K_p)^{1/2}} = \frac{1}{(1.48 \text{ x } 10^4)^{1/2}} = 8.23 \text{ x } 10^{-3}}$$

3. In the graph below the endothermic reaction BR*(g)* ⇌ B*(g)* + R*(g)* is represented. Initially only BR*(g)* is present in the reaction vessel. The marks along the *x*-axis are in 1 minute increments. The initial [BR] (*y-axis)* is 2.0 M. The reaction begins about 1.5 minutes in this case.



a) At what point (indicate a letter) does the reaction attain equilibrium? NOTE: You can also label the graph if your prefer.

The reaction attains equilibrium at point C. At point C the amounts of reactants and products are not changing. The reaction is still happening, however, every time a molecule of BR separates into a B atom and an R atom in the system, somewhere else in the system an atom B and an atom of R collide to form a molecule of BR.

b) Indicate whether K for the reaction is greater than 1, less than 1 or equal to1. Explain.

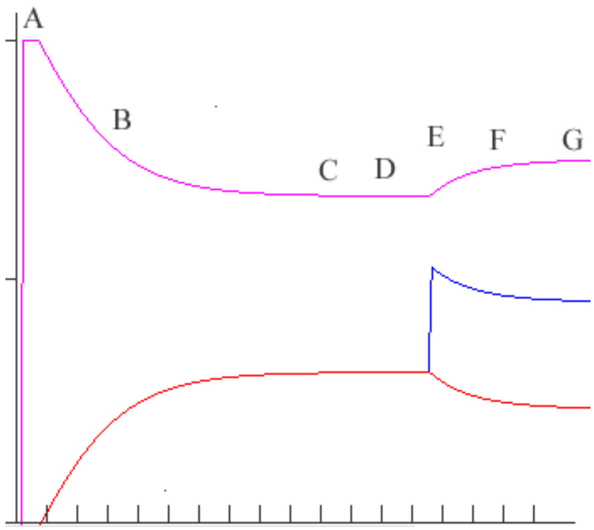
$$K_c = \frac{[B][R]}{[BR]}$$

At equilibrium the amounts of B and R are smaller compared to the amount of BR. In the equilibrium expression the numerator has two small numbers and the denominator has a larger number, so K_c is less than 1.

c) At point 'B' indicate how Q compares to K. Explain.

At point B Q < K_c so the reaction quotient must get larger. For this to happen the numerator must increase and the denominator must decrease, so the reaction will continue going from left to right.

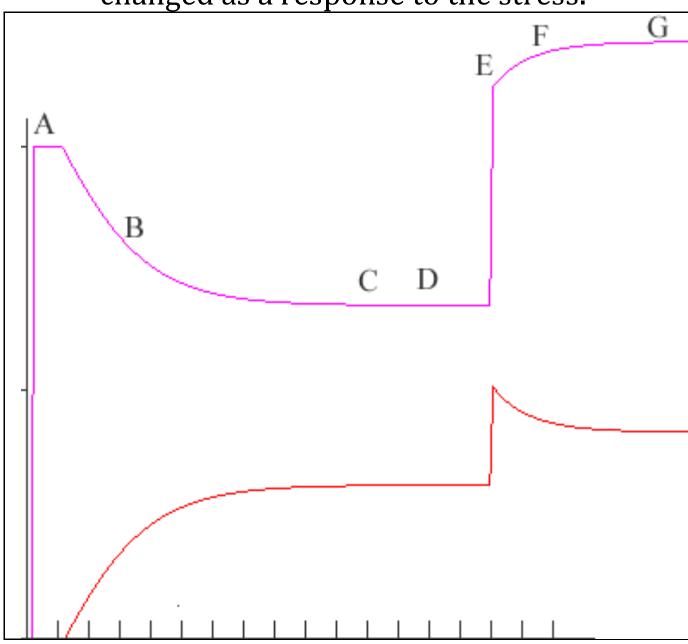
d) In this new view the same reaction has occurred. Indicate the stress (at point E) that was imposed on the system, and explain how the system changed as a response to the stress.



Explain:

As a reminder the top line is tracking the amount of BR (reactant) and the bottom line tracks the amounts of B and R. At point E the stress is an increase in the amount of one of the products (B). With an increase in the amount of B, Q > K_c and the reaction shifts right to left, and the amounts of the products decrease (point F) and the amount of reactants increase.

e) In this new view the same reaction has occurred. Indicate the stress (at E) that was imposed on the system, and explain how the system changed as a response to the stress.



Explain:

See below

At point E in this chart both the concentration of reactants and products increase. This can happen if the volume of the container is decreased.

$$Q = \frac{[B][R]}{[BR]} = \frac{[\frac{\text{mol B}}{\text{Volume}}][\frac{\text{mol R}}{\text{Volume}}]}{[\frac{\text{mol BR}}{\text{Volume}}]} = \frac{[\text{mol B}][\text{mol R}]}{[\text{molBR}]} \cdot \frac{1}{\text{volume}}$$

When the volume of the container is decreased Q will increase and will be greater than K, so the reaction will shift right to left to re-establish equilibrium.

4. a) The following reversible reaction occurs at 25. ˚C.

$$2HOCl(g) \rightleftharpoons H_2O\ g) + Cl_2O(g)$$

A reaction vessel that contains 0.500 atm of HOCl initially is allowed to attain equilibrium at 25 ˚C. Analysis indicates 0.0650 atm of HOCl are present at equilibrium. Calculate K_p for the reaction as written.

ICE table with Initial Conditions

	$2HOCl(g)$	$\rightleftharpoons$	$H_2O\ g)$	+	$Cl_2O(g)$
Initial	**0.500 atm**		**0 atm**		**0 atm**
Change					
Equilibrium	**0.0650 atm**				

ICE Table with Change row

	$2HOCl(g)$	$\rightleftharpoons$	$H_2O\ g)$	+	$Cl_2O(g)$
Initial	**0.500 atm**		**0 atm**		**0 atm**
Change	**-0.435 atm**		**+0.217 atm**		**+0.217 atm**
Equilibrium	**0.0650 atm**				

ICE Table with all equilibrium amounts

	$2HOCl(g)$	$\rightleftharpoons$	$H_2O\ g)$	+	$Cl_2O(g)$
Initial	**0.500 atm**		**0 atm**		**0 atm**
Change	**-0.435 atm**		**+0.217 atm**		**+0.217 atm**
Equilibrium	**0.0650 atm**		**+0.217 atm**		**+0.217 atm**

$$K_p = \frac{P_{H_2O} \cdot P_{Cl_2O}}{P^2_{HOCl}} = \frac{0.217 \cdot 0.217}{(0.0650)^2} = 11.1$$

b) After the reaction in 4a attains equilibrium, some HOCl is added so the new partial pressure of HOCl is 0.200 atm. Calculate the new equilibrium amounts of the system when equilibrium is re-established.

ICE table with Initial Conditions

	$2HOCl(g)$	$\rightleftharpoons$	$H_2O\,g)$	+	$Cl_2O(g)$
Initial (@ equilibrium)	**0.0650 atm**		**0.217 atm**		**0.217 atm**
New initial	**0.200 atm**		**0.217 atm**		**0.217 atm**
Change	**-2x**		**+x**		**+x**
Equilibrium	**0.200 – 2x**		**0.217 + x**		**0.217 + x**

$$K_p = \frac{P_{H_2O} \cdot P_{Cl_2O}}{P^2_{HOCl}} = \frac{0.217 + x \cdot 0.217 + x}{(0.200 - 2x)^2} = 11.1$$

Taking the square root of both sides;

$$= \frac{0.217 + x}{0.200 - 2x} = 3.33$$

$0.217 + x = 3.33\,(0.200 - 2x)$

$0.217 + x = 0.666 - 6.66x)$

$7.66x = 0.449$

$x = 0.0586$ **atm**

At equilibrium;

$P_{HOCl} = 0.200$ **atm** $- 2 \cdot 0.0586$ **atm** $= 0.0828$ **atm**

$P_{H_2O} = P_{Cl_2O} = 0.217$ **atm** $+ 0.0586$ **atm** $= 0.276$ **atm**