The Effect of Temperature on the Position of the Equilibrium and the K_{eq}

Example #1:

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + \text{heat}$

Which way would the equilibrium shift if heat was added from an outside source? (Remember that this is an exothermic reaction.)

Answer = left.

Why? **The reaction would try to use up the added heat (see LeChatelier's Principle) by making more H_2 and Cl_2, thus using up HCl and heat.**

What would this do to the value of the K_{eq}?

Answer = make it smaller. To see this, write the K_{eq} expression for the reation:

$K_{eq} = [HCl]^2 / ([H_2]\ [Cl_2])$

As the equilibrium shifts to the left, the [HCl] goes down and both the $[H_2]$ and $[Cl_2]$ increase. This makes the numerator smaller and the denominator larger. The K_{eq} decreases in value and heat is added to an exothermic reaction.

Example #2:

$N_2O_4(g) + \text{heat} \rightleftharpoons 2NO_2(g)$

Which way would the equilibrium shift if heat was added from an outside source? (Remember that this is an endothermic reaction.)

Answer = right.

Why? **The reaction will use up the added heat by making more NO_2 at the expense of N_2O_4.**

What would this do to the value of the K_{eq}?

Answer = make it larger. To see this, write the K_{eq} expression for the reation:

$K_{eq} = [NO_2]^2 / [N_2O_4]$

As the equilibrium shifts to the right, the $[NO_2]$ goes up and the $[N_2O_4]$ goes down. This makes the numerator larger and the denominator smaller, resulting in a larger value for the K_{eq} after the position of the equilibrium has shifted.

Notice that there are two questions that must be asked when the effect of heat on the value of the K_{eq} is discussed. (1) Is the reaction endothermic or exothermic? and (2) Is heat added or removed?

Here is a chart showing the effect on the value of the K_{eq} from the interplay between these two questions:

	Add Heat	Remove Heat
Endothermic	increase	decrease
Exothermic	decrease	increase

As can be seen, two combinations of the two questions yield decrease as the answer and two combinations yield increase.

For myself, when I do these, I like to write the chemical equation (in a generic way) as exothermic or endothermic. Right next to the equation, I will write the equilibrium expression. Like this:

Endothermic	heat + A $\rightleftharpoons$ B	K_{eq} = [B] / [A]
Exothermic	A $\rightleftharpoons$ B + heat	K_{eq} = [B] / [A]

When answering AP questions, I would first discuss the effect (either increase or decrease) of adding or removing heat on the amounts of A and B. Then, I would move to the K_{eq} expression to discuss the effect on the constant of increasing and decreasing the amounts of A and B.

There are two more possible combinations of the two question above. Here they are:

Example #3:

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ + heat

Which way would the equilibrium shift if heat was removed from the reaction vessel?

What would this do to the value of the K_{eq}?

(answer = shift right/increase)

Example #4:

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

Which way would the equilibrium shift if heat was removed from the reaction vessel?

What would this do to the value of the K_{eq}?

(answer = shift left/decrease)