Quantifying the Relationship between K and T (add to notes at the end of page 75 or end of lecture 7).

LeChatelier's Principle gives us a way to argue the direction in which a reaction will shift with change in temperature. But is there a way to quantify this? Of course, and it is shown below without derivation (which awaits those of you who have to take physical chemistry in a couple of years.) Here it is, the van't Hoff equation:
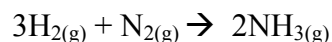
$$\ln\frac{K_2}{K_1} = \frac{\Delta H_r^\circ}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

Note a few things about to note about the equation:

- It is of a form identical to the Clausius Clapeyron, which makes sense in that the Clausius Clapeyron explains the temperature dependence of a physical equilibrium phenomenon (vapor pressure) and van't Hoff generalizes this to any equilibrium phenomenon.
- Also note that the qualitative picture of the direction in which a reaction shifts from LeChatelier's principle is consistent with the Van't Hoff equation.
- The change in enthalpy, which you can determine using anything from a bomb calorimeter calculation to a heat of formation calculation to a bond energy calculation, has a sign associated with it that will flip positive or negative depending on the direction in which you write the reaction and consequently whether the reaction as written is exothermic or endothermic.

Sample Problem:

The equilibrium constant K for the synthesis of ammonia is 6.8×10^5 at 298 K.

$$3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$$

Predict its value at 400. K.

Solution. The standard reaction enthalpy for the forward reaction is

$$\Delta H_r^\circ = 2\Delta H_f^\circ(NH_3, g) = 2(-46.11 \text{ kJ·mol}^{-1})$$
$$= -92.22 \text{ kJ·mol}^{-1} \text{ or } -92.22 \times 10^3 \text{ J·mol}^{-1}$$

Therefore,

From $\ln(K_2/K_1) = (\Delta H_r°/R)\{(1/T_1) - (1/T_2)\}$, $\ln\dfrac{K_2}{K_1} = \dfrac{\overbrace{-9.222 \times 10^4 \text{ J·mol}^{-1}}^{-92.22 \text{ kJ·mol}^{-1}}}{8.3145 \text{ J·K}^{-1}\text{·mol}^{-1}} \times \left\{\dfrac{1}{298 \text{ K}} - \dfrac{1}{400.\text{ K}}\right\}$

$= -9.49$

Take antilogarithms (e^x). $K_2 = K_1 e^{-9.49} = (6.8 \times 10^5) \times e^{-9.49} = 51$

The answer is close to the experimental value of 41 but is not exact because $\Delta H_r°$ is not actually constant over the temperature range. This same complication arose when performing a Clausius Clapeyron calculation and resulted in the boiling point of water being predicted as 105°C.