

Quantifying the Relationship between K and T (add to notes at the 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:

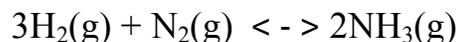
$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^\circ}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$

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 (exothermic to the left as T goes up and endothermic to the right as T goes up) 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.



Predict its value at 400. K.

Solution. The standard reaction enthalpy for the forward reaction is

$$\begin{aligned}\Delta H_r^\circ &= 2\Delta H_f^\circ(\text{NH}_3, \text{g}) = 2(-46.11 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= -92.22 \text{ kJ}\cdot\text{mol}^{-1} \text{ or } -92.22 \times 10^3 \text{ J}\cdot\text{mol}^{-1}\end{aligned}$$

Therefore,
From

$$\ln(K_2/K_1) = (\Delta H_r^\circ/R)\{(1/T_1) - (1/T_2)\},$$

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\overbrace{-92.22 \text{ kJ}\cdot\text{mol}^{-1}}^{-9.222 \times 10^4 \text{ J}\cdot\text{mol}^{-1}}}{8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}} \times \left\{ \frac{1}{298 \text{ K}} - \frac{1}{400. \text{ K}} \right\} \\ &= -9.49\end{aligned}$$

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 ΔH_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.

What LeChatelier Tells Us About How to Synthesize Ammonia

Given $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{heat}$,

applying LeChatelier's principle allows us to make predictions about how to drive this incredibly important reaction thermodynamically to make as much ammonia as possible

Change the Concentration:

Le Chatelier says that is we need to increase the amount of hydrogen and nitrogen while constantly removing the ammonia.

Shift the Pressure:

Le Chatelier says that is we need to increase pressure to drive the reaction to the right and make more ammonia.

Shift the Temperature:

Le Chatelier says that is we need to decrease the temperature to drive the reaction to the right and make more ammonia.

SO THE ANSWER IS—OOPS, KINETICS GETS IN THE WAY.

There you have it. The Haber process should be performed under pressure at low temperature while constantly removing the ammonia. The problem? As we will learn, if we want to make a lot of ammonia **FAST**, we need to increase the temperature which is in conflict with the thermodynamic requirement that we operate a low temperature. The solution?

Use a **catalyst** that will allow the reaction to occur at high rates at low temperature.

So let's wait until after we learn about kinetics to give a complete answer to the question about how to make ammonia using the Haber process.