Worksheet: Chemical equilibrium in the Haber Process

Name(s) ________________________________

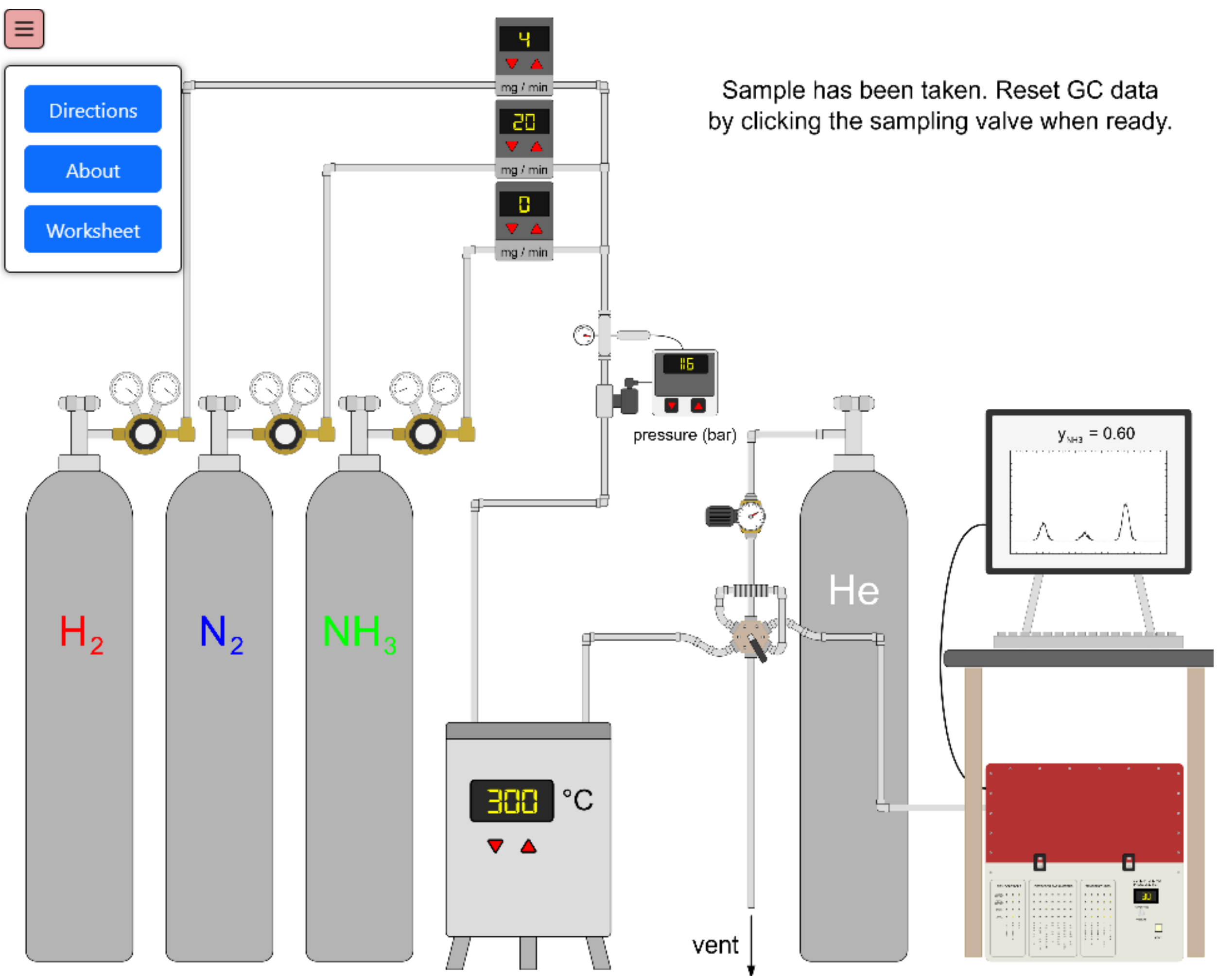
This experiment calculates chemical equilibrium constants for the gas-phase Haber reaction ($N_2 + 3H_2 \rightarrow 2NH_3$) from measurements of equilibrium concentrations. The heat of reaction is determined by measuring the equilibrium constant over a range of temperatures.

Student learning objectives

1. Be able to calculate an equilibrium constant from equilibrium concentrations.
2. Be able apply the van't Hoff equation to determine the heat of reaction.

Equipment

This catalytic reaction takes place at high pressures and elevated temperatures. Hydrogen and nitrogen are fed to the reactor to form ammonia. Ammonia can also be added to the reactor feed since in commercial reactors, unreacted N_2 and H_2 (and a fraction of the NH_3) recycle back to the feed. A gas chromatograph measures the composition of the reactor outlet stream.



Questions to answer before starting the experiment

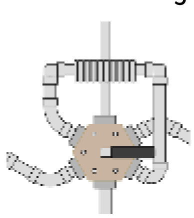
How does the equilibrium constant change with temperature for an exothermic reaction? Explain.

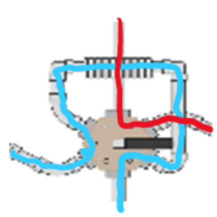
How does the equilibrium constant change with pressure for a gas-phase reaction?

What are the units of an equilibrium constant?

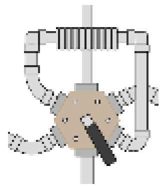
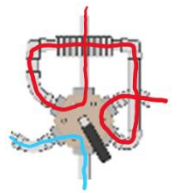
Run the experiment

1. Set the temperature of the sand bath heater by clicking on the up or down arrows. Record the temperature (^oC) in Table 1 below. Use a temperature of at least 280^oC so the reaction rate reaches equilibrium in a reasonable time.
2. Click the valves on top of the H_2 and N_2 tanks to open the tanks.
3. Optionally, also click the valve to open the NH_3 tank.
4. Open the valve on top of the He tank.
5. Select the flow rates using the red arrows on the mass flow controllers. Record in Table 1 the feed mass flow rates. Keep in mind that these are mass flow rates; a 0.21:1 mass ratio is a 3:1 H_2/N_2 molar ratio.
6. Calculate the feed molar flow rates and record in Table 1.
7. Use the red arrows on the pressure gauge/controller to select an operating pressure. To obtain a reasonable equilibrium conversion use a pressure of at least 50 bar. Record the pressure in Table 1.
8. Initially, the reactor effluent flows to a vent.
9. The display indicates the system is reaching equilibrium. Then the GC screen will show "Sample ready." The valve should be in the position below to fill the sample loop with the reactor effluent. The figure on the right shows the flow paths. Blue represents the reactor effluent flow through the sample loop, and red represents the He flow path.





9. Click on the switching valve to inject a sample into the GC. The valve will then be in the position shown below as He flushes the sample loop into the GC, and the reactor effluent flows to the vent. The blue represents the reactor effluent path, and the red represents the He path.

10. Record in Table 2 the mole fractions of H_2, N_2, and NH_3 obtained by the GC. Also convert the temperature to kelvin and record the temperature and pressure in Table 2.
11. Calculate the equilibrium pressures of N_2, H_2, and NH_3 and record in Table 2
12. Calculate the equilibrium constant and record in Table 2:

$$K_{eq} = \frac{\left(\frac{P_{NH3}}{1\ bar}\right)^2}{\left(\frac{P_{H2}}{1\ bar}\right)^3 \left(\frac{P_{N2}}{1\ bar}\right)}$$

    In this equation, partial pressures are in units of bar, and the equation is usually written as indicated below, where the pressures must be in bar and the equilibrium constant is dimensionless:

$$K_{eq} = \frac{P_{NH3}^2}{P_{H2}^3 P_{N2}}$$

    This equation assumes ideal gases, which is not a good assumption at the high pressures used for ammonia formation, but this assumption simplifies the calculations.

13. Repeat these measurements for a large enough range of temperatures so the heat of reaction can be determined from equilibrium constants as a function of temperature. Use different pressures to see the effect of pressure. Record the values in Tables 1 and 2.

Table 1 Feed conditions

			Feed rates (mg/min)			Feed rates (mol/min)		
Experiment	Temperature (^oC)	Pressure (bar)	N_2	H_2	NH_3	N_2	H_2	NH_3
#1								
#2								
#3								
#4								
#5								
#6								
#7								
#8								
#9								

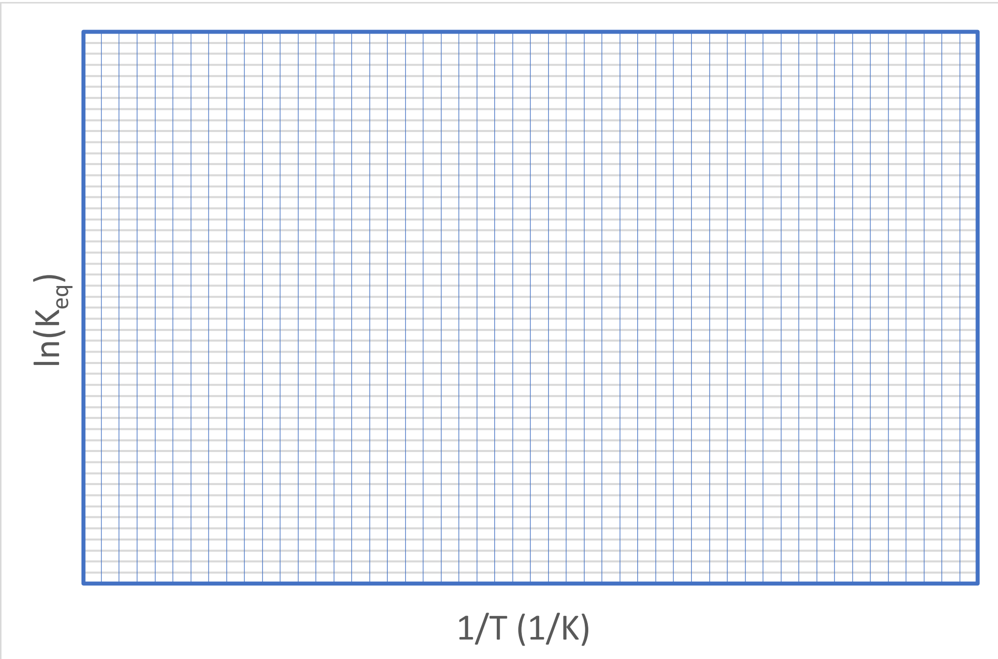
Table 2 Equilibrium conditions

			Equilibrium composition			Equilibrium pressure (bar)			
Experiment	T (K)	P (bar)	y_{N2}	y_{H2}	y_{NH3}	P_{N2}	P_{H2}	P_{NH3}	K_{eq}
#1									
#2									
#3									
#4									
#5									
#6									
#7									
#8									
#9									

What can you conclude about the effect of pressure on the equilibrium constant?

Data Analysis:

Plot ln(K_{eq}) versus inverse temperature.



Does a straight line fit the data?

Calculate the heat of reaction from the van't Hoff equation by linear regression:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where K_2 (dimensionless) is the equilibrium constant at temperature T_2

K_1 (dimensionless) is the equilibrium constant at temperature T_1

T_1 and T_2 are absolute temperatures (K)

ΔH_{rxn} = heat of reaction (J/mol)

R = ideal gas constant (J/mol K)

ΔH_{rxn} = _________ J/mol = _______ kJ/mol

Questions to answer

1. Where might these measurements have errors?

2. What safety precautions would you take to conduct this experiment in the laboratory?