

## Worksheet: Chemical equilibrium in the Haber Process

Name(s) \_\_\_\_\_

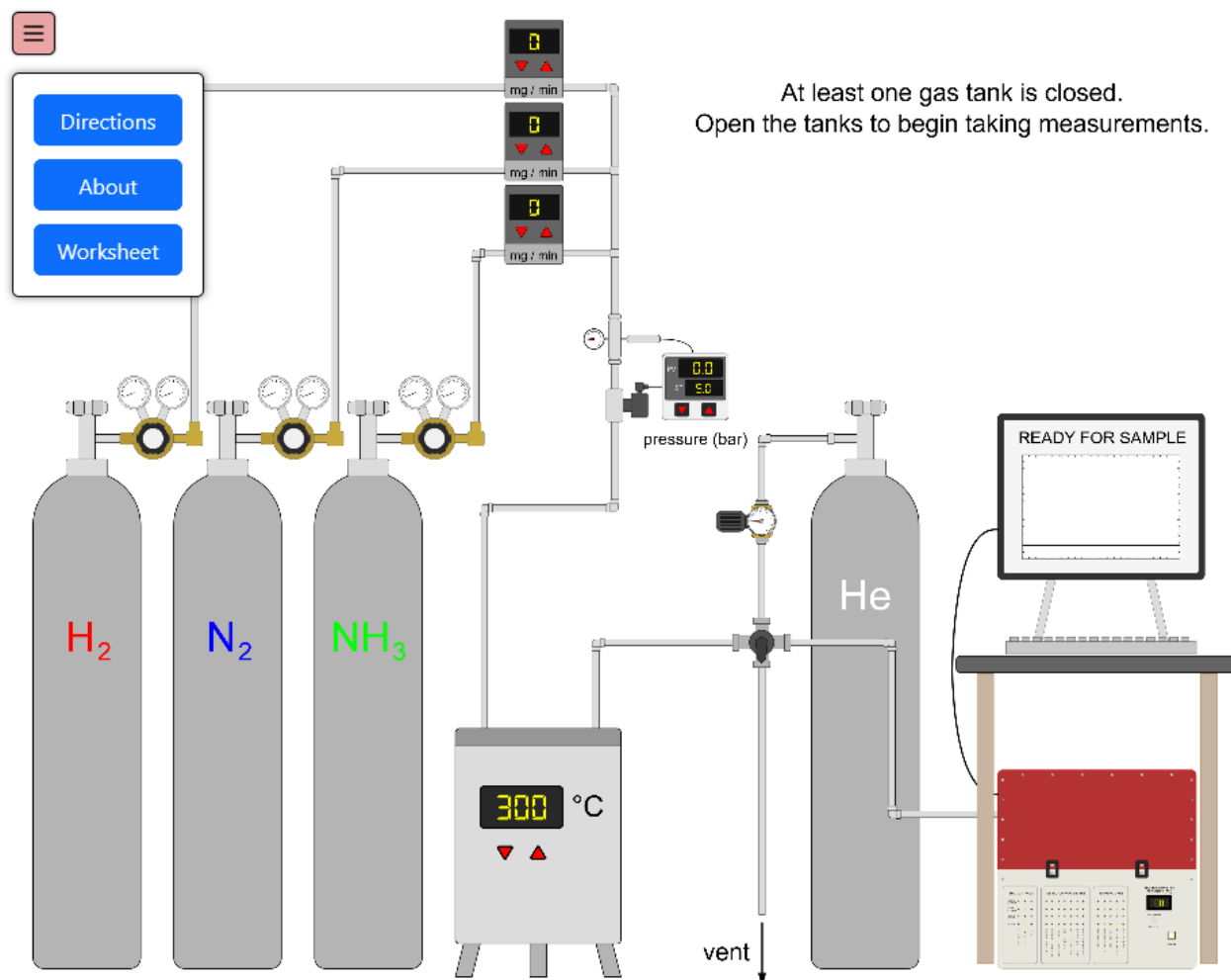
This experiment calculates chemical equilibrium constants for the gas-phase Haber reaction ( $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ ) from measurements of equilibrium concentrations. The heat of reaction is determined by measuring the equilibrium constant over a range of temperatures.

### Student learning objectives

1. Be able to calculate an equilibrium constant from equilibrium concentrations.
2. Be able apply the van 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, the unreacted  $\text{N}_2$  and  $\text{H}_2$  are recycled back to the feed and the recycle stream contains some  $\text{NH}_3$ . A gas chromatograph measures the composition of the outlet stream from the reactor.



### 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?

### Before starting

1. Set the temperature of the sand bath heater by clicking on the up or down arrows. Record the temperature in Table 1 below.
2. Click the valves on top of the H<sub>2</sub> and N<sub>2</sub> tanks to open the tanks.
3. Optionally, click the valve to open the NH<sub>3</sub> tank. Record the mass flow rate in Table 1.
4. Open the valve on top of the He tank. The He flow feeds a sample of gas into the gas chromatograph to measure the composition of the gas leaving the reactor.
5. Select an operating pressure using the up and down arrows on the pressure gauge/controller. Record the pressure in Table 1.
6. Select the flow rates using the up and down arrows on the mass flow controllers. Record in Table 1 the mass flow rates to the reactor. Calculate the molar flow rates and record in Table 1.
7. When the system starts up, the effluent from the reactor flows to a vent.
8. Allow time for the system to reach equilibrium; the GC screen should read READY FOR SAMPLE.
9. Switch the valve (**how?**) to take a sample and inject it into the GC.
10. Record in Table 2 below the mole fraction of NH<sub>3</sub> obtained by the GC.
11. Calculate the mole fractions of N<sub>2</sub> and H<sub>2</sub> in the effluent using the feed composition and stoichiometry and record in Table 2.
12. Calculate the equilibrium pressures and record in Table 2
13. Calculate the equilibrium constant and record in Table 2

$$K_{eq} = \frac{\left(\frac{P_{NH_3}}{1 \text{ bar}}\right)^2}{\left(\frac{P_{H_2}}{1 \text{ bar}}\right)^3 \left(\frac{P_{N_2}}{1 \text{ bar}}\right)}$$

In this equation, the pressure is 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.

$$K_{eq} = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

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

Repeat these measurements for a range of temperatures and pressures and record in Tables 1 & 2.

**Table 1 Feed conditions**

Experiment	Temperature (K)	Pressure (bar)	Feed rates (mg/min)			Feed rates (mol/min)			
			N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>	
#1									
#2									
#3									
#4									
#5									
#6									
#7									
#8									
#9									

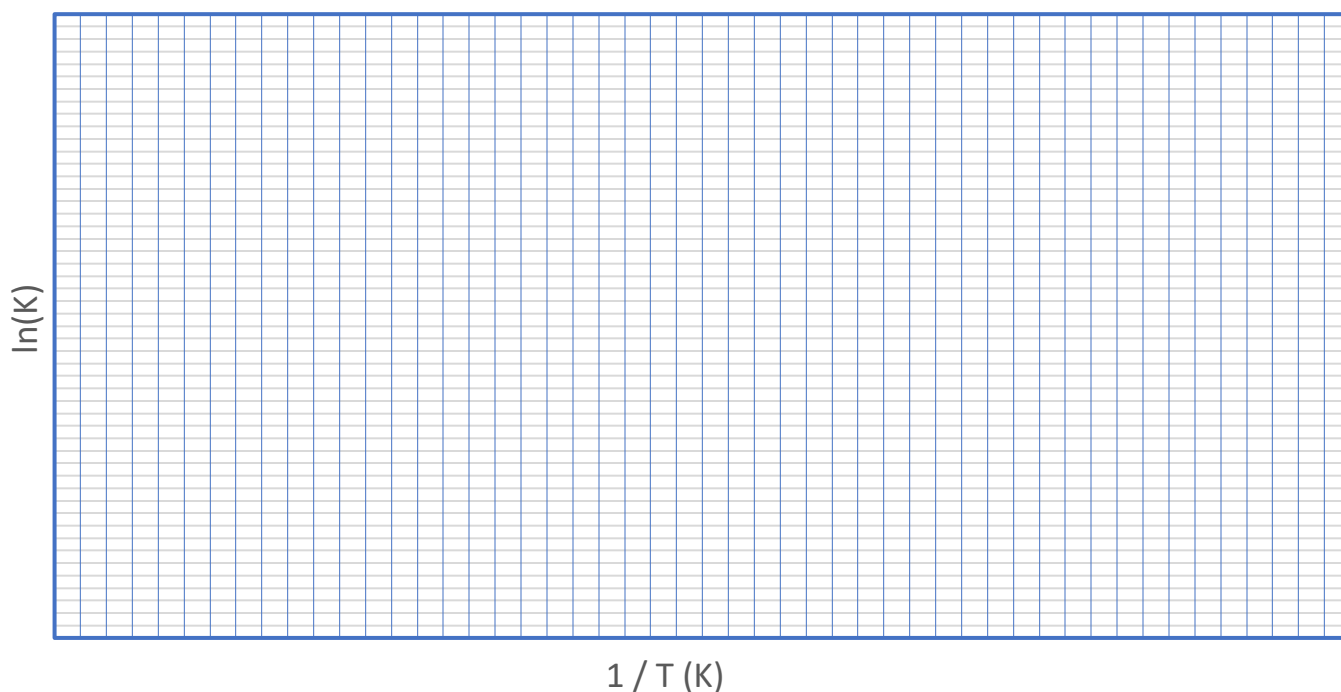
## 2 Equilibrium conditions

			Equil. composition			Equilibrium pressure (bar)			$K_{eq}$
Experiment	T (K)	P (bar)	NH <sub>3</sub>	N <sub>2</sub>	H <sub>2</sub>	P <sub>N2</sub>	P <sub>H2</sub>	P <sub>NH3</sub>	
#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.



Calculate the heat of reaction from the van Hoff equation, using all your data.

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

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)

$\Delta H_{rxn}$  = heat of reaction (J/mol)

R = ideal gas constant (J/mol K)

$\Delta H_{rxn}$  = \_\_\_\_\_ 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?