Worksheet: Chemical equilibrium N_2O_4 dissociation worksheet
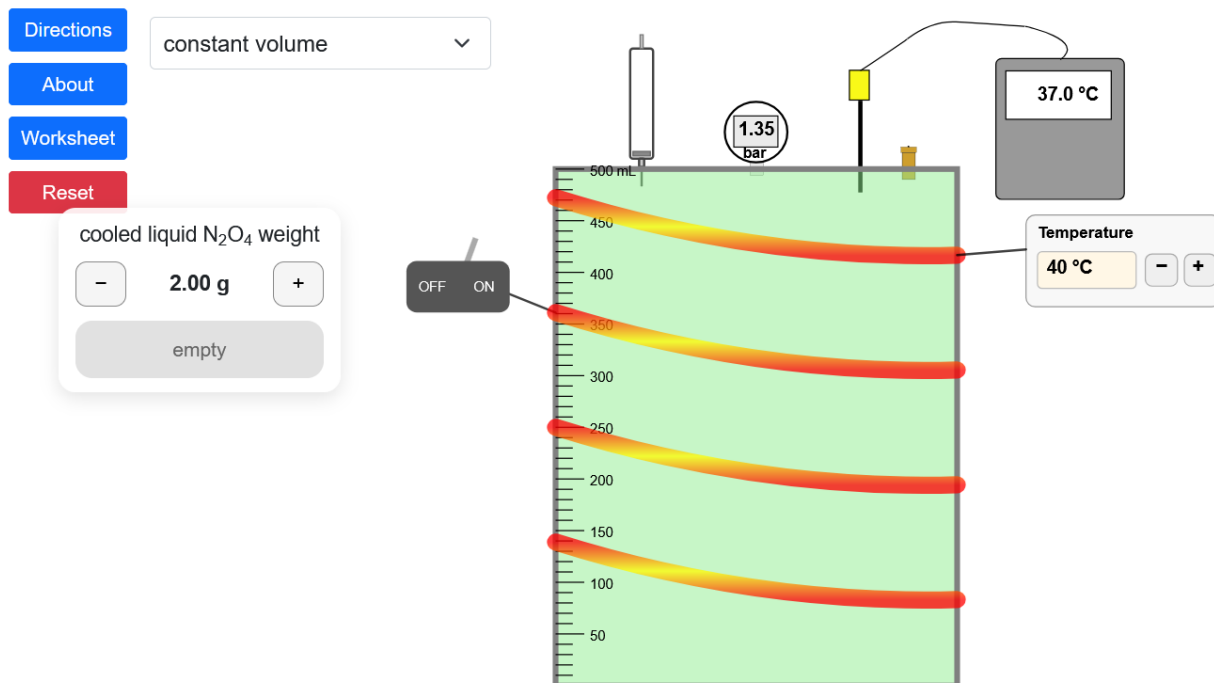
Name(s)_____

This experiment measures equilibrium pressures in a constant-volume system and equilibrium volumes in a constant-pressure system for a gas-phase reaction with a mole change ($N_2O_4 \rightarrow 2\ NO_2$). Equilibrium constants calculated from these measurements at a range of temperatures are used to calculate the heat of reaction and the entropy change.
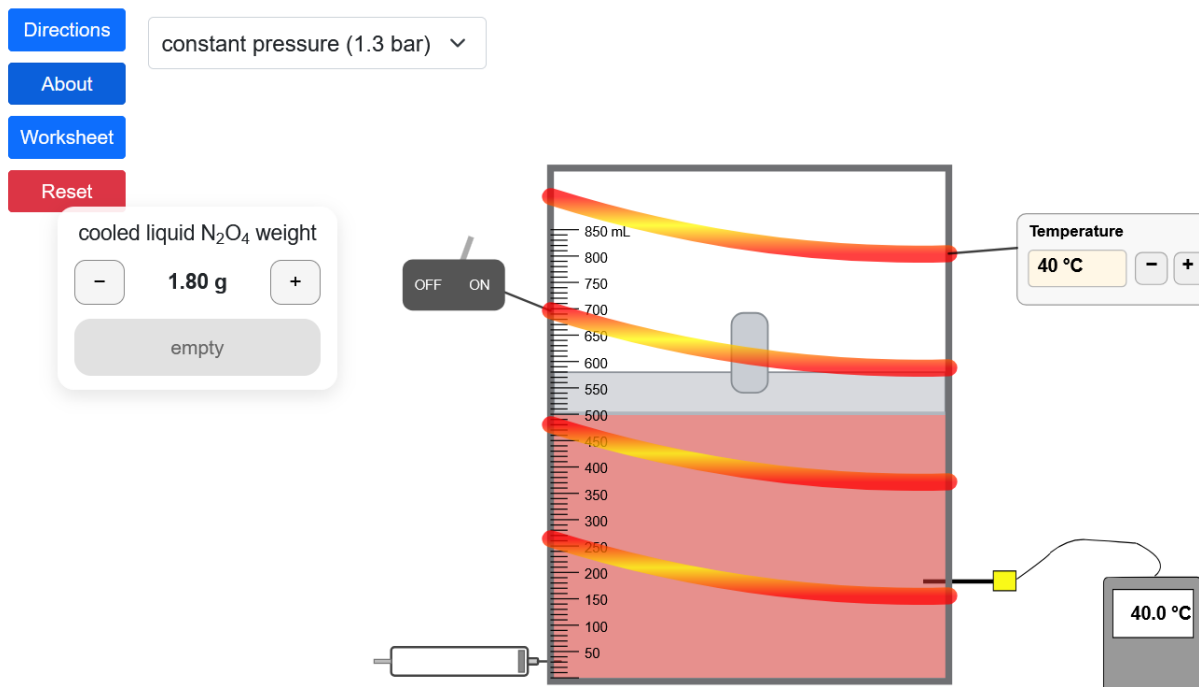
Student learning objectives

1. Be able to apply the ideal gas law.
2. Determine the extent of reaction from equilibrium pressures or equilibrium volumes for a gas-phase reaction with a mole change.
3. Calculate equilibrium constants from pressures, volumes, and extents of reaction.
4. Calculate enthalpy of reaction (heat of reaction) and entropy of reaction from equilibrium constants over a range of temperatures.

Equipment

Constant volume reactor with a pressure gauge, a heating sleeve, and a temperature sensor. A syringe injects liquid N_2O_4 into the reactor. The reactor contains a pressure-relief valve to prevent over pressure of the reactor.

Constant pressure reactor with a piston, a heating sleeve, and a temperature sensor. A syringe injects liquid N_2O_4 into the reactor.

Questions to answer before starting the experiment

1. If you add an inert gas at constant temperature to the gas-phase reaction A--> 2B that is at equilibrium in a constant volume reactor, which direction does equilibrium shift? Why?

2. If you add an inert gas at constant temperature to the gas-phase reaction A--> 2B that is at equilibrium in a constant pressure reactor, which direction does equilibrium shift?

3. For the gas-phase reaction A --> 2B at constant temperature in a piston/cylinder, when the pressure increases, which direction does the reaction proceed? Why?

Experiments

System 1: Equilibrium at constant volume

1. In a constant-volume reactor, the pressure increases as the temperature increases (ideal gas law) and also because of the number of moles increases as N_2O_4 dissociates to reach equilibrium.

2. Inject 1.6 to 2.0 g of cooled liquid N_2O_4 into an evacuated 500-mL container at 25°C. Record the amount of N_2O_4 injected _____ g and calculate the moles injected _____ mol.

3. Allow the system to go to equilibrium and record the pressure in Table 1.

4. Calculate the total number of moles $(n_{N2O4e} + n_{NO2e})$ at equilibrium from the ideal gas law.

$$P = \frac{(n_{N2O4e} + n_{NO2e})RT}{V}$$

where R = ideal gas constant = 0.08314 (bar-L)/(mol K)

T = temperature (K)

V = reactor volume = 0.50 L

5. Since $(n_{N2O4e} + n_{NO2e}) = (n_{N2O4i} - X + 2X) = (n_{N2O4i} + X)$, where X is the extent of reaction (units of mol), calculate the extent of reaction from the total number of moles and the moles of N_2O_4 injected and record in Table 1.

$$X = n_{N2O4i} - n_{N2O4e}$$

where n_{N2O4i} = mole of N_2O_4 injected

n_{N2O4e} = moles of N_2O_4 at equilibrium

n_{NO2e} = 2X = moles of NO_2 at equilibrium

6. Calculate the equilibrium constant and record the value in Table 1.

$$K_{eq} = \frac{P_{NO2}^2}{P_{N2O4}} = \frac{(y_{NO2}P)^2}{y_{N2O4}P} = \frac{\left(\dfrac{2X}{n_{N2O4i} + X}\right)^2 P^2}{\left(\dfrac{n_{N2O4i} - X}{n_{N2O4i} + X}\right)P} = \frac{4X^2 P}{(n_{N2O4i} + X)(n_{N2O4i} - X)}$$

7. Turn on the heater and raise the temperature to 35°C, allow time for the reaction to equilibrate, repeat steps 3 to 6, and record values in Table 1.

8. Repeat step 7 for temperature of 45°C, 55°C, and 65°C.

Table 1

Temperature (°C)	Pressure (bar)	X (mol)	K_{eq}	Temperature (K)
25				298
35				308
45				318
55				328
65				338
75				348

System 2: Equilibrium at constant pressure

1. In a constant-pressure reactor, the volume increases as the temperature increases (ideal gas law) and also because of the number of moles increases as N_2O_4 dissociates to reach equilibrium.

2. Inject 1.6 to 2.0 g of cooled liquid N_2O_4 into an empty piston/cylinder at 25°C. The pressure exerted by the piston is 1.3 bar. Record the amount of N_2O_4 injected _____ g and calculate the moles injected _____ mol.

3. Allow the system to go to equilibrium at constant pressure and measure the volume and record in Table 2.

4. Calculate the total number of moles ($n_{N2O4e} + n_{NO2e}$) at equilibrium from the ideal gas law.

5. Calculate the extent of reaction X from the total number of moles ($n_{N2O4i} + X$) and the moles of N_2O_4 injected and record in Table 2.

6. Calculate the equilibrium constant and enter the value in Table 2.

7. Turn on the heater and raise the temperature to 35°C, repeat steps 3 – 6 and record the values in Table 2.

8. Repeat step 7 for temperatures of 45°C, 55°C, 65°C, and 75 °C.

Table 2

Temperature (°C)	Volume (L)	X (mol)	K_{eq}	Temperature (K)
25				298
35				308
45				318
55				328
65				338
75				348

Analysis

Use the equilibrium constants in Tables 1 and 2 to calculate ΔH_{rxn} and ΔS_{rxn} from a plot of $\ln K_{eq}$ versus 1/T and the van't Hoff equation:

$$\ln K_{eq} = -\frac{\Delta H_{rxn}}{RT} + \frac{\Delta S_{rxn}}{R}$$

where R = ideal gas constant (J/(mol K)

Questions to answer

1. How close are your calculated values for ΔH_{rxn} and ΔS_{rxn} to values in the NIST Webbook?

2. What are the safety concerns with conducting this reaction? Are N_2O_4 or NO_2 toxic?

3. What assumptions in these measurements might affect the accuracy of the equilibrium constants measured?