

9.7: The Dumas Bulb Method for Measuring Decomposition Equilibrium

A classic example of an experiment that is employed in many physical chemistry laboratory courses uses a Dumas Bulb method to measure the dissociation of $N_2O_4(g)$ as a function of temperature (Mack & France, 1934). In this experiment, a glass bulb is used to create a constant volume container in which a volatile substance can evaporate, or achieve equilibrium with other gases present. The latter is of interest in the case of the reaction



The reaction is endothermic, so at higher temperatures, a larger degree of dissociation is observed.

The procedure is to first calibrate the internal volume of the Dumas bulb. This is done using a heavy gas (such as SF_6) and comparing the mass of the bulb when evacuated to the mass of the bulb full of the calibrant gas at a particular pressure and temperature.

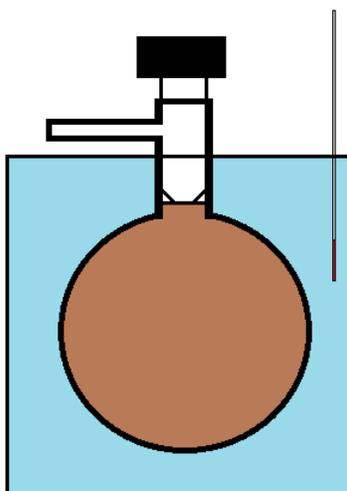


Figure 9.7.1:

The Dumas bulb is then charged with a pure sample of the gas to be investigated (such as N_2O_4) and placed in a thermalized bath. It is then allowed to come to equilibrium. Once Equilibrium is established, the stopcock is opened to allow gas to escape until the internal pressure is set to the pressure of the room. The stopcock is then closed and the bulb weighed to determine the total mass of gas remaining inside. The experiment is repeated at higher and higher temperatures (so that at each subsequent measurement, the larger degree of dissociation creates more molecules of gas and an increase in pressure in the bulb (along with the higher temperature), which then leads to the expulsion of gas when the pressure is equilibrated.

The degree of dissociation is then determined based on the calculated gas density at each temperature.

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2(n - 1)}$$

where ρ_1 is the measured density and ρ_2 is the theoretical density if no dissociation occurs (calculated from the ideal gas law for the given temperature, pressure, and molar mass of the dissociating gas) and n is the number of fragments into which the dissociating gas dissociates (ie.g., $n = 2$ for Equation \req{eq1}). The equilibrium constant is then calculated as

$$K = \frac{4\alpha^2}{1 - \alpha^2} \left(\frac{p}{1.00 \text{ atm}} \right)$$

Finally, a van't Hoff plot is generated to determine the reaction enthalpy.

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