

Physical Chemistry

Lecture 11

Adiabatic Processes, Joule Expansion, Joule-Thomson Expansion

Isothermal, reversible expansion of an ideal gas

- ◆ Work on the system

$$w = - \int_{path} P dV_m = -RT \int_{V_{m1}}^{V_{m2}} \frac{1}{V_m} dV_m = -RT \ln \left(\frac{V_{m2}}{V_{m1}} \right)$$

- ◆ Internal energy change

$$\Delta U_m = 0$$

- ◆ Heat transferred found by difference

$$q = \Delta U_m - w = RT \ln \left(\frac{V_{m2}}{V_{m1}} \right)$$

Adiabatic process

- ◆ A process in which there is no heat transfer into the system
- ◆ $q = 0$
- ◆ Differential

$$dU_m = dw = -P_{ext} dV_m$$

Adiabatic, reversible process for an ideal gas

- ◆ $q = 0$
- ◆ Reversibility requires $P_{ext} = P$
- ◆ Differential

$$dU_m = -PdV_m$$

- ◆ For an ideal gas, the energy does not depend on V_m

$$C_{Vm} dT = - \frac{RT}{V_m} dV_m$$

Adiabatic, reversible process for an ideal gas (2)

- ◆ Rearrange differential and integrate to give

$$\int_{T_1}^{T_2} \frac{C_{Vm}}{T} dT = -R \ln \left(\frac{V_{m2}}{V_{m1}} \right)$$

- ◆ If the gas is **monatomic**, C_{Vm} is usually independent of temperature (or nearly so)

$$C_{Vm} \ln \left(\frac{T_2}{T_1} \right) = -R \ln \left(\frac{V_{m2}}{V_{m1}} \right)$$

Joule expansion

- ◆ Expansion at constant internal energy
- ◆ To determine the changes, one must know

$$\left(\frac{\partial T}{\partial V_m} \right)_{U_m} = - \left(\frac{1}{C_{Vm}} \right) \left(\frac{\partial U_m}{\partial V_m} \right)_T$$

- ◆ For an ideal gas, this is zero and the temperature does not change
- ◆ For a real gas, this is nonzero and the temperature does change during the expansion

Joule expansion of a van der Waals gas

- ◆ Determine the appropriate derivative

$$\left(\frac{\partial U_m}{\partial V_m}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P = \frac{a}{V_m^2}$$

- ◆ Integrate over volume, assuming a volume-independent molar heat capacity

$$\Delta T = \int_{V_{m2}}^{V_{m1}} \left(\frac{\partial T}{\partial V_m}\right)_{U_m} dV_m = \frac{a}{C_{Vm}} \int_{V_{m2}}^{V_{m1}} \frac{1}{V_m^2} dV_m = \frac{a}{C_{Vm}} \left(\frac{1}{V_{m2}} - \frac{1}{V_{m1}}\right)$$

Joule expansion of CO₂

- ◆ Treat as a van der Waals gas
- ◆ Information
 - $a = 0.3649 \text{ Pa}\cdot\text{m}^6/\text{mol}$
 - $C_{Vm} = 28.09 \text{ joule/K}\cdot\text{mol}$
- ◆ Consider a doubling of the volume from 22.4 L/mol to 44.8 L/mol

$$\Delta T = \frac{0.3684 \text{ Pa}\cdot\text{m}^6}{28.09 \text{ joule/K}} \left(\frac{1}{0.0448 \text{ m}^3} - \frac{1}{0.0224 \text{ m}^3}\right) = -0.29 \text{ K}$$

- ◆ A tiny, but measurable increase

Joule-Thomson experiment

- ◆ Adiabatic expansion of a gas through an orifice
- ◆ Isenthalpic process
 - $H_1 = H_2$
- ◆ Temperature change given by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

- ◆ Ideal gas: $\Delta T = 0$
- ◆ Real gas: $\Delta T \neq 0$



Joule-Thomson effect

- ◆ Used for air conditioning, cooling
- ◆ Joule-Thomson coefficient, μ_{JT} , determines size of effect
 - Usually positive – cooling upon expansion
 - Can be negative
 - Typical size – 1 K/bar

Standard states

- ◆ Can calculate **changes** in variables with thermodynamic mathematics
- ◆ To make a scale of energy, one must define the value at a particular set of conditions
- ◆ Standard state – a state where the properties are defined

Standard states

- ◆ Solids and liquids
 - The material at the temperature under a pressure of 1 bar
- ◆ Gases
 - The equivalent ideal gas at the temperature and at a pressure of 1 bar
- ◆ Sometimes see other standard states defined in some circumstances

Summary

- ◆ Can calculate changes in state variables under various conditions
 - Isothermal
 - Adiabatic
 - Joule or Joule-Thomson experiment
- ◆ To define scales for thermodynamic parameters, one must specify **standard state**