

Physical Chemistry

Lecture 12

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

$$dU_m = -P dV_m$$

- ◆ 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 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

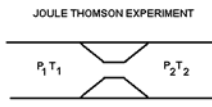
$$\Delta T = \frac{0.3684 \text{ Pa}\cdot\text{m}^6}{28.09 \text{ joule/K}} \left(\frac{1}{0.0448 \text{ m}^3} - \frac{1}{0.0224 \text{ m}^3}\right) = -0.29 \text{ K}$$

- ◆ A tiny, but measurable increase

Joule-Thomson experiment

- ◆ Adiabatic expansion of a gas through an orifice
- ◆ Treat as a sequence of two steps:
 - Compress gas at constant pressure, P_1 , to $V=0$ ($w_1=P_1V_1$)
 - Expand gas at constant P_2 to V_2 ($w_2=-P_2V_2$)
- ◆ Because of the adiabaticity of the process: □
- ◆ This gives: □
- ◆ or

JOULE THOMSON EXPERIMENT



$$\Delta U = U_2 - U_1 = w_1 + w_2$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

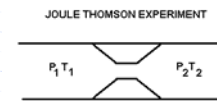
$$H_2 = H_1$$

Joule-Thomson experiment

- ◆ Adiabatic expansion of a gas through an orifice
- ◆ Isenthalpic process
 - $H_1 = H_2$
- ◆ Temperature change given by
- ◆ Ideal gas: $\Delta T = 0$
- ◆ Real gas: $\Delta T \neq 0$

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

JOULE THOMSON EXPERIMENT



$$\Delta T = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_H dP$$

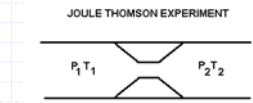
Joule-Thomson coefficient

- ◆ Joule-Thomson coefficient

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

- ◆ The size of the coefficient determines temperature change for a pressure drop
- ◆ One gets μ_{JT} from measurements in Joule-Thomson experiments

JOULE THOMSON EXPERIMENT

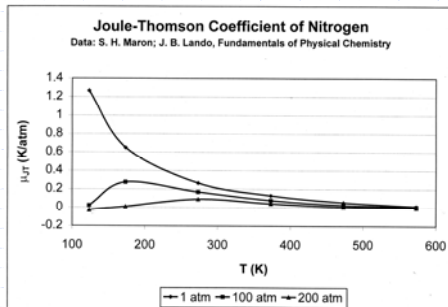


$$\Delta T = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_H dP = \int_{P_1}^{P_2} \mu_{JT} dP$$

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

Joule-Thomson effect



Ranque-Hilsh vortex tube

◆ Mechanical device that separates a compressed gas into hot and cold streams



◆ Two explanations

- Outer air is under higher pressure than the inner air (because of centrifugal force); the temperature of the outer air is higher than of the inner air
- Both vortices rotate at the same angular velocity and direction, the inner vortex has lost angular momentum, the decrease of which is transferred as kinetic energy to the outer vortex

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**