

59-240
Lecture 6
Work and Heat

Heat capacity

Cannot measure heat directly
Gives a connection between ΔU and ΔT Definition
Extensive property
partial derivative
constant over small ΔT
molar heat capacity, $C_{V,m}$ ($J K^{-1} mol^{-1}$)
specific heat capacity, $C_{V,m}^S$ ($J K^{-1} g^{-1}$)
 $C_V = \left(\frac{\partial U}{\partial T} \right)_V$
 $q_V = C_V \Delta T$ at constant V
Large C_V : Large $q > 0$, Smaller $\Delta T > 0$
Small C_V : Small $q > 0$, Larger $\Delta T > 0$
Heat capacity infinite at phase transitions (has no meaning!)

Calorimetry

Walls of bomb are diathermic Adiabatic bomb calorimeter
Outer walls of calorimeter are adiabatic
Calibrated by determining the calorimeter constant
Basic layout and workings
or...compare against known **heat capacity**

Heat transactions

$dU = dq + dw_{exp} + dw_e$
If isochoric, $\Delta V = 0$, $w = 0$
Ignore extra sources of work, $w_e = 0$
 $dU = dq$ or $\Delta U = q_V$

Expansion work

$dU = dq + dw$
Frictionless piston
 $dw = -p_{ex} dV$
 $w = -\int_{V_i}^{V_f} p_{ex} dV$
Free expansion (into vacuum)
 $w = 0$
types of work - large variety. all with generalized force and generalized displacement

Expansion against constant p

$w = -p_{ex} \Delta V$
piston indicator diagram
irreversible process

Reversible vs. Irreversible:

Reversible
Theoretical
Infinitesimally away from equilibrium
Idealization
Easy to model mathematically
Set up with infinitesimals; integrate for observable real processes
Irreversible
Real process
Finite departures from equilibrium
Difficult to model mathematically in some cases

Reversible expansion

$w = -\int_{V_i}^{V_f} p dV$

Isothermal rev. exp.

$\Delta U = 0, \Delta T = 0, q = -w, \Delta V > 0$
 $w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \left(\frac{V_f}{V_i} \right)$
Max. work obtained from rev. process in comparison to irrev. process