

Physical Chemistry

Lecture 8

Heat flow and heat capacity

First law of thermodynamics

- ◆ The internal energy, U , of a system remains constant unless work is done on (by) it or heat flows into (from) it.
- ◆ Conservation of energy in a process
- ◆ Internal energy is a state function independent of the path

$$U(T_2, V_{m2}) - U(T_1, V_{m1}) = \int dU_{\text{along path}}$$

Heat flow and work

- ◆ Energy is changed by heat flow or work

$$\Delta U = q + w$$

- ◆ Work discussed previously
- ◆ Heat flow is any energy change not attributable to work

Heat capacity

- ◆ Heat capacity (C) – measure of how heat flow affects the temperature of a system

- Differential definition:

$$C = \lim_{\Delta T \rightarrow 0} \frac{q}{\Delta T}$$

- ◆ Usually reported: intensive quantities

- C_m – heat capacity on a molar basis
- c – specific heat, heat capacity on a weight basis, often per gram

Heat capacity and internal energy

- ◆ In the absence of mechanical work, there is no volume change
- ◆ Change internal energy via heat flow, when volume is constant:

$$\Delta U = U(T_2, V) - U(T_1, V) = q = \int_{T_1}^{T_2} C_v dT$$

- ◆ C_v , heat capacity at constant volume, $= (\partial U / \partial T)_v$
- ◆ $C_{v,m}$, molar heat capacity at constant volume
 - intensive variable $= (\partial U_m / \partial T)_v$
- ◆ The manner in which a system absorbs energy depends on the conditions of the process:

$$\left(\frac{\partial U_m}{\partial T} \right)_v \neq \left(\frac{\partial U_m}{\partial T} \right)_p$$

Sources of heat capacity

- ◆ Internal energy has contributions from various energy-storage modes

$$U = U_t + U_r + U_v + U_e + \dots$$

- Translation, U_t
- Rotation, U_r
- Vibration, U_v
- Electronic, U_e

- ◆ Heat capacity at constant volume is a sum of contributions

$$C_v = C_{v,t} + C_{v,r} + C_{v,v} + C_{v,e} + \dots$$

Heat capacity contributions in the equipartition limit

Type of Energy	Number of Modes	Energy in Equipartition	$C_{v,m}$
Translation	3	3 (RT/2)	3R/2
Vibration (linear)	3N - 5	(3N-5)2(RT/2)	(3N-5)R
Rotation (linear)	2	2(RT/2)	R
Vibration (nonlinear)	3N - 6	(3N-6)2(RT/2)	(3N-6)R
Rotation (nonlinear)	3	3(RT/2)	3R/2

Heat capacity of an ideal gas

◆ Internal energy has contributions from only translation, i.e. kinetic energy

◆ Found from kinetic theory

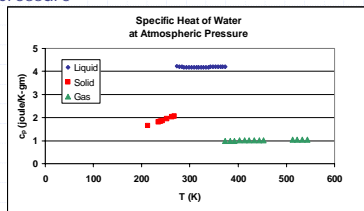
$$U_{t,m} = \frac{3}{2}RT$$

◆ Heat capacity for translation

$$C_{v,t,m} = \left(\frac{\partial U_{t,m}}{\partial T} \right)_v = \left(\frac{\partial}{\partial T} \left(\frac{3}{2}RT \right) \right)_v = \frac{3}{2}R$$

Temperature-dependent heat capacity

- ◆ The molar heat capacity, or the specific heat, is a state variable
- ◆ May depend on state variables such as temperature or pressure



Heat capacity of gaseous organic molecules

- ◆ Heat capacity reflects the manner in which energy is absorbed
- ◆ Roughly constant on a per-bond basis
- ◆ Reflects the nature of energy absorption

Molecule	$C_{p,m}$ (joule/K-mole)	$C_{p,m}$ per bond
Ethane	52.93	7.56
Propane	73.89	7.59
n-Butane	97.91	7.53
2-Methylpropane	97.28	7.53
n-Hexane	143.80	7.57
2,3-Dimethylbutane	141.25	7.43
n-Octane	181.88	7.26
2,2,3,3-Tetramethylbutane	193.68	7.75
Cyclobutane	72.68	6.06
Ethene	43.72	8.74 (7.29)
Propene	64.18	8.02 (7.13)
But-1-ene	86.06	7.82 (7.17)
cis-But-2-ene	79.33	7.21 (6.61)
Trans-But-2-ene	88.20	8.01 (7.36)
2-Methylpropene	89.50	8.13 (7.46)

Summary

- ◆ Internal energy only changed by work or heat flow
- ◆ Heat flow affects temperature of the system
 - Described by heat capacity
- ◆ Determine internal-energy change by integration of the heat capacity at constant volume
- ◆ Heat capacity is a function of state variables
- ◆ Heat capacity depends on how the molecules absorb energy