CHEM 331
Physical Chemistry
Revision 1.0

# $1^{st}$ Law of Thermodynamics

## PV Work

$$W = -\int P_{op}dV$$

$$W_{rev} = -\int Pdv$$

## Definition of Heat

$\Delta U = W_{adiab}$ State A $\longrightarrow$ State B along an Adiabatic Path

$Q = \Delta U - W$ State A $\longrightarrow$ State B along a General Path

## $1^{st}$ Law of Thermodynamics

$$\Delta U = Q + W$$

## Functional Form of U

$$\begin{aligned} dU &= \delta Q + \delta W \\ &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_v\, dT + \Pi_T\, dV \\ &= \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP = (C_v + \Pi_T V\alpha)\, dT + (-V\alpha T + V\kappa P)\, dP \quad ^{***} \end{aligned}$$

## Enthalpy

$$H = U + PV$$

$$dH = \delta Q_p$$

## Functional Form of H

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_p\, dT - C_p\, \mu_{JT}\, dP$$

## Thermodynamic Equations of State

$$\left(\frac{\partial U}{\partial V}\right)_T = \Pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad ^{***}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_p\,\mu_{JT} = -T\left(\frac{\partial V}{\partial T}\right)_P + V \quad ^{***}$$

## Heat Capacities

$$C_x = \frac{\delta Q_x}{dT}$$

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P = \frac{\alpha^2 TV}{\varkappa} \quad ^{***}$$

Equipartition Theorem

$U = \frac{1}{2}\,nRT$ for each degree of freedom

Law of Dulong & Petit

$C_v \sim 6.2$ cal/K mol

Debye Law

$C_p = a\,T^3$ below 15K

## Ideal Gases

$PV = nRT$

$U(T)$ or $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$H(T)$ or $\left(\frac{\partial H}{\partial P}\right)_T = 0$

$C_p - C_v = R$

$C_v = 3/2\ nR$ if monatomic

## Notes

*** Indicates the formula presented will be derived at a later point in the course.