

Physical Chemistry (Chem 132A)



Lecture 3 Wednesday, October 4

First Law of Thermodynamics

The internal energy of an ISOLATED system is constant

COURSE WEBSITE



<https://canvas.eee.uci.edu/courses/6058>

Github website generated by Shane Flynn

https://github.com/swflynn/Teaching_UCI/tree/master/Chem132_A_2017



Equations from last lecture

From last lecture:

$$\mathbf{dU = dq + dw = dq \text{ (at constant volume)} \quad \Delta U = q_v}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

**Definition of constant volume
heat capacity.**

$$w = - \int_{V_i}^{V_f} p_{ex} dV = -p_{ex} \int_{V_i}^{V_f} dV = -p_{ex}(V_f - V_i) \quad \text{Constant pressure}$$

For a REVERSIBLE expansion/compression

	Ideal gas	Isothermal
$w = - \int_{V_i}^{V_f} p dV$	$w = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$	$= - nRT \ln \frac{V_f}{V_i}$

Relationship between change in temperature and q



$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT = C_V dT$$

$$\Delta U = \int dU = \int_{T_1}^{T_2} C_V dT = C_V \int_{T_1}^{T_2} dT = C_V \Delta T$$

$$\mathbf{q_V = C_V \Delta T}$$

Chemistry in an open system by constant pressure



$$H \equiv U + pV \quad \text{DEFINITION OF Enthalpy (H)}$$

U, p, and V are all state functions so H is a state function

For a reaction involving ideal gases at constant T:

$$\Delta H = \Delta U + \Delta n_g RT$$

$$dH = dU + d(pV) = dq + dw + pdV + Vdp$$

If only expansion/compression work: $w = dw = -pdV$

$$dH = dq - pdV + pdV + Vdp$$

$$dH = dq + Vdp$$

$$dH = dq_p$$

$$\Delta H = q_p$$



Temperature dependence of ΔH

$$C_p \equiv \left(\frac{\partial H}{\partial T} \right)_p \quad \text{Definition of constant pressure heat capacity}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT = C_p \Delta T \quad \text{If } C_p \text{ is constant with } T$$

THERMOCHEMISTRY



TEXTBOOK Chapter 2C

Standard Enthalpies

Enthalpies of Formation

$$\Delta_r H^0 = \sum_{\text{Products}} \nu \Delta_f H^0 - \sum_{\text{Reactants}} \nu \Delta_f H^0$$

You should have LOTS of experience with this from previous courses. Review this so you are very familiar with these sorts of calculations.

$\Delta_r H$ at T other than 298.15K



$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT \quad \text{Eq 2C.6 (note typo in the text)}$$

$$\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^0 dT$$

$$\Delta_r C_p^0 = \sum_{\text{products}} \nu C_p^0 - \sum_{\text{reactants}} \nu C_p^0$$

This allows you to calculate standard enthalpy changes for a reaction at temperatures other than 298.15

State functions and Exact Differentials



U is an example of a state function and it can be viewed as a function of p, V, and T, all of which are also state functions.

However, there is an Equation of State that relates p, V, and T

For example for an ideal gas: $pV = nRT$

So we can write the change in U in the following manner

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT = \pi_T dV + C_V dT$$

π_T is called the “internal pressure”



$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT = \pi_T dV + C_V dT$$

If we are interested in how U varies with T at constant p? Divide the above equation by dT holding p constant

$$\left(\frac{\partial U}{\partial T} \right)_p = \pi_T \left(\frac{\partial V}{\partial T} \right)_p + C_V$$

$$\left(\frac{\partial V}{\partial T} \right)_p$$

Describes how the volume of the system changes with T. Usually tabulated as:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

Called the expansion coefficient

THE END



SEE YOU Friday