

Chemical Thermodynamics - I

BASICS

Section - 1

Internal Energy :

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the **internal energy**, U of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as : $\Delta U = q + w$... (I)

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (**isolated system**) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.

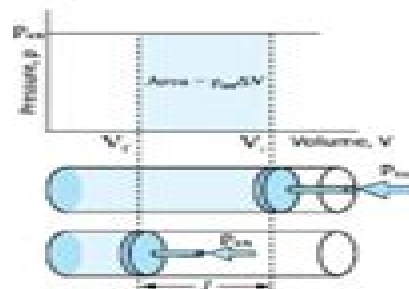
The equation, $\Delta U = q + w$ is mathematical statement of the first law of thermodynamics, which states that *the energy of an isolated system is constant*.

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how!

Pressure-Volume work :

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p . If external pressure is p_{ex} which is greater than p , piston is moved inward till the pressure inside becomes equal to p_{ex} . Let this change be achieved in a single step and the final volume be V_f .

During this compression, suppose piston moves a distance, l . **Figure :** Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, p_{ex} (in single step) is equal to the shaded area.



We also know, $\text{pressure} = \frac{\text{force}}{\text{area}}$ Therefore, $\text{force on the piston} = p_{ex} \cdot A$

If w is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{ex} \cdot A \cdot l = p_{ex} \cdot (-\Delta V) = -p_{ex} \Delta V = -p_{ex} (V_f - V_i) \quad \dots (II)$$

Basic Thermodynamics Module 1 Nptel

Evelyn Guha



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1. Understanding the eBook Basic Thermodynamics Module 1 Nptel
 - The Rise of Digital Reading Basic Thermodynamics Module 1 Nptel
 - Advantages of eBooks Over Traditional Books
2. Identifying Basic Thermodynamics Module 1 Nptel
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Basic Thermodynamics Module 1 Nptel
 - User-Friendly Interface
4. Exploring eBook Recommendations from Basic Thermodynamics Module 1 Nptel
 - Personalized Recommendations
 - Basic Thermodynamics Module 1 Nptel User Reviews and Ratings
 - Basic Thermodynamics Module 1 Nptel and Bestseller Lists
5. Accessing Basic Thermodynamics Module 1 Nptel Free and Paid eBooks
 - Basic Thermodynamics Module 1 Nptel Public Domain eBooks
 - Basic Thermodynamics Module 1 Nptel eBook Subscription Services

- Basic Thermodynamics Module 1 Nptel Budget-Friendly Options
- 6. Navigating Basic Thermodynamics Module 1 Nptel eBook Formats
 - ePub, PDF, MOBI, and More
 - Basic Thermodynamics Module 1 Nptel Compatibility with Devices
 - Basic Thermodynamics Module 1 Nptel Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Basic Thermodynamics Module 1 Nptel
 - Highlighting and Note-Taking Basic Thermodynamics Module 1 Nptel
 - Interactive Elements Basic Thermodynamics Module 1 Nptel
- 8. Staying Engaged with Basic Thermodynamics Module 1 Nptel
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Basic Thermodynamics Module 1 Nptel
- 9. Balancing eBooks and Physical Books Basic Thermodynamics Module 1 Nptel
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Basic Thermodynamics Module 1 Nptel
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Basic Thermodynamics Module 1 Nptel
 - Setting Reading Goals Basic Thermodynamics Module 1 Nptel
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Basic Thermodynamics Module 1 Nptel
 - Fact-Checking eBook Content of Basic Thermodynamics Module 1 Nptel
 - Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
- 14. Embracing eBook Trends

- Integration of Multimedia Elements
- Interactive and Gamified eBooks

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