

Internal Energy, Heat, Work and Enthalpy

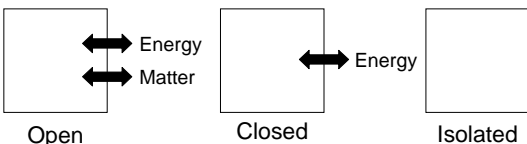
CHEM 323 Physical Chemistry I

Thermodynamics

- Study of Interactions between Matter and Energy
- Classical Physics Approach
 - Matter has mass takes up space
 - Energy is a property of matter resulting from motion (kinetic) or position (potential)
 - Energy has no mass, no volume
 - Matter and energy are not interconverted
- Start with Ideal Cases work to Real

Fundamental Definitions

- System and Surroundings
 - *System* part of the universe of interest
 - *Surroundings* rest of the universe



- System's Walls
 - *Diathermic* permeable to energy as heat
 - *Adiabatic* impermeable to energy as heat

Energy

- Capacity of System to do Work, w
 - Apply a force through a distance, $w = F \cdot d$
 - Measured in its orderly transfer between system and surroundings
- Types of Energy
 - Kinetic energy ($E_{kin} = 1/2 \cdot m \cdot v^2$)
 - Potential energy (position-dependent)
- Quantum Mechanics
 - Boltzmann distribution

More on Heat and Work

- Types of Work
 - Expansion work
 - Non-expansion work (Table 2.1 in text)
- Define *Temperature*, T
 - System's average thermal energy
 - *Equipartition Theorem*
- Define *Heat*, q , as Energy Flow caused by ΔT across diathermic Barrier
 - Chaotic molecular motion
 - Thermal equilibrium

Internal Energy

- Define U as total Energy in the System
 - Sum of all kinetic and potential inside system
 - State function, $U(p, n, V, T)$
 - Simplify to $U(V, T)$, but still not measurable
- Define ΔU as Change in U between some initial State, U_i , and some final State, U_f
 - Or $\Delta U = U(V_f, T_f) - U(V_i, T_i)$
 - Depends only on initial and final states
 - Verified experimentally

First Law of Thermodynamics

- First Formulation
 - For an isolated system $\Delta U = 0$
 - Proof?
- Second Formulation
 - For an adiabatic system the work needed to change from one specific state to another is independent of how the work is done
- Third Formulation
 - For all systems $\Delta U = q + w$
 - Mechanical equivalence of heat

Acquisitive Sign Convention

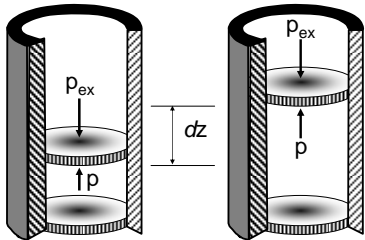
- Work
 - $w < 0$ system does work (energy leaves system and goes to surroundings)
 - $w > 0$ work is done on the system (energy enters system from surroundings)
- Heat
 - $q > 0$ heat enters system, its thermal energy increases (*endothermic*)
 - $q < 0$ heat exits system, its thermal energy decreases (*exothermic*)
- Sign Expectations!

First Law in Differential Form

- Formulation $\Delta U = q + w$ is for macroscopically-observable Changes
- Need
 - To expand definition of work
 - Define $U(V, T)$ more fully
- Change to $dU = dq + dw$
 - Infinitesimal changes
 - Not measurable, but mathematically handy

Expansion Work

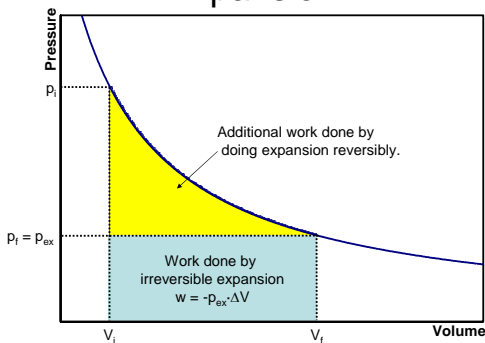
- Model
- Definitions?
- Assumptions?



Expressions for Work

- General Expression: $w = -\int_{V_i}^{V_f} p_{ex} dV$
- Free Expansion: $w = 0$
- Expansion against Constant Pressure:
 $w = -p_{ex}(V_f - V_i)$
- Reversible Expansion: $w = -\int_{V_i}^{V_f} p dV$
- Isothermal Reversible Expansion
 - Examine for an ideal gas

Isothermal Reversible Expansion



Heat with Constant Volume

- From the First Law
 - At constant volume $dV = dw_{\text{expansion}} = 0$
 - No other work allowed
 - Result: $dU = dq_v$, or $\Delta U = q_v$
- Remember $U(V, T)$
 - Since V constant $(\partial U / \partial V)_T = 0$
 - Dependence of U on T defines *constant volume heat capacity*, C_v

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

Heat with Constant Pressure

- Expansion Work is allowed
 - Still let other work be 0
- Define change in *Enthalpy*, ΔH , as q_p
 - Proof of $H = U + pV$
 - Can H be measured?
- Since $H(p, T)$ and with p constant
 - Define constant pressure heat capacity, C_p

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Dependence of U and H on T

- Need to integrate C_p and C_v Expressions

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p dT \quad \int_{U_1}^{U_2} dU = \int_{T_1}^{T_2} C_v dT$$

- Problem: C_p and C_v depend on T
- Solutions
 - For small T changes H doesn't change much
 - Use empirical equation (constants tabulated)

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

Calorimetry

- Ideal Relationships between ΔT and Thermodynamic Quantities
 - Constant volume (ΔU)
 - Constant pressure (ΔH)
 - Connection: $\Delta H = \Delta U + p\Delta V$
- Real-Life Calorimetry
 - Calorimeter constant
 - Specific heat capacities
 - When to use the total mass

Focus on Enthalpy

- Relevance to Chemistry
 - Bonding and intermolecular interactions
- Can only Measure $\Delta H (= q_p)$
 - Define standard enthalpy change ΔH°
 - Standard states
- For Chemical or Physical Change define $\Delta_x H^\circ$ as
$$\Delta_x H^\circ = \sum_{\text{products}} \nu_i H_{m,i}^\circ - \sum_{\text{reactants}} \nu_j H_{m,j}^\circ$$
 - Implications

Focus on Enthalpy

- Hess's Law
 - Enthalpy change for any process is sum of the enthalpy changes for each step in process
 - Why does this work?
- Standard Enthalpies of Formation, $\Delta_f H^\circ$
 - Definition
 - Reference state
 - Why do this?

$$\Delta_x H^\circ = \sum_{\text{products}} \nu_i \Delta_f H_i^\circ - \sum_{\text{reactants}} \nu_j \Delta_f H_j^\circ$$

Focus on Enthalpy

- Temperature Dependence of ΔH given by Kirchhoff's Law

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

where

$$\Delta_r C_p^0 = \sum_{\text{products}} \nu_i C_{p,m,i}^0 - \sum_{\text{reactants}} \nu_j C_{p,m,j}^0$$

- For small T changes ΔH changes little
- Use empirical expression for C_p if needed

Expanding the Differential

- Exact and Inexact Differentials
- Correspondence to State and Path Functions
 - Why don't we write Δq and Δw ?
- Proof of Function Type
 - Experimentally
 - Mathematically
 - Examples: U and w

Consequences

- Since $U(V, T)$ is a State Function

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

- Graphical interpretation

- Define Internal Pressure, $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$
- With $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$dU = \pi_T dV + C_V dT$$

Consequences

- Variation of U at constant Pressure
 - Assume system is closed (n constant)

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

- Define Expansion Coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$
- Universally-applicable Result

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

- Meaning

Extension to Enthalpy

- Since $H(p, T)$, we can write

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

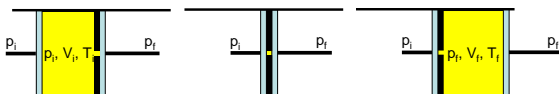
- Isothermal Compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$
 - Consequences
- Joule-Thomson Coefficient $\mu = \left(\frac{\partial T}{\partial p}\right)_H$
- Variation of H with T at constant V (n)

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha \mu}{\kappa_T}\right) C_p$$

Joule-Thomson Effect

- Isenthalpic Adiabatic Expansion of Gas
 - Gas forced through small opening from high pressure to low pressure
 - Real gases *usually* cool
 - All real gases have ΔT proportional to Δp
 - Used to liquefy gases

- Model



Joule-Thomson Effect

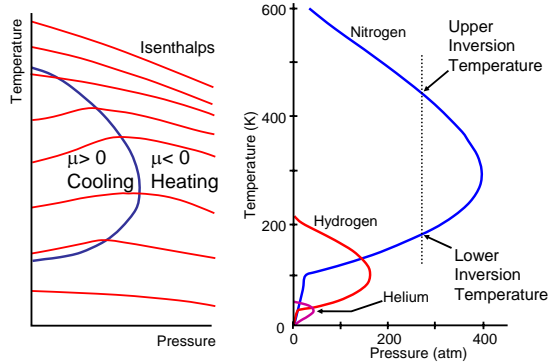
- Usually measure Isothermal Joule-Thomson Coefficient

$$\mu_T = \left(\frac{\partial H}{\partial p} \right)_T$$

- Conversion $\mu_T = -C_p \mu$
- Process

- Inversion Temperature(s)
 - Joule-Thomson coefficient changes sign
 - Depends on gas, pressure, intermolecular interactions

Inversion Temperatures



Relating C_V and C_p

- Heat Capacity Ratio
 - Adiabatic versus isothermal expansion of an ideal gas

$$\gamma = \frac{C_{p,m}}{C_{v,m}}$$

- Difference of Heat Capacities
 - Meaning

$$C_p - C_v = \frac{\alpha^2 TV}{\kappa_T}$$
