University of Washington
Department of Chemistry
Chemistry 452/456
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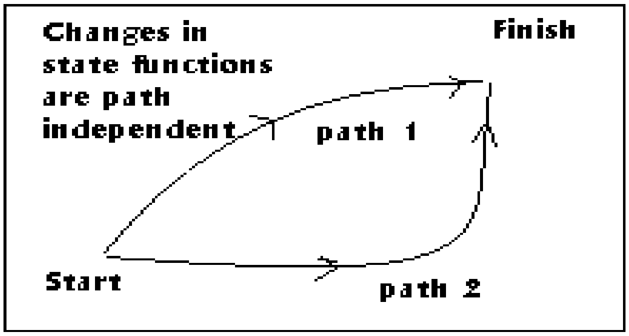
Lecture 2. 6/26/13
EDR: Ch. 2

A. Differentials and State Functions

- Thermodynamics allows us to calculate energy transformations occurring in systems composed of large numbers of particles, systems so complex as to make rigorous mechanical calculations impractical.
- The limitation is that thermodynamics does not allow us to calculate trajectories. We can only calculate energy changes that occur when a system passes from one equilibrium state to another.
- In thermodynamics, we do not calculate the internal energy U. We calculate the change in internal energy ΔU, taken as the difference between the internal energy of the initial equilibrium state and the internal energy of the final equilibrium state: $\Delta U = U_{final} - U_{initial}$
- The internal energy U belongs to a class of functions called state functions. State function changes ΔF are only dependent on the initial state of the system, described by $P_{initial}$, $V_{initial}$, $T_{initial}$, $n_{initial}$, and the final state of the system, described by P_{final}, V_{final}, T_{final}, and n_{final}. State function changes do not depend upon the details of the specific path followed (i.e. the trajectory).
- Quantities that are path-dependent are not state functions.
- Thermodynamic state functions are functions of several state variables including P, V, T, and n. changes in the state variable n is are not considered at present. We will concentrate at first on single component/single phase systems with no loss or gain of material. Of the three remaining state variables P, V, T only two are independent because of the constraint imposed by the equation of state.



- Changes in state functions can be expressed using the notation of differntials.
- For a differential of the state function U: $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ which physically means if the temperature or the volume of a material change the energy changes.

- A differential (in two dimensions…we can generalize to high dimensions, if necessary) has the general form $M\left(x,y\right)dx + N\left(x,y\right)dy$.
  - If $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$ the differential is exact (Euler's Criterion). It follows that exact differentials have the form
    $$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy = M\left(x,y\right)dx + N\left(x,y\right)dy$$
  - All state functions are exact differentials. The path integrals of exact differentials are invariant to path. From this fact it follows that for a state function F $\Delta F = F_{final} - F_{initial} = \int_{initial}^{final} dF$.
  - Proof by Construction: Consider a differential $dZ = 2xy \cdot dx + x^2 dy$ integrated on two paths where Path I is x=y and Path II is x^2=y. The integrations are from (x,y)=(0,0) to (x,y)=(1,1).

  - Path integral along Path I:

$$\Delta Z_I = \oint_I dZ = 2\int_0^1 xy \cdot dx + \int_0^1 x^2 dy$$
$$= 2\int_0^1 x^2 dx + \int_0^1 y^2 dy = 1$$

  - Path integral along Path II:

$$\Delta Z_{II} = \oint_I dZ = 2\int_0^1 xy \cdot dx + \int_0^1 x^2 dy$$
$$= 2\int_0^1 x^3 dx + \int_0^1 y dy = 1$$

So the integral of an exact differential is independent of path and only dependent on the initial and final states. This is an important property of state functions.

  - Contrast this behavior with the inexact differential $xy \cdot dx + xy \cdot dy$. Note that because the differential is inexact there exists no function Z such that $dZ = xy \cdot dx + xy \cdot dy$
  - Now for path 1: $\int_0^1 xy \cdot dx + \int_0^1 x^2 dy = \int_0^1 x^2 dx + \int_0^1 y^2 dy = \frac{2}{3}$
  - For path 2: $\int_0^1 xy \cdot dx + \int_0^1 x^2 dy = \int_0^1 x^3 dx + \int_0^1 y^{3/2} dy = \left.\frac{x^4}{4}\right|_0^1 + \left.\frac{2y^{5/2}}{5}\right|_0^1 = \tfrac{1}{4} + \tfrac{2}{5} = \frac{13}{20}$
  - Another example: Given n exact differential, find the function

$$dZ = M(x,y)\,dx + N(x,y)\,dy = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$$

$$\therefore M(x,y) = \left(\frac{\partial Z}{\partial x}\right)_y \Rightarrow Z(x,y) = \int M(x,y)\,dx + K(y)$$

$$or \ldots K(y) = Z(x,y) - \int M(x,y)\,dx$$

$$\therefore \frac{dK}{dy} = \left(\frac{\partial Z}{\partial y}\right)_x - \frac{\partial}{\partial y}\left(\int M(x,y)\,dx\right)_x = N(x,y) - \frac{\partial}{\partial y}\left(\int M(x,y)\,dx\right)_x$$

$$and \ldots Z(x,y) = \int M(x,y)\,dx + K(y) = \int M(x,y)\,dx + \int\left(N(x,y) - \frac{\partial}{\partial y}\left(\int M(x,y)\,dx\right)_x\right)dy$$

Suppose $dZ = 2xy \cdot dx + x^2 dy$. Then

$$Z(x,y) = \int M(x,y)\,dx + \int\left(N(x,y) - \frac{\partial}{\partial y}\left(\int M(x,y)\,dx\right)_x\right)dy$$

$$= \int 2xy\,dx + \int\left(x^2 - \frac{\partial}{\partial y}\left(\int 2xy\,dx\right)_x\right)dy$$

$$= x^2 y + \int\left(x^2 - \frac{\partial}{\partial y}\left(x^2 y\right)_x\right)dy = x^2 y + \int\left(x^2 - x^2\right)dy = x^2 y$$

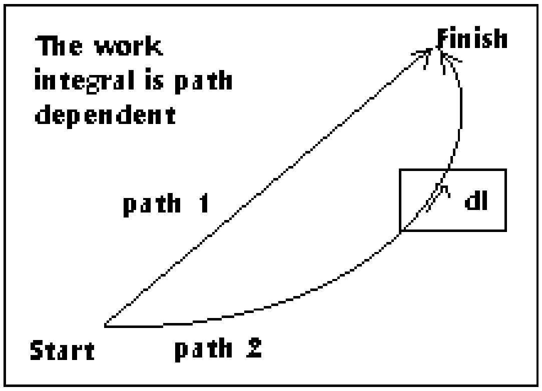
B.The Laws of Thermodynamics

- The First law of thermodynamics identifies the way in which a state variable, the internal energy can change, then makes a statement about how the internal energy of the universe can change
- There exists a state function called the internal energy U. For a system, ΔU_{system}=w+q, where w is the work done on or by the system and q is the heat which flows into or out of the system.
- The Great Invariance Principle: The amount of energy in the universe is a constant. Therefore $\Delta U_{universe}=\Delta U_{system}+\Delta U_{surroundings}=0$.
- As a result of the Invariance Principle, a device whose net effect is to produce work without an accompanying exchange of heat with the surroundings (also called a perpetual motion machine of the first kind), cannot exist.

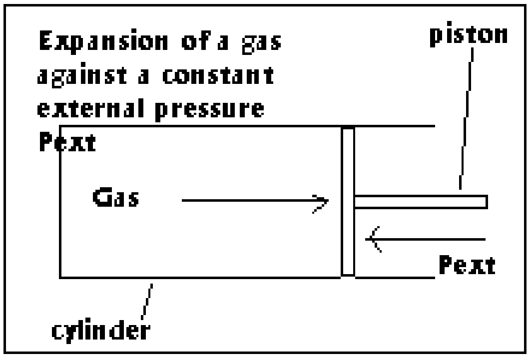
Work: In thermodynamics, work refers to mechanical and/or electrical contact between a system and the surroundings. Work is a form of energy. In the mechanical sense, work is defined as the product of the external force F applied to a mass times the distance d that the mass is compelled to move by the force. Mathematically this is expressed as $w = \int_{start}^{finish} \vec{F} \cdot d\vec{\ell}$.

- More precisely, work is calculated for complicated pathways by evaluating the work integral, which is calculated as follows.

- F is the force acting on the mass along the path. The path is divided into very small, linear displacement dl (see diagram).
- F and dl are both vectors. Work is a scalar, the inner product of F and dl for the work involved in moving the mass m by a small amount dl.
- The work along a complicated path is calculated by summing (integrating) the inner products $\vec{F}\cdot d\vec{\ell}$ from the start of the path to the finish: $w = \int_{start}^{finish} \vec{F}\cdot d\vec{\ell}$
- Work is NOT a state function. The work integral is path dependent.



- For gases it is more convenient to express work in terms of pressure and volume.



- Suppose a gas is confined within a cylinder. The initial volume of the cylinder is $V_{initial}=Al_i$ where A is the cross sectional area of the cylinder and l_i is the distance from the bottom of the cylinder to the initial position of the piston.
- The gas expands against a piston. To expand, the gas must apply sufficient force to overcome the external force F_{ext} that the atmosphere exerts on the piston. If the gas displaces the position of the piston to l_f, the displacement is $\Delta l=l_f-l_i$. The work is $w = \int_{\ell_i}^{\ell_f} \vec{F}_{ext}\cdot d\vec{\ell} = F_{ext}\left(\ell_f-\ell_i\right) = F_{ext}\Delta\ell = F_{ext}\Delta\ell\frac{A}{A} = P_{ext}\Delta V$ where $\Delta V = A\Delta\ell = A\left(\ell_f-\ell_i\right) = V_f - V_i$.
- Sign Convention: work can be done on the system by the surroundings (i.e. the gas in the cylinder is compressed) or work can be done by the system on the

surroundings (the gas expands). To keep track of whether work is being done on or by the system a sign convention is used.

- Work done BY the system: $w<0$.
- Work done ON the system: $w>0$.
- To enforce this convention the work definition must have a sign added…

$$work = w = -\int_{V_{initial}}^{V_{final}} P_{ext}\, dV \,.$$

If the external pressure is constant: $w = -P_{ext} \int_{V_{initial}}^{V_{final}} dV = -P_{ext}\Delta V$

- Electrical work is performed when charge is transported over of potential gradient.
  - Electrical work is expressed as $w_{elec} = -n\Im E$ where n is the number of moles of electrons transported, $\Im$=96, 485 Coulombs/mole, called Faraday's constant, which measures the electrical charge per mole of electrons, and E is the potential difference in Volts.
  - Electrical work is important in calculations of energy changes associated with the active transport of ions across membranes.

A. Heat: If the system is in thermal contact with the surroundings, heat q can be transferred to the system from the surrounding or vice versa.

- Like work, heat is NOT a state function
- If the system is thermally insulated from the surroundings heat cannot be exchanged so q=0 and $\Delta U = w$. A process for which q=0 is called *adiabatic*.
- Sign convention
  - If heat is transferred from the system to the surroundings…q<0.
  - If heat is transferred from the surroundings to the system…q>0.

Statement of the First Law of Thermodynamics (pressure-volume work only)

$$dU_{sys} = \delta q + \delta w$$

where the δ notation indicates δq and δw are inexact differentials. Upon integration…

$$\Delta U_{system} = q + w = q - \int P_{ext} dV$$

Comment and Question: The First Law says the energy of a system changes when work is done on or by the system and/or heat is transferred into or out of the system. How are energy changes ΔU detected? *An energy change is detected as changes in state variables, P, V, T, and/or n.* What is the relationship between ΔU, and ΔP, ΔV, ΔT, Δn?

C.Energy Changes and State Variable Changes

- Assume the system consists of a single component (i.e. a single kind of gas) and assume the amount of gas in the system is fixed, i.e. Δn=0…so n is a constant.

- ΔU can be expressed in terms of ΔP, ΔV, and ΔT. But the equation of state makes only two of these changes independent. Then U is a function of two independent variables. Let these variables be V and T, i.e. U(V,T).
- Hence we express dU in terms of changes in V and T i.e.
  $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = nC_V dT + \pi_T dV$ or
  - C_V is called the *molar heat capacity at constant volume*. It is defined as the increase in energy that occurs per unit increase in temperature for 1 mole of a substance held at constant volume. Mathematically $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. The value of C_V depends on the substance. The subscript V denotes constant volume.
    - Ideal Gas (monatomic): From Lectures 1 and Ch. 1 the kinetic energy n moles of a monatomic ideal gas is $U = \frac{3}{2}RT$. Therefore $\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\left(\frac{3}{2}\right)nRT\right)_V = \frac{3}{2}nR$. Therefore $C_V = \frac{3}{2}R$.
    - Heat Capacity and Degrees of Freedom. The heat capacity reflects the degree to which a substance can be thermally excited. For a monatomic ,ideal gas three degrees of translational freedom must be thermally excited. Hence, according to the Equipartition Principle $C_V = DOF * \frac{R}{2}$., where DOF indicates the number of degrees of freedom.
    - A diatomic gas has six degrees of freedom, 3 translational, two rotational, and two vibrational. Therefore $C_V = DOF * \frac{R}{2} = 7 * \frac{R}{2}$ But for a diatomic ideal gas $C_V = \frac{5R}{2}$ at low temperatures. Why? Because at low temperatures vibrational energy levels are not excited above the ground state energy.

- Internal Pressure: the molar internal pressure at constant temperature π_T should not be confused with the external pressure P_{ext}. or the pressure exerted by a gas against an external pressure. Internal pressure reflects the change in energy that occurs per unit change in volume of the system at constant temperature i.e. $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$.
  - Physical Interpretation of Internal Pressure: Molecules in a gas experience interactions with each other (see Lecture 3). As the distances between molecules change, their potential energy changes. Therefore, if the volume of a gas changes, the intermolecular distances change and the energy changes as a result. This gives rise to the internal pressure.
  - For an ideal gas, molecules do not interact with each other, and so their energy does not change if the volume is changed at constant temperature. Therefore for an ideal gas, the energy is only dependent on temperature, and the internal pressure is zero.