University of Washington
Department of Chemistry
Chemistry 452/456
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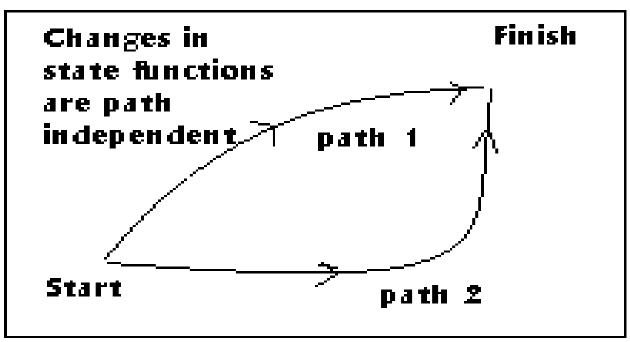
Lecture 2. 6/25/14
EDR: Ch. 2
DeVoe: Ch. 2

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 $M(x,y)dx + N(x,y)dy$.
    - 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 $dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy = M(x,y)dx + N(x,y)dy$
    - 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: $\int_0^1 xy\cdot dx+\int_0^1 x^2dy=\int_0^1 x^3dx+\int_0^1 y^{3/2}dy=\left.\frac{x^4}{4}\right|_0^1+\left.\frac{2y^{5/2}}{5}\right|_0^1=\frac{1}{4}+\frac{2}{5}=\frac{13}{20}$
- Another example: Given n exact differential, find the function

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

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

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

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

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

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

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

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

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

B.Energy Changes and State Variable Changes

- Assume the system consists of a single component (i.e. a single kind of gas) and assume also that the system is closed so 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.