Lecture 3 6/25/10

A. Reversible and Irreversible Work

- Reversible Process: A process that occurs through a series of equilibrium states, and thus can be reversed by an infinitesimal change in the applied forces.

- Irreversible Process: A process that does NOT proceed through a series of equilibrium states, and thus CANNOT be reversed by an infinitesimal change in the applied forces.

Most thermodynamic processes are irreversible. Except for the initial and final states the system is not at equilibrium. In irreversible changes thermodynamic quantities cannot be easily calculated except at the initial and final states, i.e. because the system is not at equilibrium during the passage from the initial to the final state, state variables like P, V, and T are not able to be related mathematically through an equation of state (e.g. PV=nRT).

In reversible processes, the system undergoes infinitesimal changes of the state variables along the path between the initial equilibrium state and the final equilibrium state. The system thus passes through a sequence of equilibrium states and unlike the irreversible case, state variables are related by an equation of state all along the path and are thus calculable.

Understanding the nature of reversible and irreversible changes is crucial to understanding the Second Law.

Examples. In the course of performing a given process (e.g. a gas expansion) if the process is performed reversibly, the amount of work produced by the system is greater than if the system performs the same process irreversibly i.e. $-w_{rev} > -w_{irrev}$. Note the negative signs. That is because work performed by the system is negative. The amount of work performed is thus –w.

Let's demonstrate this fact with an example…Suppose 2 moles of an ideal gas expands isothermally from an initial volume of 10L to a final volume of 20L. Calculate the work performed by the gas (i.e. the system) if the work is performed a) irreversibly…against a constant external pressure of 1 atm. b) reversibly. Assume T=300K.

Solution.

a) This work is calculated in the usual
way… $w_{irrev} = -\int\limits_{10L}^{20L} P_{ext}dV = -P_{ext}\int\limits_{10L}^{20L}dV = -(1atm)(20L-10L) = -10L\cdot atm = -1010J$

b) The reversible work is calculated in the same way…at first…

$w_{rev} = -\int\limits_{10L}^{50L} P_{ext}dV$. But a reversible expansion passes through a sequence of equilibrium

steps, where at each step $P_{gas}=P_{ext}$. This means that the external pressure is not constant, but equal to the gas pressure, i.e. the pressure exerted by the system, which is composed of an ideal gas, at every step of the expansion. This means…

$w_{rev} = -\int\limits_{10L}^{20L} P_{ext}dV = -\int\limits_{10L}^{20L} P_{gas,idealt}dV = -\int\limits_{10L}^{20L} \frac{nRT}{V}dV = -nRT\int\limits_{10L}^{20L} \frac{dV}{V}$.

Each step in the calculation above follows from the information given. $P_{ext}=P_{gas}$ because the expansion is performed reversibly. Then we substitute nRT/V for P_{gas} because the gas is ideal. Finally we move nRT out of the integrand because n and R are constants. T is also a constant because the expansion is performed isothermally, i.e. $\Delta T=0$.

The resulting integral has the general form $\int \frac{dx}{x} = \ln x + cons\tan t$. This means that

$w_{rev} = -nRT\int\limits_{10L}^{20L} \frac{dV}{V} = (2moles)(8.31J / mole \cdot K)(300K)(\ln 20 - \ln 10)$

$= -(2moles)(8.31J / mole \cdot K)(300K)\ln\left(\frac{20}{10}\right) = -(2493J)\ln 2 = -3456J$

Conclusions: Note $-w_{rev}=-(-3456J)=3456J$. Note also $-w_{irrev}=-(1010J)=1010J$. Therefore $-w_{rev}>-w_{irrev}$, as stated above.

Comments:
- The difference between reversible work and irreversible work can be appreciated from a diagram of the two pathways…In the figure below the expansion of a gas follows two pathways…one irreversible and the other reversible. Each path begins at (V1,P1) and ends at (V2,P2).
- The irreversible path follows a sudden drop in pressure from P1 to P2, followed by a expansion from V1 to V2. The amount of work accomplished is –(-P2(V2-V1)=P2(V2-V1).

- In the second path the external pressure is dropped incrementally in five steps, and in each step the external pressure and gas pressure are matched. At each step the volume increases by a small amount ΔV. In this process the total work is
$-w_{rev} = \Delta V\left(P_{ext,1} + P_{ext,2} + P_{ext,3} + P_{ext,4} + P_{ext,5}\right)$
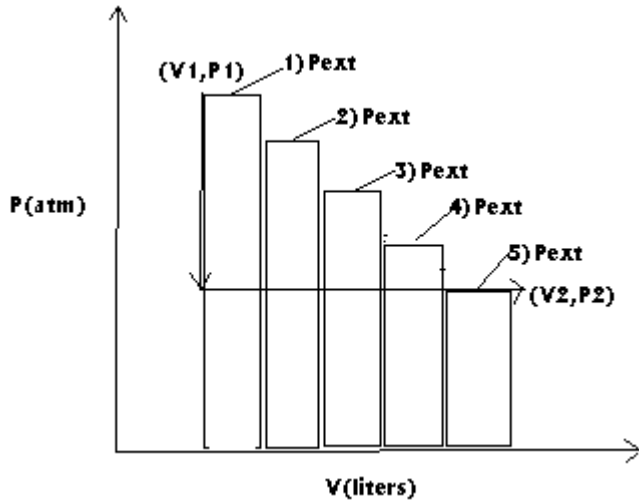
- Graphically, the amount of reversible work performed is $-w_{rev}$ and equals the sum of the five rectangular boxes. The amount of irreversible work $-w_{irrev}$ is simply P2(V2-V1). Clearly the area corresponding to $-w_{rev}$ is larger than the area corresponding to $-w_{irrev}$. Thus $-w_{rev} > -w_{irrev}, \ldots$ as claimed above.
- Note in general…for N steps in the reversible path… $w_{rev} = -\left(P_{ext,1}\Delta V + P_{ext,2}\Delta V + \ldots + P_{ext,N}\Delta V\right)$. As we increase the number of steps the volume change DV gets smaller and smaller which we represent as dV…to indicate the volume change is very small…

- $$w_{rev} = -\sum_{i=1}^{N} P_{ext,i}dV \xrightarrow{N\to\infty, dV\to 0} -\int_{V_1}^{V_2} P_{ext}dV = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

  Valid for an isothermal, reversible expansion of an ideal gas…

B. More reversible processes: Example Problems

Summary:
- A reversible change is a change whose direction can be perturbed by an infinitesimal change in the applied forces.
- Reversible changes involve passage through a series of equilibrium states.
  - Example: Isothermal expansion of an ideal gas
    $$reversible\,work = w_{rev} = -\int_{V_1}^{V_2} P_{ext}dV = -\int_{V_1}^{V_2} P_{gas}dV = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$
  - If a process occurs reversibly the work performed by the system is greater than if the process is performed irreversibly i.e. $-w_{rev} > -w_{irrev}$.

Note that if a process is performed reversibly, the change in the energy ΔE is the same as for when the process is performed irreversibly…assuming the initial and final states are the same. This is because ΔE is a state function… $\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$

Some Examples:
- A reversible, isothermal expansion/contraction
- Isothermal implies ΔT=0.

Five moles of an ideal monatomic gas expand reversibly and isothermally from a an initial pressure of 10 atm to a final pressure of 1 atm. Calculate the work done, the heat flow, ΔU and ΔH. Assume T=298K.

Solution: For an ideal gas $\Delta E = n\bar{c}_V \Delta T \ and \ \Delta H = n\bar{c}_P \Delta T$. An isothermal change implies ΔT=0, so ΔH=ΔE=0. Then use

$$\Delta U = 0 = q + w \Rightarrow \therefore w = -q$$

$$dw = -P_{ext}dV = -P_{gas}dV = -nRT\frac{dV}{V}$$

$$w = -nRT \ln\left(\frac{V_{final}}{V_{initial}}\right) = nRT \ln\left(\frac{P_{final}}{P_{initial}}\right)$$

$$= -(5moles)(8.31J/mole\cdot K)(298K)\ln(10) = -28.5kJ$$

$$\therefore q = -w = 28.5kJ$$

- A reversible adiabatic expansion/contraction
- Adiabatic implies q=0. That is, the system is thermally insulated from the surroundings and heat cannot be exchanged between the system and the surroundings.

For an ideal gas $dU = nC_V dT \ and \ dw_{rev} = -P_{ext}dV = -nRT\frac{dV}{V}$

Because the process is adiabatic dq=0 so dU=dw$_{rev}$. Equate the two expressions above…

$$nC_V dT = -nRT\frac{dV}{V} \ or \ C_V\frac{dT}{T} = -R\frac{dV}{V}$$

Integrate both sides of the equation: $C_V\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V}$

to obtain: $C_V \ln\left(\frac{T_2}{T_1}\right) = -R\ln\left(\frac{V_2}{V_1}\right) \ or \ \ln\left(\frac{T_2}{T_1}\right)^{\bar{c}_V} = \ln\left(\frac{V_2}{V_1}\right)^{-R}$

where we use the fact that xln(y)=ln(y)^x. Now remove the logarithms altogether…

$$\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_2}{V_1}\right)^{-R} = \left(\frac{V_1}{V_2}\right)^{R} = \left(\frac{V_1}{V_2}\right)^{C_P - C_V}$$

where we used the fact that $C_P - C_V = R$ for an ideal gas. Now just do some more algebra…

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P - C_V}{C_V}} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \quad where \ \gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = \frac{5}{3} \ \text{for an ideal gas}$$

This is the equation that you use to obtain the initial and final temperatures and volumes for an adiabatic expansion/contraction. You can rearrange this expression to get… $T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$ and you can use the ideal gas law to get pressure into the

expression $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$. Note for an ideal gas $\gamma = \frac{5}{3}$. Now let's solve a problem…

> Five moles of an ideal monatomic gas, initially at T=298K, expand reversibly and adiabatically from an initial pressure of 10 atm to a final pressure of 1 atm. Calculate the final volume and temperature, the work done w, ΔE, and ΔH.

Solution: Now we can use all these relationships to answer the question…but we have to decide how to use all these equations. We have the initial and final pressures so it is tempting to use $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ to get the volumes. We do not know either of the volumes so we can only get the ratio using this equation. But we can get the initial volume from the ideal gas law because we know the initial pressure and temperature.

Therefore… $V_1 = \frac{nRT_1}{P_1} = \frac{(5moles)(0.0821L \cdot atm / mole \cdot K)(298K)}{10atm} = 12.2L$

We can use the adiabatic equation $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ to get the final volume…

$$V_2^{\gamma} = \frac{P_1}{P_2} V_1^{\gamma} = (10)(12.2L)^{5/3} \therefore V_2 = (10)^{3/5}(12.2L) = 48.7L$$

And we can get the final temperature from the ideal gas

law… $T_2 = \frac{P_2 V_2}{nR} = \frac{(1atm)(48.7L)}{(5moles)(0.0821L \cdot atm / mole \cdot K)} = 119K$

We get the state function and work expression because we know the temperature

change… $w = \Delta U = nC_V \Delta T = (5moles)\left(\frac{3}{2}\right)(8.31J / mole \cdot K)(119K - 298K) = -11,200J$

$$\Delta H = nC_P \Delta T = (5moles)\left(\frac{5}{2}\right)(8.31J / mole \cdot K)(119K - 298K) = -18,600J$$