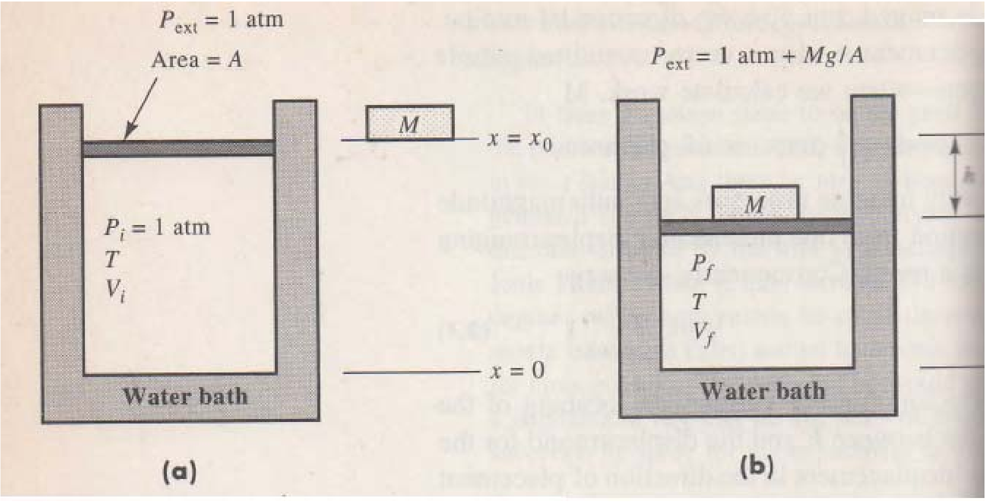
University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2014

Lecture 4 6/30/14 Irreversible & Reversible Work
EDR 2.6-2.10
DeVoe: 3.2

A. Irreversible Compression/Expansion Work on Gases

- Whenever a process is referred to as "irreversible" it indicates that has been a substantial displacement from equilibrium. As the name implies such a process has a clearly designated direction and the displacement has been so substantial from equilibrium that no minimal adjustment of state variables like P, T, or V will be sufficient to restore the system to the preceding condition. Most processes that we experience are irreversible.
- To illustrate work associated with irreversible processes we use the expansion compression of ideal gases. Real gases can also be used but add needless complications at this stage, so we will stay with PV=nRT for now.

Figure 1: Irreversible compression of an ideal gas in a cylinder enclosed by a piston and weighted with a mass m.



- Suppose a gas is confined within a cylinder. The initial volume of the cylinder is $V_{initial}=Ax_0$ where A is the cross sectional area of the cylinder and x_0 is the distance from the bottom of the cylinder to the initial position of the piston.
- The piston is initially static because the system is initially at mechanical equilibrium, as shown in the Figure above, left.The piston does not move because the initial pressure of the gas P_i equals the external pressure P_{ext}. For convenience these two pressure will be 1 atm.

- Now suppose a mass m is placed on the piston. The external force, which is pointed downwards, which we take to be the –x direction, is

$$F_{disp} = -\left(P_i A + mg\right) \tag{4.1}$$

- Assume the temperature T of the cylinder remains constant and that the piton moves from x_0 to x_0-h at which point it comes to a stop at a new mechanical equilibrium where the final pressure of the gas is

$$P_f = P_i + \frac{mg}{A} \tag{4.2}$$

- We can now calculate the work using the work integral:.

$$w_{compress} = \int_{x_0}^{x_0-h} F_{disp}dx = -\int_{x_0}^{x_0-h}\left(P_i A + mg\right)dx = -\left(P_i A + mg\right)\left(-h\right) = -\left(P_i + \frac{mg}{A}\right)\left(-Ah\right) \tag{4.3}$$

- Note that the initial volume of the cylinder is $V_i = Ax_0$ and the final volume is $V_f = A\left(x_0 - h\right)$. Therefore $\Delta V = V_f - V_i = -Ah$ and equation 4.3 can be written

$$w_{compress} = -\left(P_i + \frac{mg}{A}\right)\left(-Ah\right) = -P_{ext}\Delta V \tag{4.4}$$

- Equation 4.4. states if a constant external pressure is applied to gas, the work is dependent on the external pressure and the volume change. Note when work is done on the gas by compressing it, ΔV<0 so w>0 as expected. The work performed is the shaded area under the curve in Figure 2;

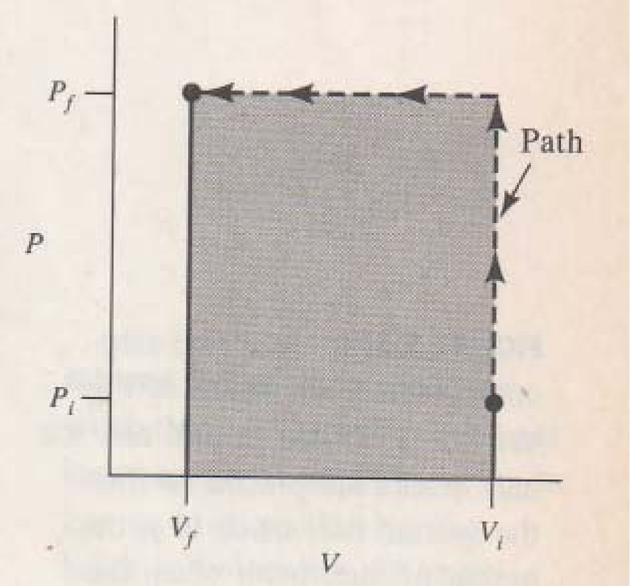


Figure 2: path followed by te irreversible compression of an ideal gas by a piston and a mass. The work given in equation 4.4 is the shaded area under the curve.

Example: Calculate the work performed when a constant external pressure of 200atm compresses one mole of an ideal gas to half of its initial volume. Assume T=300K and remains constant.

Solution; When the gas is compressed to one half its volume

$2V_f = V_i \Rightarrow \Delta V = V_f - V_i = -V_f$. Also $P_f = P_{ext}$ so that

$$w = -P_{ext}\Delta V = -P_f\left(-V_f\right) = P_f V_f = nRT$$

$$= \left(1.00mol\right)\left(8.31JK^{-1}mol^{-1}\right)\left(300K\right) = 2.46kJ$$

- Once the piston ceases moving at x=x_0-h, and the gas pressure is given by equation 4.2, we remove the mass from the piston. Now the external pressure is back to its initial value i.e. $P_{ext} = P_i = 1atm$ but the gas pressure is higher so the psiton moves upwards. It continues to move until the volume increases by ΔV=Ah and restoring the piston position to x=x_0. Now the work is:

$$w_{expand} = -P_{ext}\Delta V = -P_i Ah \qquad (4.5)$$

- Note the work is negative because the system (i.e. the gas) did the work. We can similarly represent the work of expansion by the area under the curve in Figure 3, but the area is $-w_{expand}$, because an area must be a positive quantity.

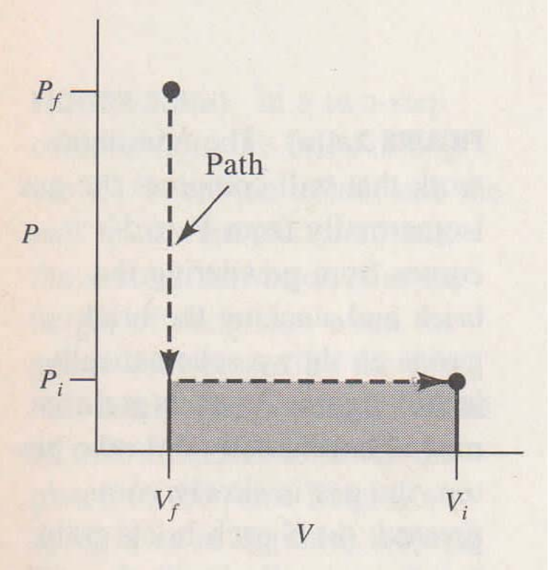


Figure 3: Graphical representation of the expansion work given in equation 4.5.

- Now suppose we compress the gas as before and follow this with an expansion back to the original position of the piston. This is called a cycle and the total work done in the cycle is the sum of the compression and expansion works given in equations 4.4 and 4.5.

$$w_{cycle} = w_{compress} + w_{expand} = \left(P_i + \frac{mg}{A}\right)Ah - P_i Ah = mgh \qquad (4.6)$$

- Equation 4.6 means work has been done on the gas during this cycle equivalent to lifting the mass by a distance h. This work can be represented by the difference between the area in Figure 2 and the area in Figure 3.
- Note that for the internal energy $\Delta U = U_f - U_i$. For a cyclic process $U_f = U_i$ so that $\Delta U_{cycle} = 0$. Unlike path functions which are non-zero for a cycle, all state function changes are zero over a cycle.

B. Reversible Work

- Most real 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.

- Although reversible changes cannot be realized physically, they represent a theoretical limit where the work required for compression is minimal and the work performed by expansion is maximum. In real, irreversible gas expansions/compressions piston motions are rapid and the gas pressure within a cylinder is not uniform due to turbulence and pressure gradients induced by the rapid piston motion. This makes the simple treatments of work in equations 4.1-4.6 invalid.

- In reversible changes piston motions are so slow as to result in uniform gas pressures. But more than that, reversibility fundamentally changes our formulation of work. Suppose instead of adding the mass to the piston in one step, we break the mass into very small piece and add the small masses gradually to the piston. As each small mass is added the gas is only slightly perturbed from equilibrium. In this deliberate process, the compression occurs via a large number of steps and the work is now represented by the integral:

$$w = -\int_{V_i}^{V_f} P_{ext}\,dV \tag{4.7}$$

- At each step we add an infinitesimal mass dm to the piston and we can formulate the external pressure as:

$$P_{ext} = P_{gas} + \frac{dmg}{A} \approx P_{gas} \tag{4.8}$$

- Apply 4.8 to 4.7 and assume the gas is ideal:

$$w = -\int_{V_i}^{V_f} P_{ext}\,dV = -\int_{V_i}^{V_f} P_{gas}\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\ln\left(\frac{V_f}{V_i}\right) \tag{4.9}$$

Examples. Assume 1 mole of an ideal gas is compressed reversibly by a constant external pressure of 200 atm to half its initial volume. Calculate the compression work and compare to the irreversible compression work calculated above.

Solution:

$$w_{compress} = -nRT\ln\left(\frac{V_f}{V_i}\right) = -(1mol)(8.31JK^{-1}mol^{-1})(300K)\ln\left(\frac{1}{2}\right)$$

$$= (-2.46J)(-0.693) = 1.71J$$

The reversible compression performed upon the gas (i.e. the system) requires less work than if the compression is performed irreversibly. For a compression: $w_{irrev} > w_{rev}$

- The difference between reversible work and irreversible work can be appreciated from a diagram of the two pathways…In Figure 4 below the compression of a gas follows a curved path where at each step the gas is approximately at equilibrium . Along this “quasi-static’ path the temperature is constant (isothermal) and the ideal gas law states: $PV = nRT = \text{constant}$

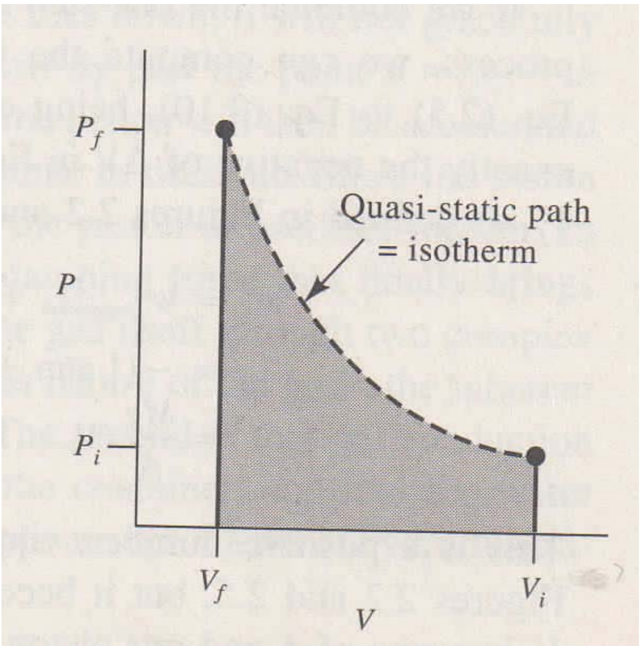


Figure 4: Path followed by isothermal reversible compression of an ideal gas. Compression goes along the dotted line from right to left. Reversible compression work is the shaded area under the curve. Reversible expansion goes from left to right and $-w_{expand}$ work of expansion is the area under the curve.

- Comparing Figure 4 to figure 2, reversible compression requires less work than irreversible compression. However for a reversible expansion the are under the curve in Figure 4 is $-w_{expand}$, and comparing Figure 4 to Figure 3, the wamount of work produced by reversible expansion is greater than the work produced by irreversible expansion.
- In general the work produced by a reversible process is greater in amount than the work produced by an irreversible process so for an expansion: $-w_{rev} > -w_{irrev}$, …as claimed above.

C. 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 $\Delta U = nC_V \Delta T$ and $\Delta H = nC_P \Delta T$. An isothermal change implies ΔT=0, so ΔH=ΔU=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…

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

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