Work and heat

Chapter 2 of Atkins: *The First Law: Concepts*

Sections 2.3-2.4 of Atkins (7th, 8th & 9th editions)

Expansion Work
>	**General Expression for Work**
>	**Free Expansion**
>	**Expansion Against Constant Pressure**
>	**Reversible Expansion**
>	**Isothermal Reversible Expansion**

Heat Transactions
>	**Calorimetry**
>	**Heat Capacity**

Work and heat

Must focus upon **infinitessimal changes** in state and energy, and be able to connect the contributions of small changes in heat and work to the total energy

Work done on a system: dw
Energy supplied as heat: dq

$$dU \quad = \quad dq \quad + \quad dw$$

Expansion work: Work that leads to a change in volume - gas expanding, driving force against atmospheric pressure

Examples: thermal decomposition of $CaCO_3$
              combustion of octane

Expansion Work

1. Work required to move an object over distance dz against a force of opposing magnitude F:

$$dw = -F\,dz$$

Negative sign: since the system moves against the opposing force F, there will be a decrease in the internal energy of the system
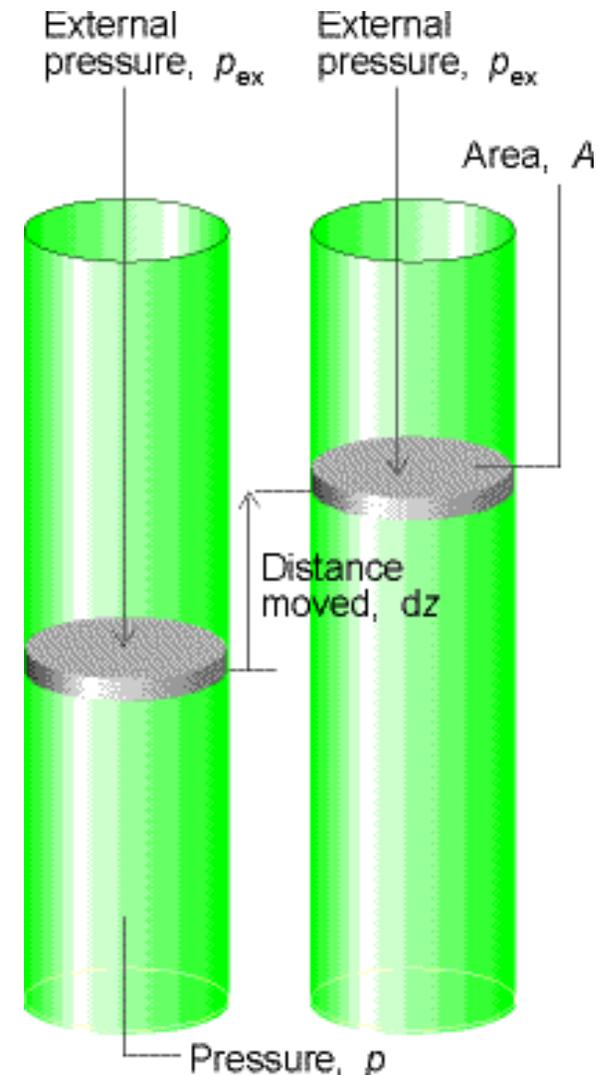
2. System: massless, frictionless, rigid, perfectly fitting piston of area A

3. Force on outer face of the piston: $F = p_{ex}A$

4. Work done against external pressure:
$$dw = -p_{ex}A\,dz$$

5. Change in volume $dV = A\,dz$

External pressure, p_{ex}
External pressure, p_{ex}
Area, A
Distance moved, dz
Pressure, p

Expansion Work

Work can now be written in terms of pressure and change in volume:

$$dw = -p_{ex}dV$$

If we need to know the total work done expanding the volume of a system, we can integrate the above expression over the initial and final volumes

$$w = -\int_{V_i}^{V_f} p_{ex}dV$$

- Force acting on the piston, $p_{ex}A$, is the same as raising a weight as the system expands (e.g., $F = mg$)
- Compressing the system is analogous, excepting that $V_i > V_f$

If we have **free expansion**, there is no opposing force, despite increase (or decrease for compression) in volume. (e.g., expand into vacuum)

$$w = 0$$

Types of Work

There are various types of work from different sources which work much in the same way, resulting from the product of:

an **intensive factor** (e.g., p) times an **extensive factor** (e.g., V)

Type of work	dw	Comments	Units
Lifting	$-mg\,dh$	mg mass and gravity	N
		dh is change in height	m
Expansion	$-p_{ex}dV$	p_{ex} is external pressure	Pa
		dV is change in volume	m^3
Surface expansion	$\gamma\,d\sigma$	γ is surface tension	$N\,m^{-1}$
		$d\sigma$ is change in area	m^2
Extension	$f\,dL$	f is the tension	N
		dL is change of length	m
Electrical	$\phi\,dq$	ϕ is electric potential	V
		dq is change in charge	C

Generalized work: $dw = -F\,dz$ where F is "generalized force" and dz is "generalized displacement"

Expansion Against Constant Pressure
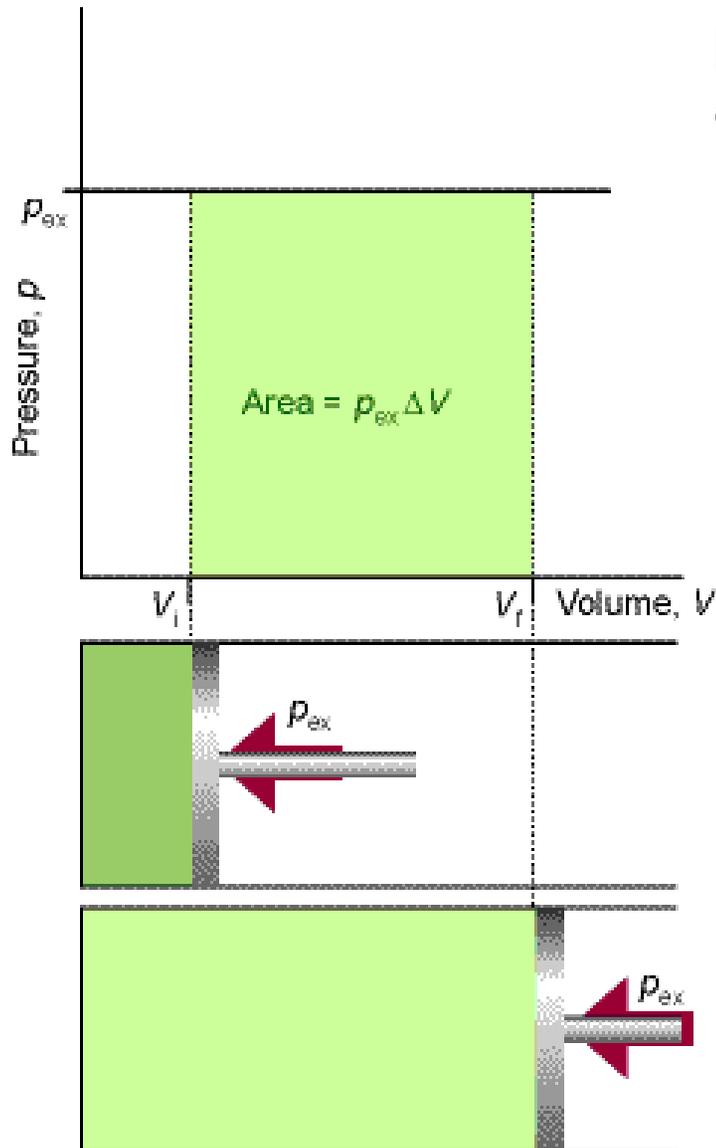
During expansion, external pressure p_{ex} is constant (e.g., atmosphere)

$$w = -p_{ex} \int_{V_i}^{V_f} dV = -p_{ex}(V_f - V_i)$$

If $\Delta V = V_f - V_i$, then the work can be written

$$w = -p_{ex}\Delta V$$

The integral above is interpreted as area, as we watch work done by a gas expanding against a constant pressure

The magnitude of work, $|w|$, is equal to the area beneath the line with $p = p_{ex}$, between final and initial volumes: p, V graphs to calculate expansion are **indicator diagrams**

Reversible Processes

Reversible process: a process during which the system is never more than infinitesimally far from equilibrium and an infinitesimal change in external conditions can reverse the process at any point - a change can be reversed by infinitesimal modification of a variable

Irreversible process: a process which cannot be reversed by an infinitesimal change in external conditions; during the process, the system makes finite departures from equilibrium

Consider a sample of gas in thermal and mechanical equilibrium with the surroundings; i.e., with $T_{gas} = T_{surroundings}$ and $p_{gas} = p_{external}$. If the external pressure is decreased infinitesimally at constant T, the gas will expand infinitesimally; if the external pressure is increased infinitesimally at constant T, the gas will be compressed by an infinitesimal amount.

Strictly speaking, a reversible process cannot be achieved, since to carry out a finite transformation in a series of infinitesimal steps would require infinite time. *All real processes are therefore irreversible*. A reversible process is an *idealization* (very useful)

Reversible Expansion

In order for the gas to expand, p_{ex} must be smaller than p (the pressure of the gas). At the same time, the system must be infinitesimally close to equilibrium throughout the expansion. This means that p_{ex} must equal $p - dp$ at all times during the expansion. Therefore,

$$w = -\int_{V_i}^{V_f} p_{ex}\,dV = -\int_{V_i}^{V_f} (p - dp)\,dV = -\int_{V_i}^{V_f} p\,dV$$

The $dpdV$ part disappears, since the integral of the product of two infintessimal quantities gives another infinitessimal quantity. Thus,

$$dw = -p_{ex}\,dV = -p\,dV \qquad\qquad w = -\int_{V_i}^{V_f} p\,dV$$

This is **work of reversible expansion**. The integral on the right can be evaluated with knowledge of how pressure of the defined gas depends on the volume (i.e., if we know the *equation of state* of the gas, p can be expressed in terms of V)!
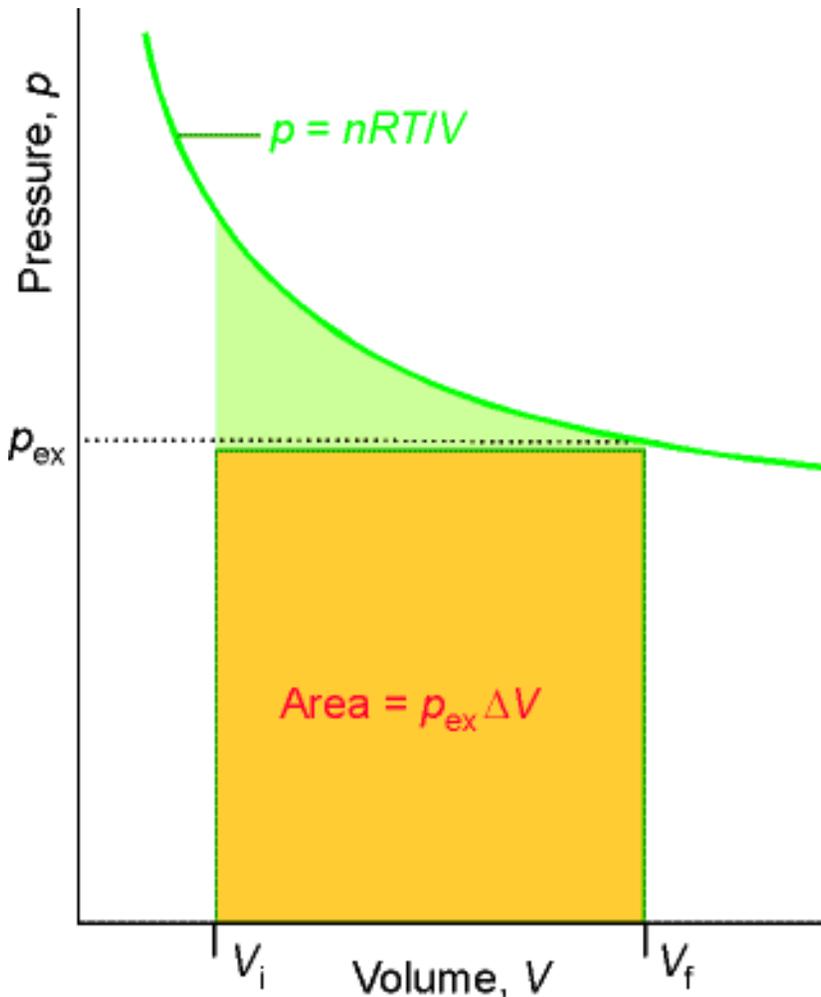
Isothermal Reversible Expansion

Expansion is **isothermal** if system is in contact with constant thermal surroundings (i.e., a constant temperature bath or heating element)

1. Each stage of expansion, $p = nRT/V$
2. Temperature T is constant, so treated outside of the integral

$$w \;=\; -nRT \int_{V_i}^{V_f} \frac{dV}{V} \;=\; -nRT \, \ln\left(\frac{V_f}{V_i}\right)$$

- When $V_f > V_i$, gas expands, and work done to expand the gas causes the system to lose internal energy, $w < 0$
- Constant supply of energy at constant T replenishes internal energy
- More work is done for a given change in volume at higher temperature
- Pressure of confined gas needs higher opposing pressure for reversibility - **so, pressure can change but $\Delta T = 0$** (*continued*)

Isothermal Reversible Expansion

Here, w is equal to the area under the $p = nRT/V$ isotherm, and this represents work of a *reversible expansion at constant temperature*, where external pressure is continually matched against the internal pressure

Yellow square: *irreversible expansion* against constant external pressure

More work and maximum pushing power is obtained from the reversible expansion (pushing power is **wasted** when $p > p_{ex}$ - more work also cannot be obtained by increasing p_{ex}, since **compression** will result!)

Maximum work obtained from system operating between specific initial and final states is obtained when change is reversible

Heat Transactions

Internal energy can be written as:

$$dU \;=\; dq \;+\; dw_{exp} \;+\; dw_e$$

dq heat: energy transferred across boundary due to difference in T
dw_{exp} work due to expansion
dw_e extra sources of work (e.g., electrical current)

- At constant V, $dw_{exp} = 0$ (system cannot expand)
- If no additional work (no battery, etc.), $dw_e = 0$

$$dU \;=\; dq$$

Write $dU = dq_v$, which implies infinitessimal change at constant volume. Thus for a measurable finite change:

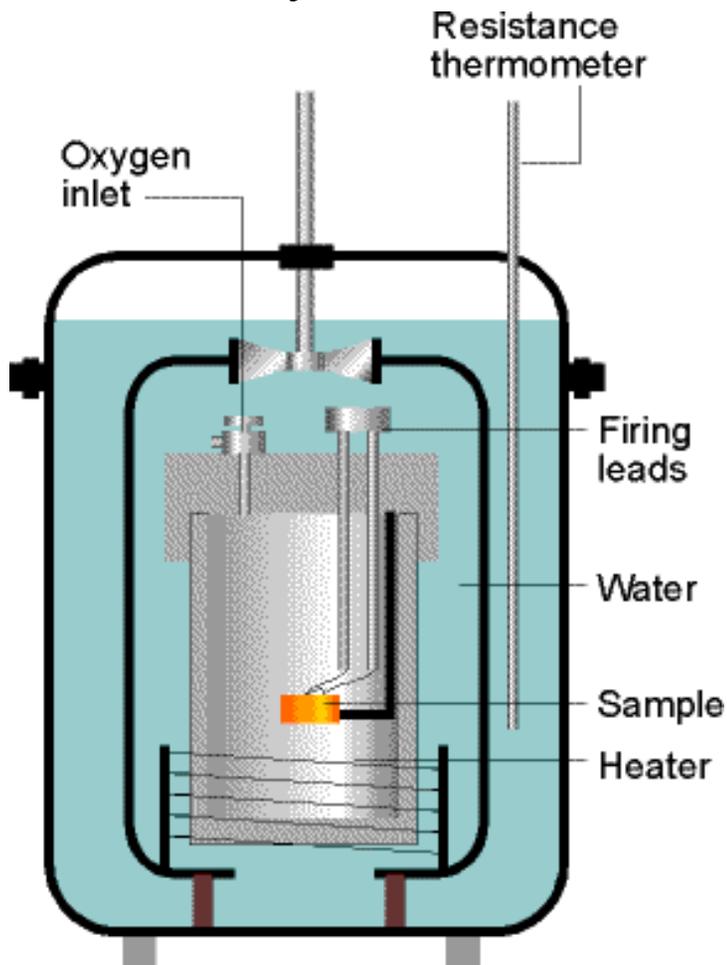$$\Delta U \;=\; q_V$$

| $q > 0$ (heat supplied to system) | $q < 0$ (heat lost from system) |

Calorimetry

How do we study changes in energy due to addition or subtraction of heat in a system? We can use an **adiabatic bomb calorimeter**

Adiabatic: Implies that the device is isolated from the outside world, such that no thermal transfer of energy can take place between system and surroundings

Bomb: The sturdy vessel with constant volume inside which very vigorous reactions, combustions and explosions can take place at high pressure

Calorimeter: From the cgs unit of energy, the **calorie**, implying the measurement of energy

Resistance thermometer

Oxygen inlet

Firing leads

Water

Sample

Heater

How does the calorimeter work? *

1. Reaction is conducted in the constant volume **bomb**
2. Bomb is immersed in a stirred water bath, forming the calorimeter
3. Calorimeter is immersed in a second water bath, the temperature of which is continuously adjusted to the temperature of the bomb bath, thereby ensuring an **adiabatic system**

A chemical reaction either releases or absorbs heat, causing a proportional change in temperature ΔT of the calorimeter:

Measuring ΔT allows us to determine q_V, and therefore ΔU - **BUT....**
we must calibrate the calorimeter using known energy to get the **calorimeter constant**, C

$$q \quad = \quad C\Delta T$$

1. Use electrical current I at fixed potential ϑ through a heater for time t

$$q \quad = \quad I\vartheta t$$

2. Burn an exact mass of substance with known heat output

Heat Capacity

Increasing temperature increases the internal energy of a system

The exact increase depends upon the heating conditions

Heat cannot be detected or measured directly. (There is no "heat meter".) One way to determine the magnitude of a heat transfer is to measure the work needed to bring about the same change in the thermodynamic state of the system as was produced by heat transfer.

Another approach is to deduce the magnitude of a heat transfer from the its effects; namely, a temperature change. The temperature change resulting from a particular transfer of heat is determined by the heat capacity of the system, which is defined as follows:

heat capacity (of a system):   the heat required to raise the temperature of the system by one Kelvin (or one °C)

Heat capacity is an **extensive property**

Heat Capacity & Internal Energy[†]

Here is a plot of the internal energy of a system versus temperature
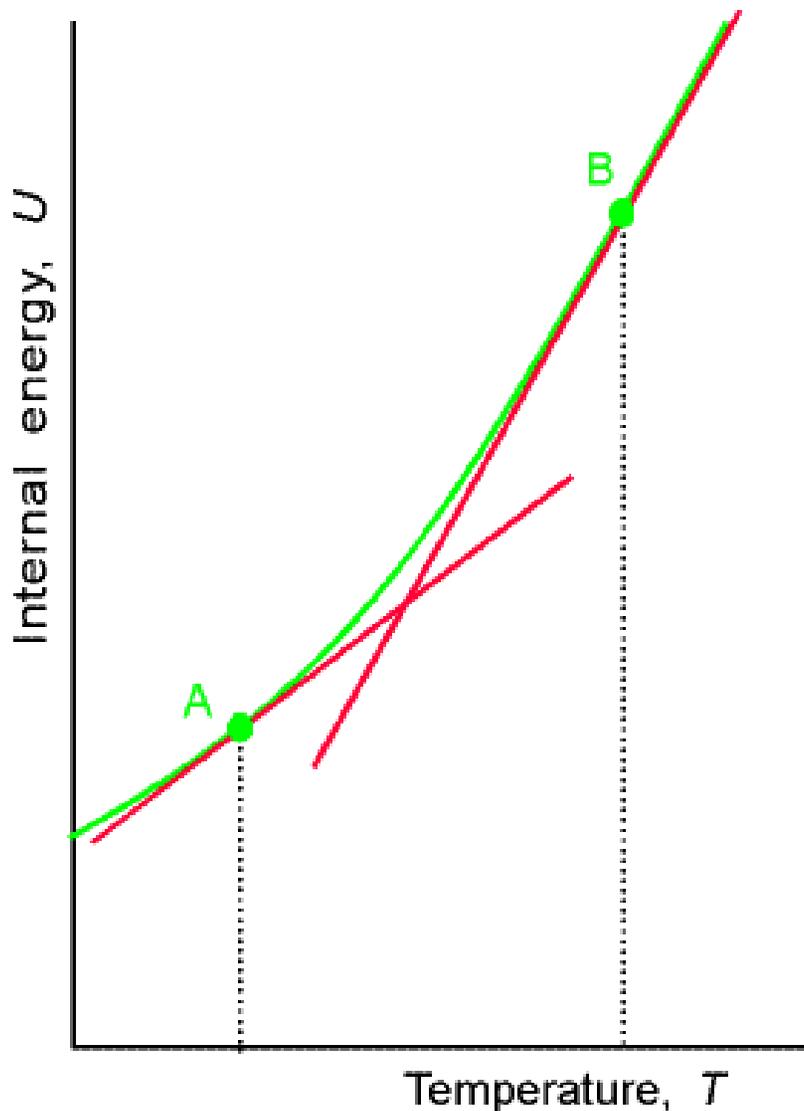
The slope of the curve at a given temperature is defined as the heat capacity of the system

The heat capacity at constant volume is formally defined as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The RHS is a **partial derivative**, which is a derivative where all variables are held constant except for one - it gives the slope of the plot of U vs. T

The heat capacity at temperature A is lower than that at temperature B

Molar Heat Capacity

Heat capacity is an *extensive property*: for instance, we know for instance that 100 g of water has 100x the heat capacity of 1 g of water

So, we can also have an *intensive property*, the **molar heat capacity at constant volume**, which is a measure of heat capacity at constant volume per mole of material: $C_{V,m}$

There is also the **specific heat capacity**, $C_{V,m}^s$, which gives us a useful measure of heat capacity per unit mass of the sample (e.g., $J\ K^{-1}\ g^{-1}$)

Generally:

Heat capacities are temperature dependent, decreasing at lower T

Over small ranges near room temperature, C_V are almost invariant to changes in temperature

Relating *U* and *T* at Constant *V* [*,†]

Heat capacity is used (say in a calorimeter) to relate internal energy changes and changes in temperature

As usual, an infintessimal change in temperature changes energy slightly

$$dU \quad = \quad C_V \, dT \qquad \text{at constant volume}$$

Over a measurable range of temperatures

$$\Delta U \quad = \quad C_V \, \Delta T \qquad \text{at constant volume}$$

Change in energy can be noticed with heat supplied at a constant *V*

$$q_V \quad = \quad C_V \, \Delta T$$

1. Supply a controlled known amount of heat to the sample (say with an electric current in a heater)
2. Monitor the resulting increase in temperature
3. The ratio: heat supplied/temperature increase is the heat capacity

Large heat capacity: large supply of heat, small change in measured *T*
Small heat capacity: small supply of heat, large change in measured *T*
Infinite heat capacity: at a phase transition, energy changes phases!

Molecular Interpretation of Heat Capacity

We previously showed that the internal energy of a system is given by $U_m = U_m(0) + (3/2)RT$, so

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = \frac{3}{2}R$$

For non-linear polyatomic molecules:

$$C_{V,m} = 3R$$

$C_{V,m}$ is independent of temperature, and ca. 24.94 J K^{-1} mol^{-1}

When vibration is considered as well, for frequency ν:

$$C_{V,m} = Rf^2 \qquad f = \left(\frac{h\nu}{kT} \right) \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/2kT}}$$

At $T = 0$, $f = 0$, and $f \approx 1$ when $kT \gg h\nu$ (so vibrational contributions to heat capacity are 0 at $T = 0$, and climb steadily to the classical value with increasing T - more and more energy levels become accessible and it appears that the vibrations are no longer quantized