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First Law of Thermodynamics

This is the law of conservation of energy

1st Law: Energy can be converted from one form to another but can be neither created nor destroyed.

Energy is classified into one of two forms:

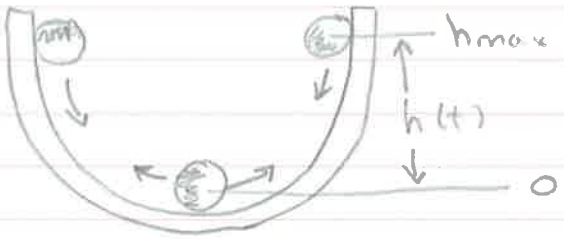
Potential Energy: depends on objects position or composition.

Kinetic Energy: depends on objects motion, that is,

$$E_{kinetic} = \frac{1}{2} m v^2$$

(m: mass, v: velocity)

Consider a marble rolling in a bowl



at any instant, the marble has a potential Energy:

$$E_{potential} = m g h(t)$$

($h(t)$: height; m: mass; g: gravity acceleration)

and a kinetic Energy:

$$E_{kinetic} = \frac{1}{2} m v^2(t)$$

(v: velocity)

When marble is at h_{max}, the potential energy is at the maximum and kinetic energy is zero.

When marble is at $h = 0$, the potential energy is zero, & kinetic is maximum.

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In absence of friction, the marble would continue rolling up & down forever with its energy converting back & forth between kinetic & potential

The total energy, however, would be constant (time independent)

$$E_{total} = mgh(t) + \tfrac{1}{2}mv^2(t)$$ (frictionless system)

In the real world, where there is friction between the marble & the bowl, the marble eventually stops rolling.

Since energy must be conserved, where did it go?

It gets "dissipated" into the marble and the bowl. That is, it is transferred to the internal energy associated with random atomic motion in the marble and bowl.

To correctly describe the situation to include friction and obey the 1st law we include the internal energy, U, of the system (marble & bowl).

$$E_{TOTAL} = U(t) + mgh(t) + \tfrac{1}{2}mv^2(t)$$

$U(t)$: internal Energy — microscopic degrees of freedom

$mgh(t) + \tfrac{1}{2}mv^2(t)$: Energies associated with macroscopic coordinates not averaged to zero over time due to random motion of atoms & molecules in system.

Other macroscopic coordinates

R - center of mass	Q - total charge
Θ - orientation	P - Polarization
V - volume	M - magnetization
A - surface Area	

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Work

by lifting the marble up to start it rolling we put energy into the marble. This type of energy transfer is called:

WORK

Work is not a form of energy, but rather it is a process in which energy is transferred between the system & surroundings.

Work is an Energy Transfer Process

$$\text{Work} = (\text{Force}) \times (\text{distance applied})$$

The energy that we initially transferred to the marble & bowl (system) by lifting the marble (work) to start it rolling is eventually transferred (i.e., dissipated) to the internal energy of the marble & the bowl.

Because energy must be conserved, the difference in the internal energy of the system (marble & bowl) before we lift the marble & start it rolling, and after it comes to equilibrium (i.e. stops rolling) must be equal to the work we performed on the system.

$$\Delta U = U_{final} - U_{initial} = W$$

W: work performed on system

In this example, the initial & final states of the system look the same to the naked eye. That is, a marble sitting on the bottom of the bowl & not rolling.

However, on close inspection, one would notice that the marble & bowl of the final state will have a slightly higher temperature due to the increased internal energy.

Temperature is a measure of the degree of random motion of atomics & molecules in a substance.

Heat

Another way we could obtain the same change in internal energy of the system (marble & bowl) is to heat the system.

By placing it in contact with an object that has a higher temperature, such as a hot plate, until we get the same change in temperature as we did with work.

Heat - energy transfer by means of a temperature difference between system & surroundings.

$$\Delta U = U_{final} - U_{initial} = q \leftarrow \text{heat is energy transferred.}$$

Remember: Heat is NOT A Form of energy, but rather is an energy transfer process.

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Only two "forms" of energy - kinetic & Potential

two ways to transfer energy - heat & work between system & surroundings

any change in energy of a system must occur through heat and/or work.

$$\Delta U_{sys} = q + w$$

- q: heat transferred across boundary
- w: thermodynamic work transferred across boundary

1st Law of Thermodynamics

if $\Delta U_{sys} < 0$ Then system lost energy to surroundings
if $\Delta U_{sys} > 0$ " " gained " from surroundings

Similarly,
if $w < 0$ Then system lost energy through work on surroundings
if $w > 0$ " " gained " " " done by surroundings

if $q < 0$ Then system lost energy through heat to surroundings
if $q > 0$ " " gained " " " from surroundings

exothermic process ≡ system releases energy as heat into surroundings ($q < 0$)

endothermic process = system receives energy as heat from surroundings ($q > 0$)

Infinitesimal Change

$$dU = dq + dw$$

- $U = \int dU$ — path independent
- $q = \int dq$ — path dependent
- $w = \int dw$ — path dependent

Both heat & work are path functions, associated with a process, not a state.

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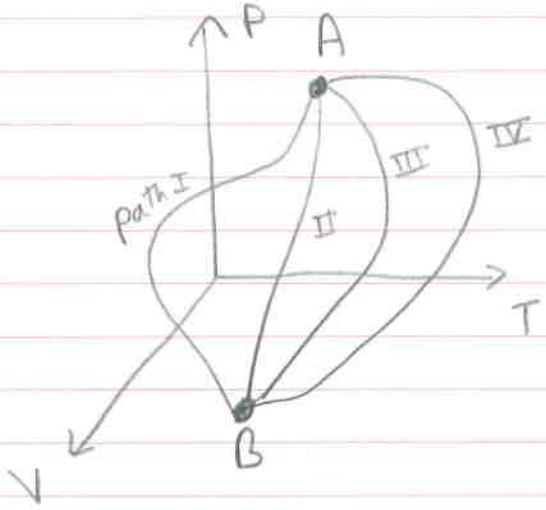
Changing The Thermodynamic EQUILIBRIUM STATE

Process = change in Thermodynamic state over time



Many paths can be taken in PVT space in going from A → B

There are many adjectives in Thermodynamics for describing processes

Expansion = path leads to volume increase $\Delta V > 0$

Compression = " " " " decrease $\Delta V < 0$

Isothermal = path where temperature of system remains constant & uniform throughout process

Isobaric = path where pressure of system remains constant & uniform throughout process

Isochoric = path where Volume of system remains constant & uniform throughout process

Adiabatic = path where no energy transfer as heat occurs between system & surroundings - more later...

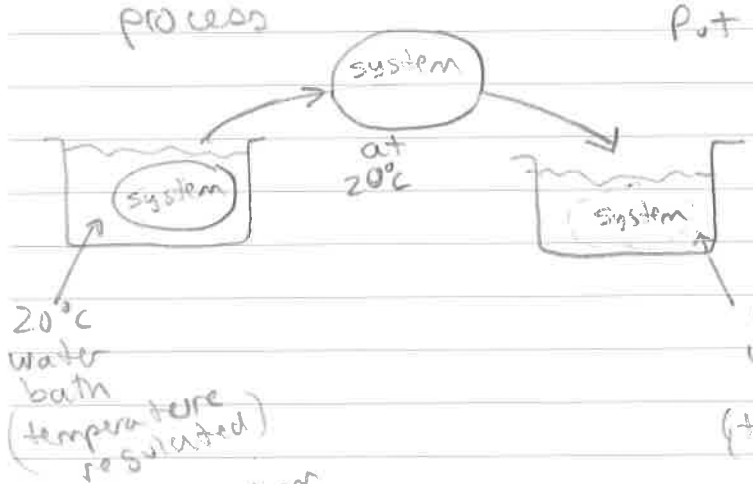
Cyclic = path which returns system to initial state

Reversible Process - system undergoing change in state and is always infinitesimally close to equilibrium.

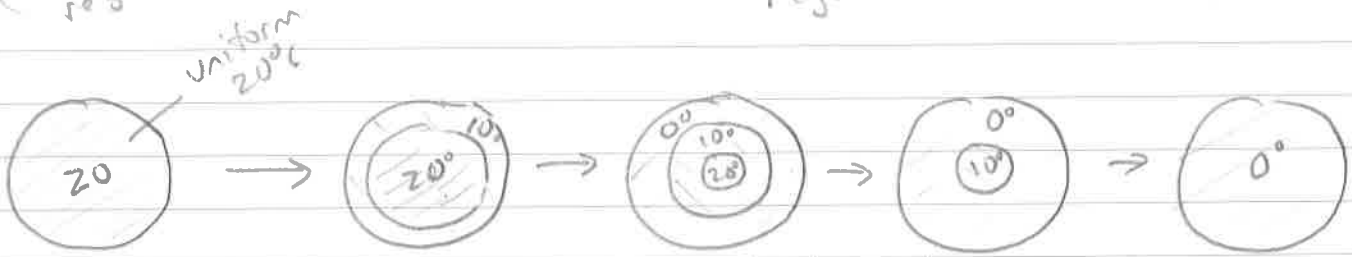
- no process is truly reversible. Idea is approached by a process occurring infinitely slow.

To better understand let's look at an irreversible process

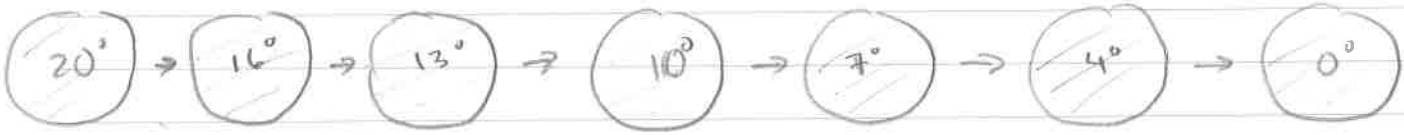
Put equilibrium system at 20°C into 0°C water bath



after some time system is at new equilibrium temp of 0°C



Reversible Process - change temperature regulated water bath infinitely slowly from 20° → 0°C



at every point in time during the process the system is fully at equilibrium at a given temperature. No temperature gradients.

a reversible process looks reasonable going backward in time, an irreversible process would look bizarre. (see above)

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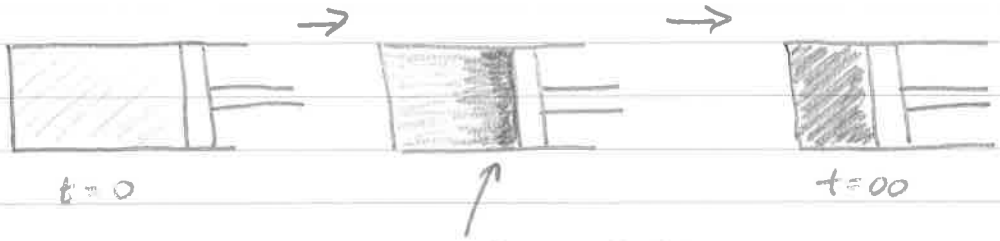
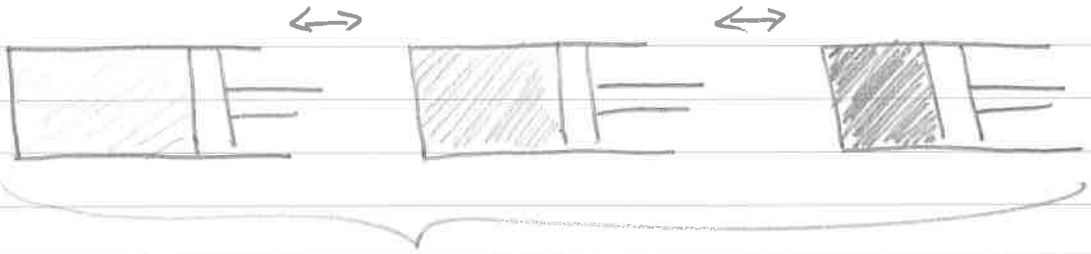
irreversible compression of a gas



as piston moves in you get high pressure region in front of piston

reversible compression of a gas



mechanical equilibrium at all times during process

what does irreversible expansion of a gas look like?

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State Functions

Property of a system that does not depend on the previous history of the system, only its present condition.

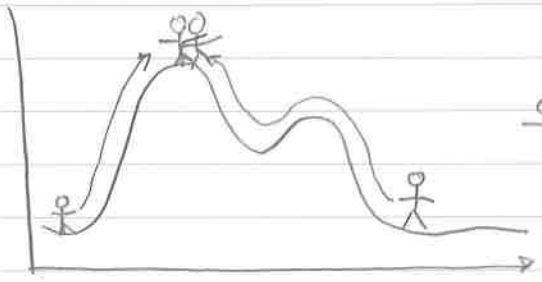
Examples

U, internal Energy

difference in U between 1 liter of water at 10°C and 1 atm at equil. and 1 liter of water at 75°C and 2 atm at equil. is the same regardless of the process used to make the transformation.

other state functions, V, T,

In contrast to state functions are path functions, which depend on the system history.



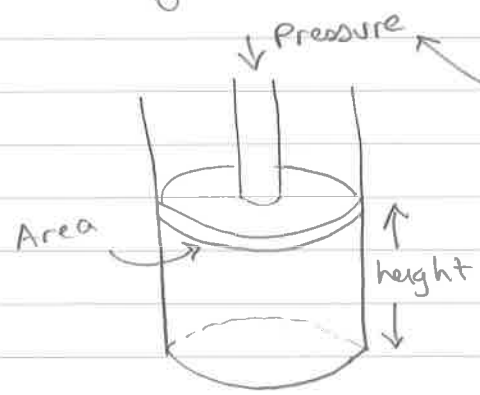
altitude is a state function
distance traveled is a path function

Work & Heat are also path functions

WORK

A common type of work, often associated with chemical reactions, occurs through gas expansion or compression

e.g. Gasoline combustion is used to create expanding gases in the cylinders of your car's engines that push out the pistons. This motion then gets translated into the motion of the car.



Pressure is force applied per unit area.

$$P = F/A \quad \leftarrow \text{area}, \quad \leftarrow \text{Force}$$

recall: Work is force applied over a distance

$$|\text{Work}| = |F \cdot \Delta h| \qquad \Delta h = h_{final} - h_{initial}$$

Use absolute value until we sort out the correct sign.

since $F = P \cdot A$ then $|\text{Work}| = |P \cdot A \cdot \Delta h|$

since $A \cdot \Delta h = \Delta V$ then $|\text{Work}| = |p \cdot \Delta V|$

$\Delta V = V_{final} - V_{initial}$

If ΔV is positive, then gas (system) is expanding and doing work on surroundings. So work should be negative

$$\boxed{W = -p\Delta V}$$ Expansion Work

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Calculate the work associated with the expansion of a gas from 46L to 64L against a constant external pressure of 15 atm.

1st we calculate the change in volume

$$\Delta V = 64L - 46L = 18L$$

Using $P = 15$ atm, we can then calculate

$$\text{Work} = -P\Delta V = (15\text{ atm})(18\text{ L})$$

$$= -270\text{ atm-L}$$

Using the conversion between atm-L and Joules:

$$1\text{ L-atm} = 101.325\text{ J}$$

Then

$$\text{Work} = -270\text{ atm-L}\left|\frac{101.325\text{ J}}{1\text{ atm-L}}\right|\frac{1\text{ kJ}}{1000\text{ J}}$$

$$\text{Work} = -27.4\text{ kJ}$$

So, when the gas expands it does 27.4 kJ of work on its surroundings.
That is, 27.4 kJ of energy flows out of the system so the work is negative.

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Differential Work

$dw = -p\,dV$ expansion work

Work is a path function

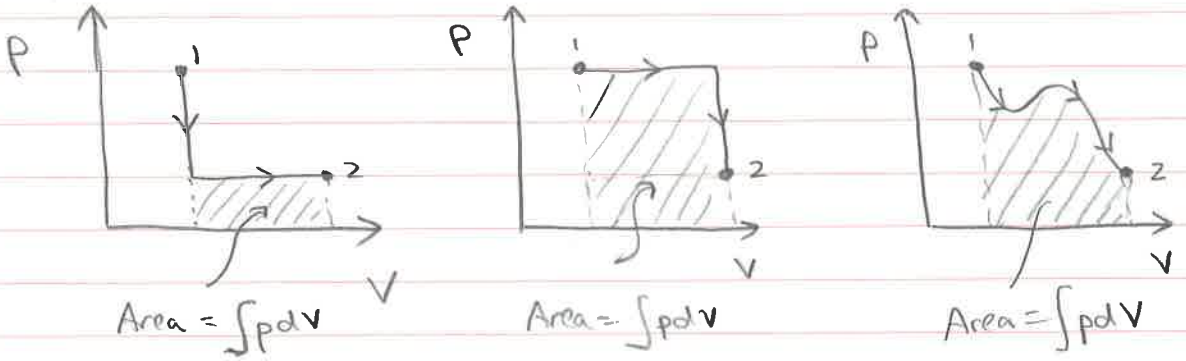
$$w = -\int_{path} p\,dV$$

if p was strictly a function of Volume V then this would be a definite integral.

Problem is that p can also depend on other variables, e.g. T, so many paths are possible

$$w = -\int p(V)\,dV$$

$$w = -\int p(T,V)\,dV$$



It can actually be harder that this. These plots imply a uniform pressure within the system throughout the process.

Both Work & Heat are path functions

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Other types of work

Kind of Work	Formula
Linear Mechanical	$dw = F\,dx$ ← displacement in x direction; F: x component of Force
Gravitational	$dw = mg\,dh$ ← change in height; g: gravity acceleration
Rotational Mechanical	$dw = \tau\,d\theta$ ← change in angle of rotation; τ: Torque
Surface	$dw = \gamma\,dA_s$ ← change in surface Area; γ: surface tension
Stretching or Compression	$dw = F\,dl$ ← change in length; F: stress; $F>0$ tension, $F<0$ compression
Electrical	$dw = \Delta\phi\,dQ_{ee}$ ← change in total charge; $\Delta\phi$: Electrical Potential difference
Electric Polarization	$dw = V\vec{E}\cdot d\vec{p}$ ← change in Polarization; $\vec{E}$: Electric Field Strength
Magnetic	$dw = \left(\frac{\mu_0}{4\pi}\right) V \cdot \vec{H} \cdot d\vec{M}$ ($\vec{H}$: magnetic field; $d\vec{M}$: change in magnetization)

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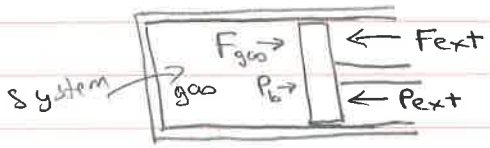
total work is sum of all these possibilities

$$W = \sum_m \int_{path} Y_m \cdot dy_m$$

- $\sum_m$: sum over macroscopic coordinates
- Y_m: work coefficient (Generalized Force)
- dy_m: work coordinate (generalized internal coordinate)

Why are Reversible Processes interesting (important)?

Let's use work to put energy into a system, and then extract work out of the system.

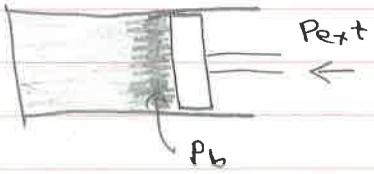


$F_{gas} = P_b A_s$ ← Piston Area

↖ Pressure right behind piston

$F_{ext} = P_{ext} A_s$

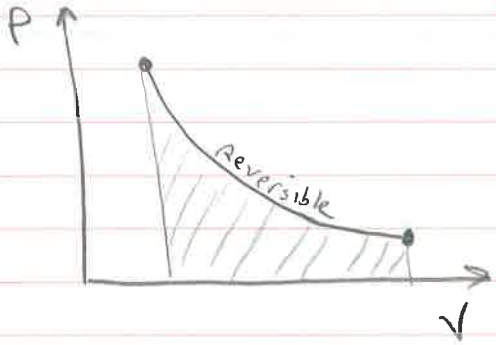
During irreversible compression the pressure behind the piston will always be slightly higher than the equilibrium pressure of the gas



Similarly, during irreversible expansion, the pressure behind the piston will always be slightly less than the equilibrium pressure of the gas

NOTE BOOK

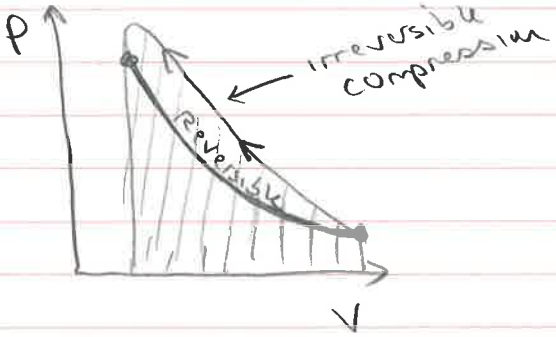
Consider Reversible Process



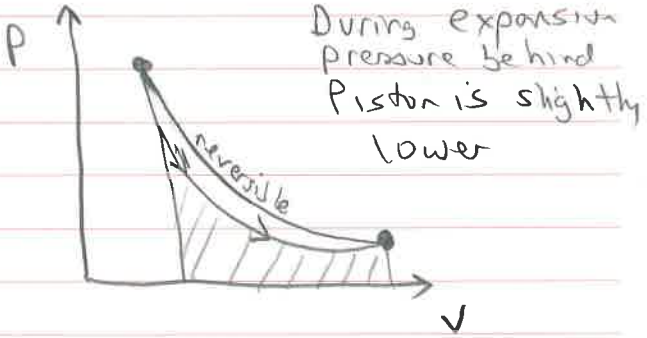
Neglecting piston friction, the work put into the system during reversible compression is exactly the same in magnitude as the work obtained from the system during reversible expansion along the same path

$$-\int_{\text{Reversible compression path}} p\,dV = -\left[-\int_{\text{Reversible expansion path}} p\,dV\right]$$

- During irreversible compression the pressure in the system behind the piston will be slightly higher



takes more work to compress irreversibly



recover less work when expanding irreversibly

When a process deviates from a reversible path the energy that could have been transferred as work gets dissipated into thermal Energy of system or surroundings.

$$\left[-\int_{\text{Irreversible compression path}} P_b\,dV\right] > -\left[-\int_{\text{Irreversible expansion path}} P_b\,dV\right]$$

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Heat

An important concept for understanding how heat is measured is heat capacity

heat capacity – amount of heat needed to raise an object's temperature by 1 degree kelvin.

heat capacity can vary quite a bit, particularly for gases, depending on whether the pressure or volume is held constant as heat is transferred.

... so we specify $C_{p,m}$ & $C_{v,m}$

$C_{p,m}$: molar heat capacity at constant pressure

$C_{v,m}$: molar heat capacity at constant volume.

$$q = n C_{p,m} \Delta T$$

q: heat transferred at constant pressure

n: #moles

$C_{p,m}$: molar heat capacity at constant pressure (heat capacity per amount)

ΔT: change in temperature.

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Sometimes we'll use $C_{P,s}$ ⇐ specific heat capacity (per mass)

$$q = m\, C_{P,s}\, \Delta T$$

- q: heat transferred at constant pressure
- m: mass in grams
- $C_{P,s}$: specific heat capacity
- ΔT: change in temperature

Compd	Temp/°C	$C_{P,s}$ / J/g-K
$H_2O_{(l)}$	15	4.1814
$H_2O_{(s)}$	-11	2.03
$CaCO_{3(s)}$	0	0.85
$MgO_{(s)}$	0	0.87
$SiO_{2(s)}$	25	0.739
$O_{2(g)}$	25	0.917

A piece of iron with a mass of 72.4 grams is heated to 100°C and plunged into 100 grams of water that is initially at 10°C. Calculate the final temperature that is reached assuming no heat loss to the surroundings. Use heat capacities $C_s(H_2O) = 4.18\,J/(g\cdot K)$ & $C_s(Fe) = 0.449\,J/(g\cdot K)$

1st we note that the heat gained by the cooler body + the heat lost by the hotter body = 0

i.e.,

$$q_{H_2O} + q_{Fe} = 0$$

Thus we can write

$$m_{H_2O} C_s(H_2O) \Delta T_{H_2O} + m_{Fe} C_s(Fe) \Delta T_{Fe} = 0$$

and at equilibrium we have $T_f(H_2O) = T_f(Fe) = T_f$

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Solving for T_f using:

$$m_{H_2O} C_s(H_2O) \left[T_f - T_i(H_2O)\right] + m_{Fe} C_s(Fe) \left[T_f - T_i(Fe)\right] = 0$$

and obtain (after some algebra)

$$T_f = \frac{m_{H_2O} C_s(H_2O) T_i(H_2O) + m_{Fe} C_s(Fe) T_i(Fe)}{m_{H_2O} C_s(H_2O) + m_{Fe} C_s(Fe)}$$

Now let's put in the numbers:

$$T_f = \frac{(100.0\,g\,H_2O)(4.18\,J/g\text{-}^\circ C)(10.0^\circ C) + (72.4\,g\,Fe)(0.449\,J/g\text{-}^\circ C)(100.0^\circ C)}{(100.0\,g\,H_2O)(4.18\,J/g\text{-}^\circ C) + (72.4\,g\,Fe)(0.449\,J/g\text{-}^\circ C)}$$

$$T_f = 16.5^\circ C$$

★★★

Calorimetry - Science of measuring heat flow (based on temperature change)

Consider a chemical reaction that releases energy into its surroundings

$$A + B \rightarrow C + D + \text{Energy}$$

The energy will be released into the surroundings through heat & work.

If we seal the reactants into a vessel strong enough that the volume cannot change, then there can be no expansion work.

Then $\Delta U = q + \cancel{w}^{0}$ at constant volume.

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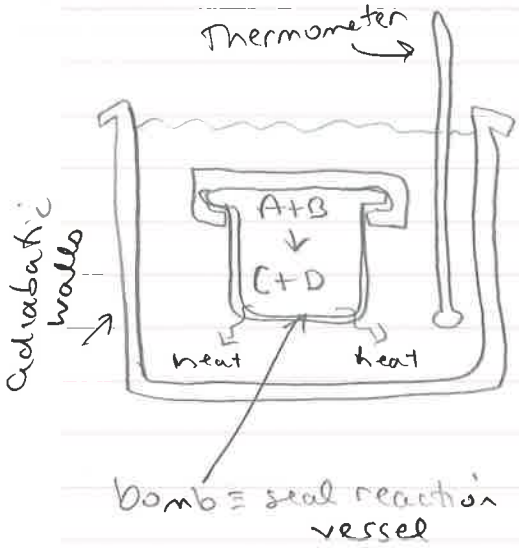
In such a situation (const. volume), all the energy MUST get released into the surroundings as heat.



$\Delta U = q$ at constant volume

Bomb Calorimetry = measure heat flow at constant volume.

Then $q = n C_{V,m} \Delta T = U$

So $n C_{V,m} = C_V = \left(\frac{\Delta U}{\Delta T}\right)_V$

↑ means at constant volume.

expressed in partial derivatives

$$C_V = \left(\frac{dU}{dT}\right)_V$$

In Calorimetry the 1st step is to calibrate the calorimeter by introducing a known quantity of heat and measure its temperature rise.

$$C_{calorimeter} = \frac{q_{KNOWN}}{\Delta T_{measured}}$$

← from reaction with known ΔU.

1.00 grams of hydrazine, N_2H_4, is burned in a bomb calorimeter.

$$N_2H_{4(g)} + O_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)} + \text{Energy}$$

and the temperature of the calorimeter increases by 3.51°C. The bomb calorimeter has a heat capacity of $C_{calorimeter} = 5.510$ kJ/°C. What is the quantity of heat evolved?

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This is easy:

$$q_{evolved} = C_{calorimeter}\,\Delta T$$

so

$$q_{evolved} = \frac{-5.510\ \text{kJ}}{^\circ\text{C}} \Big| 3.51^\circ\text{C} = -19.3\ \text{kJ}$$

What is the heat evolved per mole of N_2H_4?

$$q_{evolved\ per\ mole} = -19.3\ \text{kJ} \Big| \frac{32.0\ \text{g}}{1.00\ \text{g}\ N_2H_4} \Big| \frac{\text{mole}\ N_2H_4}{} = -618\ \frac{\text{kJ}}{\text{mole}}$$

Then we can write

$$N_2H_{4(\ell)} + O_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)} + 618\ \text{kJ}$$

We have measured an energy change of 618 kJ for this reaction (i.e., the heat evolved at constant volume).

★ Remember that ΔU is a state function (unlike q), so this number is good regardless of the history of the reactants and products; that is, 1 mole of N_2H_4 will always react with 1 mole of O_2 to give 618 kJ of energy

ENThalpy

Many chemical reactions occur at constant pressure rather than constant volume.

When gases expand out of open reaction vessels they are doing $p\Delta V$ work on the surroundings, but this work is lost from a practical point of view since it is dissipated into the surroundings

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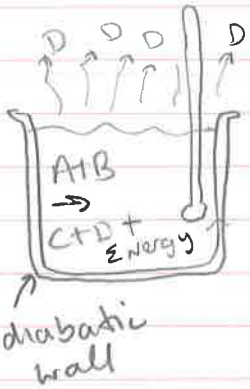
for example $A_{(aq)} + B_{(aq)} \rightarrow C_{(aq)} + D_{(g)}$



When we do a calorimetry experiment at constant (atmospheric) pressure & measure the heat given off we don't know the $p\Delta V$ work

$$\Delta U = q + w = q - p\Delta V$$

(?)

We like measuring quantities like ΔU because it is a state function (history independent)

but clearly ΔU is not so easy to measure here.

There is a nice compromise solution. If we insist that the pressure remain constant during the reaction, then we can define a new state function called Enthalpy

state function → $H = U + pV$ ← all state functions

and during any constant pressure process the change in Enthalpy will be

$$\Delta H = \Delta U + \Delta pV + p\Delta V$$

ΔpV: zero since p = constant

and since

$$\Delta U = q + w = q - p\Delta V$$

Then $\Delta H = q - p\Delta V + p\Delta V = q_p$ ← heat transfered at const. pressure.

(isobaric process)

as long as we hold pressure constant (and only allow expansion work, & no others) then the heat flow will be equal to a state function called Enthalpy

Thus, since

$$q = n C_{P,m} \Delta T = \Delta H$$ isobaric process

then

$$n C_{P,m} = C_P = \left(\frac{\Delta H}{\Delta T}\right)_P$$

or expressed in partial derivative form

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

How does C_p differ from C_v?

Let's look at an ideal gas

$$H = U + pV \approx U + nRT$$

Then

$$dH \approx dU + nRdT$$ closed system $\Delta n = 0$

$C_p dT$ $\quad$ $C_v dT$

so $\quad C_p dT \approx C_v dT + nRdT$

becomes $\quad C_p \approx C_v + nR$

$$\boxed{C_{P,m} - C_{V,m} \approx R}$$

for molar heat capacities & ideal gas

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EQUIPARTITION OF ENERGY

The equipartition Theorem says that energy is distributed, on average, equally amongst all possible molecular motions, that is, translations, rotations, vibrations, ...

In an ideal monoatomic gas there is only the possibility of translational motion.

For each particle (atom) the energy is given by

$$E_{Trans} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

Kinetic energy associated with 3 independent coordinates: p_x, p_y, p_z

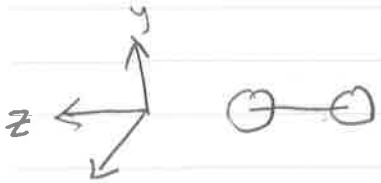
momentum in x, y, z

The EQUIPartition Theorem says there will be an average energy of $\frac{1}{2}k_BT$ associated with each coordinate that shows up squared in the total Energy

so $\overline{E} = 3\left(\frac{1}{2}k_BT\right)$

↑ for p_x^2, p_y^2, p_z^2

For a diatomic molecule, we need additional degrees of freedom (coordinates) to describe the energy



Translation of molecule's center of mass

$$E_{Trans} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

same as monoatomic gas

and also Rotational motion of molecule

$$E_{ROT} = \underbrace{\frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2}_{\text{Kinetic Energy}}$$

No $I_z \omega_z^2$ because molecule is linear. i.e. $I_z = 0$

and also vibrational motion

$$E_{vib} = \underbrace{\frac{p_r^2}{2m_r}}_{\text{Kinetic Energy}} + \underbrace{\frac{1}{2} k (r - r_0)^2}_{\text{Potential energy}}$$

r_0 ← equilibrium bond length

$r - r_0$

So for diatomic we find

p_x^2, p_y^2, p_z^2 ← translational

ω_x^2, ω_y^2 ← rotational

p_r^2, r^2 ← vibrational

so $\overline{\epsilon} = 7\left(\frac{1}{2} k_B T\right) = 7/2\, k_B T$

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Polyatomic Molecule ($X \equiv$ # atoms in a molecule)

Depends on whether molecule is linear or nonlinear

non-linear case (more general)

- 3 coordinates (p_x, p_y, p_z), $(x, y, z$ don't appear)
- 3 coordinates $(\omega_x^2, \omega_y^2, \omega_z^2)$ $(\alpha, \beta, \gamma,$ orientation don't appear)
- $(3X - 6) \times 2$ vibrational energy coordinates

($3X$: # atoms in molecule; $\times 2$: kinetic + potential)

So $$\bar{\epsilon} = 3\left(\tfrac{1}{2}k_BT\right) + 3\left(\tfrac{1}{2}k_BT\right) + (3X-6)(k_BT)$$

translation, rotation, vibration

linear case

- 3 coordinates for translation (p_x^2, p_y^2, p_z^2)
- 2 coordinates for rotation (ω_x^2, ω_y^2)
- $(3X-5) \times 2$ coordinates for vibration

So $$\bar{\epsilon} = 3\left(\tfrac{1}{2}k_BT\right) + 2\left(\tfrac{1}{2}k_BT\right) + (3X-5)(k_BT)$$

translation, rotation, vibration

Heat Capacity & Equipartition Theorem

If we set the internal energy to this average energy

$$U = \frac{3}{2} N_A k_B T = \frac{3}{2} RT \quad \text{for one mole of monoatomic gas}$$

Then we can calculate the heat capacity of the monatomic gas

$$C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} R = 12.47 \ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Gas	C_v (measured) / $J \cdot K^{-1} \cdot mol^{-1}$	
He	12.47	} all measured at Room Temperature
Ne	12.47	
Ar	12.47	

↑ impressive agreement!!

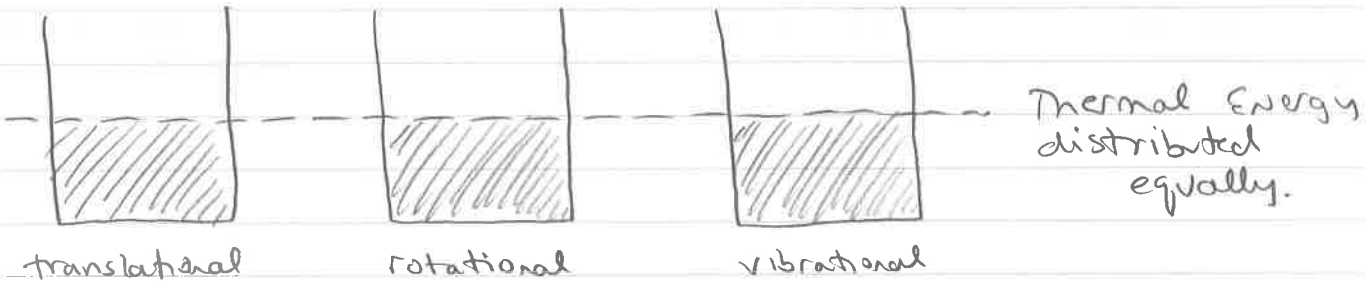
How about a diatomic gas?

$$U = \frac{7}{2} RT \quad \text{so} \quad C_v = \frac{7}{2} R = 29.10 \ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

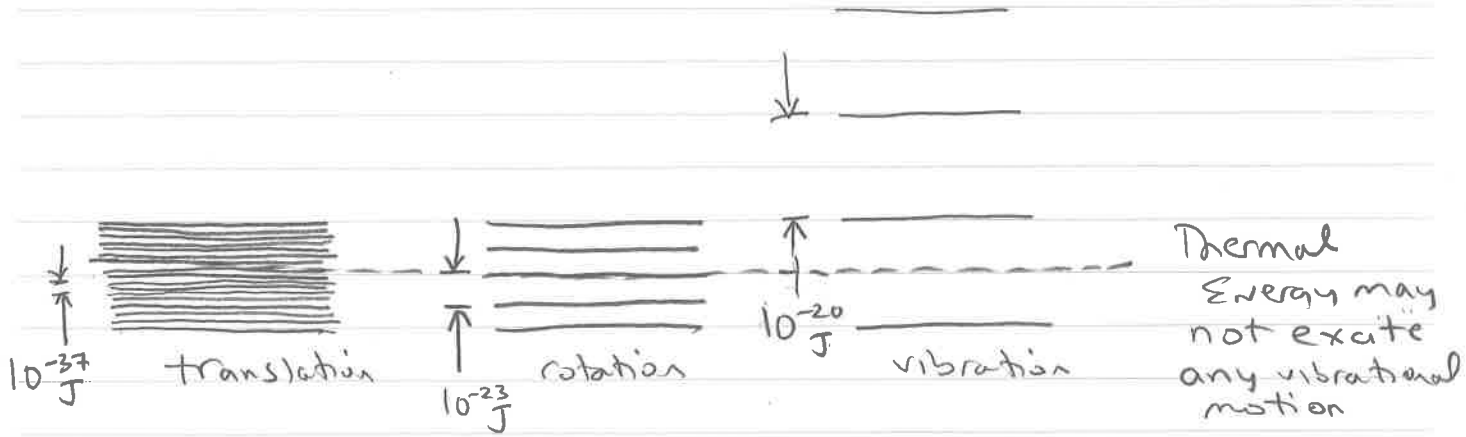
Gas	C_v (measured) / $J \cdot K^{-1} \cdot mol^{-1}$	
H_2	20.50	} all measured at Room Temperature
N_2	20.50	
O_2	21.50	

↑ hmmm. at least they are nearly identical as predicted by theory, but all values are consistently lower than predicted.

The EQUIPartition Theorem assumes the thermal energy is distributed equally amongst all type of motion.



The Quantum Theory, however, tells us that molecules can only be found in discrete energy states, and that the spacing between these states depends on the type of motion.



For diatomics

$$\bar{\epsilon} = 3\left(\tfrac{1}{2}k_B T\right) + 2\left(\tfrac{1}{2}k_B T\right) + (3\cdot 2 - 5)(k_B T)$$

Translation, Rotation, Vibration

NOT enough Thermal energy to excite at Room Temp.

so $\bar{\epsilon} = \frac{5}{2}k_B T$ at Room Temp for diatomic molecule

or

$$u = \frac{5}{2}RT = 20.79\ \text{J-K}^{-1}\text{-mol}^{-1}$$ for one mole of diatomic gas

much better agreement.

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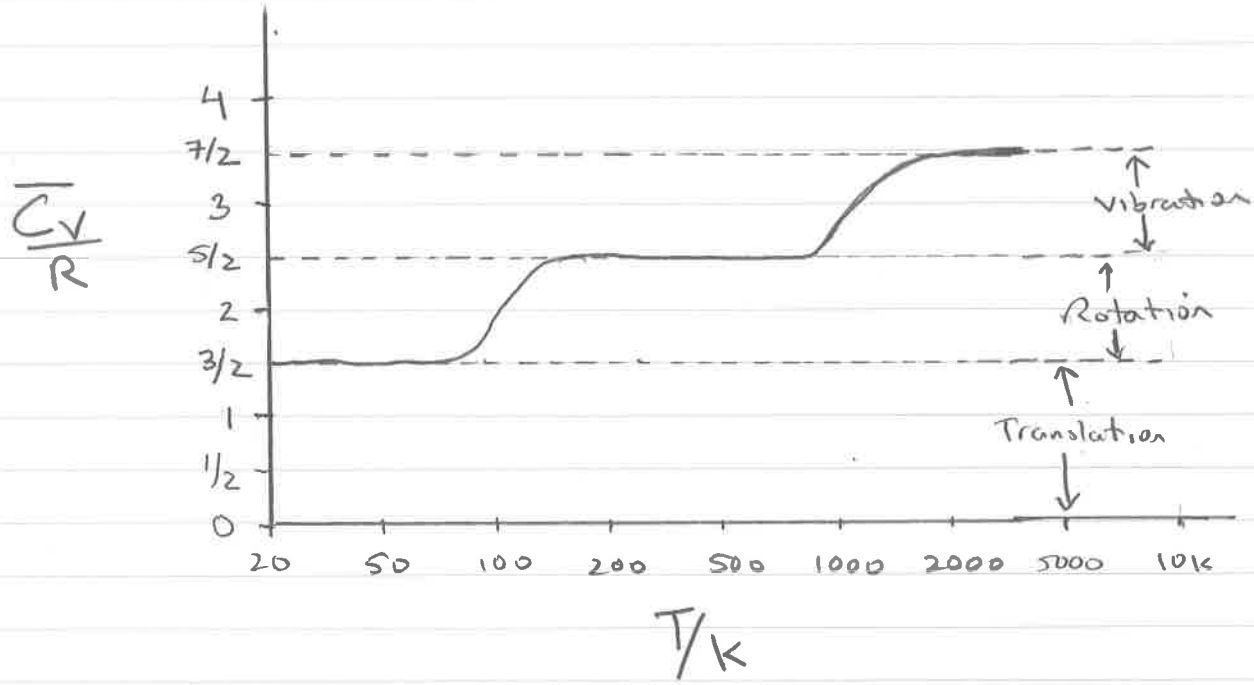
Heat Capacity of diatomic gas



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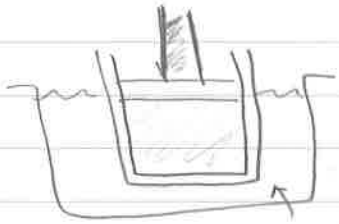
Reversible Expansion of an ideal gas

Reversible means at equilibrium at all times, so

$PV = nRT$ can be used

$$w = -\int_{path} p\,dV = -\int_{path} \frac{nRT}{V}\,dV$$



Isothermal Expansion

If piston is in constant temperature bath then

$$w = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

assume closed system
n = constant

so $$\boxed{w = -nRT\ln\frac{V_2}{V_1}}$$

work done by system in reversible, isothermal expansion of ideal gas.

also recall that $U = \frac{3}{2}RT$ or $\frac{5}{2}RT$ for ideal monatomic or diatomic gas
so if T = constant throughout process $\Delta T = 0$, then $\Delta U = 0$

so $\Delta U = 0 = q + w$ Thus $q = -w$

and $q_{Rev} = nRT\ln\frac{V_2}{V_1}$

Adiabatic Expansion

Instead of constant temperature bath, let's use adiabatic walls and calculate work on expansion

In this case, temperature will change, so can't factor it out of the integral. $w = -\int_{path} \frac{nRT}{V}\,dV$

how does T change during adiabatic expansion?

NOTE BOOK
Miquelrius

optional

With adiabatic wall we know

$$dU = dw + \cancel{dq}^{\,0}$$

and we also know $\left(\frac{\partial U}{\partial T}\right)_V = C_V$

which helps us know how the temperature changes with ΔU.

which we rearrange to

$$dU = C_V dT = dw$$

for adiabatic process

then

$$w = \int_{T_i}^{T_f} C_V dT = C_V \Delta T$$

Great!, but how do we know ΔT for adiabatic expansion? easier to measure V_f and V_i

Since

$$dw = C_V dT = -p dV$$

Let's use ideal gas and write

$$\frac{C_V}{n} dT = -\frac{RT}{V} dV$$

integral becomes

$$C_{V,m} \int_{T_i}^{T_f} \frac{dT}{T} = -R \int_{V_i}^{V_f} \frac{dV}{V}$$

Since $C_{P,m} - C_{V,m} = R$ for ideal gas

$$C_{V,m} \ln \frac{T_f}{T_i} = -(C_{P,m} - C_{V,m}) \ln \frac{V_f}{V_i}$$

rearrange

$$\ln \frac{T_f}{T_i} = \left(\frac{C_{P,m}}{C_{V,m}} - 1\right) \ln \frac{V_i}{V_f}$$

define $\gamma = C_{P,m}/C_{V,m}$

$$\boxed{T_f/T_i = \left(V_i/V_f\right)^{\gamma-1}}$$

Reversible adiabatic ideal gas expansion

MIQUELRIUS

optional

and $$\Delta T = T_f - T_i = T_i \left[\left(\frac{V_i}{V_f} \right)^{\gamma - 1} - 1 \right]$$

so $$w = C_v \Delta T = \underbrace{C_v T_i \left[\left(\frac{V_i}{V_f} \right)^{\gamma - 1} - 1 \right]}$$

work for reversible adiabatic expansion of ideal gas

We can also substitute into $(T_f/T_i) = (V_i/V_f)^{\gamma - 1}$

$$T_i = \frac{P_i V_i}{nR} \quad \text{and} \quad T_f = \frac{P_f V_f}{nR}$$

and get

$$\frac{P_f}{P_i} = \left(\frac{V_i}{V_f} \right)^{\gamma} ,$$

which rearrange to

$$\boxed{P_i V_i^{\gamma} = P_f V_f^{\gamma}}$$

Reversible adiabatic expansion of ideal gas

contrast this to Boyles Law

$$\boxed{P_i V_i = P_f V_f}$$

Reversible isothermal expansion of ideal gas.

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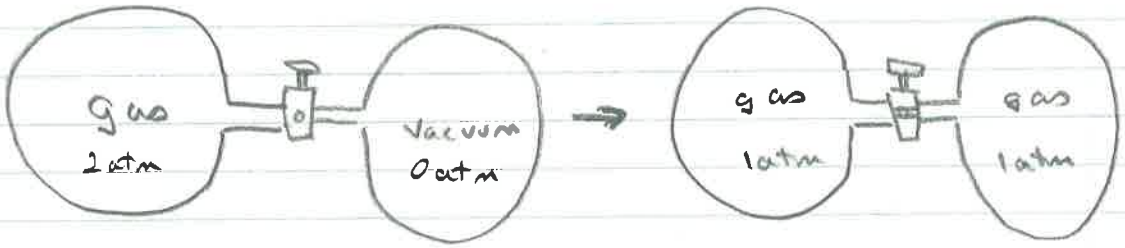
Free expansion into a vacuum



What is the work?

$w = 0$, since gas is expanding against zero pressure

$$dw = -P_{ex}\,dV$$

P_{ex}: zero

dV: Volume doubles but external pressure is zero.

A chemical reaction is a Thermodynamic process. $\underbrace{A+B}_{\text{reactants}} \rightarrow \underbrace{C+D}_{\text{products}}$

State Function

$\Delta H = H_{final} - H_{initial}$

$\Delta H = H_{products} - H_{reactants}$

Thermochemistry

Because Enthalpy is a state function we can write for a chemical reaction that

$$\Delta_r H^\circ = \sum \nu H_m^\circ(\text{products}) - \sum \nu H_m^\circ(\text{reactants})$$

- $\Delta_r H^\circ$: change in Enthalpy for reaction; $^\circ$ indicates standard state $p = 1$ bar; T not specified
- ν: reaction stoichiometry for product
- H_m°(products): molar enthalpy of product
- $\sum$: sum over all products
- ν: reaction stoichiometry for reactant
- H_m°(reactants): molar enthalpy of reactant
- $\sum$: sum over all reactants

We cannot measure absolute values of molar enthalpy for a substance, so we define

Standard molar enthalpy of formation - $\Delta_f H_m^\circ$

- enthalpy change when 1 mole of a compound is formed from its constituent elements at 1 bar and 298 K.

we assign a value of zero to $\Delta_f H_m^\circ$ for elements in their MOST STABLE allotropic form.

e.g. at T = 298 K, P = 1 bar Carbon is graphite

So $\Delta_f H_m^\circ(\text{graphite}) = 0$

Oxygen is a diatomic gas at P = 1 bar, T = 298 K so $\Delta_f H_m^\circ(O_{2(g)}) = 0$

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So the reaction

$$C_{graphite\,(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} \qquad \Delta_r H = -393.5 \text{ kJ}$$

since both graphite & O_2 are in their standard states, the $\Delta_r H$ for this reaction is the $\Delta_f H^\circ_m$ for $CO_{2\,(g)}$

$$\Delta_f H^\circ_m (CO_{2\,(g)}) = -393.5 \text{ kJ/mole}$$

another example

$$H_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \rightarrow H_2O_{(\ell)} \qquad \Delta_r H = -286 \text{ kJ}$$

↑ standard states ↑

so $\Delta_f H^\circ_m (H_2O_{(\ell)}) = -286 \text{ kJ/mole}$

So the more straightforward approach to calculating reaction enthalpy changes is to use standard molar enthalpy of formations

$$\Delta_r H^\circ = \sum \nu \, \Delta_f H^\circ_m (\text{products}) - \sum \nu \, \Delta_f H^\circ_m (\text{reactants})$$

What is $\Delta_r H^\circ$ for

$$C_3H_{8\,(g)} + 5O_{2\,(g)} \rightarrow 3CO_{2\,(g)} + 4H_2O_{(g)}$$

$$\Delta_r H^\circ = \left[3\Delta_f H^\circ_m (CO_{2\,(g)}) + 4\Delta_f H^\circ_m (H_2O_{(g)})\right] - \left[\Delta_f H^\circ_m (C_3H_{8\,(g)}) + 5\Delta_f H^\circ_m (O_{2\,(g)})\right]$$

Look up values for $\Delta_f H^\circ_m$ in tables.

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$$\Delta_r H^\circ = \left[3\left(-393.5 \frac{kJ}{mole}\right) + 4\left(-241.8 \frac{kJ}{mole}\right)\right]$$

$$-\left[\left(-103.85 \frac{kJ}{mole}\right)\right] = -2220\ kJ$$

In fact, it's not even necessary to use $\Delta_f H^\circ_m$ values, if you know $\Delta_r H$'s for reactions that sum to your desired reaction.

Hess' Law - change in enthalpy is same whether reaction takes place in one step or in a series of steps,

e.g. $N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$ $\quad \Delta_r H = 68\ kJ$

but could also carry out in 2 steps

① $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ $\quad \Delta_r H_1 = 180\ kJ$

② $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ $\quad \Delta_r H_2 = -112\ kJ$

which sum to

$N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$ $\quad \Delta_r H_T = 68\ kJ$

$\Delta_r H_T = \Delta_r H_1 + \Delta_r H_2$

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Bond Enthalpies

In a chemical reaction we'll have bonds broken, bonds formed, & energy either absorbed or emitted by the reaction.

Let's look closer at the enthalpy change associated with each individual bond broken or formed.

Process	ΔH (kJ/mole)
$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)}$	435
$CH_{3(g)} \rightarrow CH_{2(g)} + H_{(g)}$	453
$CH_{2(g)} \rightarrow CH_{(g)} + H_{(g)}$	425
$CH_{(g)} \rightarrow C_{(g)} + H_{(g)}$	339
	1652

The enthalpy change associated with breaking a C-H bond is slightly dependent on what molecule it is in. Thus, we take an average change in enthalpy when a CH bond breaks as

$$D_{C-H} = 1652/4 = 413 \text{ kJ/mole}$$

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JB

Other average bond enthalpy changes found this way are

BOND	ΔH / kJ/mole	BOND	ΔH / kJ/mole
H-H	432	C-H	413
H-F	565	C-C	347
H-Cl	427	C-N	305
		C-O	358

You can also nicely see the bond enthalpy with multiple bonding.

BOND	ΔH / kJ/mole	BOND	ΔH / kJ/mole
C-C	347	C-N	305
C=C	614	C=N	615
C≡C	839	C≡N	891

We can use these bond enthalpies to calc approximate enthalpy changes for reactions.

$$H_{2(g)} + F_{2(g)} \rightarrow 2\,HF_{(g)}$$

Count bonds broken & formed

$$\underset{\text{broken}}{H-H} + \underset{\text{broken}}{F-F} \rightarrow 2\,\underset{\text{formed}}{H-F}$$

$$\Delta_r H = \sum \Delta H(\text{bonds broken}) - \sum \Delta H(\text{bonds formed})$$

So $\Delta_r H = [(1\text{ mole})(432\text{ kJ/mole}) + (1\text{ mole})(154\text{ kJ/mole})] - [(2\text{ moles})(565\text{ kJ/mole})]$

(D_{H-H}, D_{F-F}, D_{H-F})

Many of the standard state enthalpies are given at 298 K. What if you needed to calc $\Delta_r H$ at a different temperature?

Generally, $\left(\frac{\partial H}{\partial T}\right)_P = C_p$

so if we need to adjust an enthalpy to a new temperature we only need to integrate

$$\int_{H_1}^{H_2} dH = \Delta H = \int_{T_1}^{T_2} C_p \, dT$$

to get the enthalpy of a substance at a new T.

for a reaction we take the same approach

$$\Delta_r H = \sum \nu H(\text{products}) - \sum \nu H(\text{reactants})$$

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_P = \sum \nu \left(\frac{\partial H(\text{products})}{\partial T}\right)_P - \sum \nu \left(\frac{\partial H(\text{reactants})}{\partial T}\right)_P$$

$$= \sum \nu C_p(\text{Products}) - \sum \nu C_p(\text{reactants})$$

So we define for a given reaction

$$\Delta C_p = \sum \nu C_p(\text{Products}) - \sum \nu C_p(\text{reactants})$$

Then we can calc.

$$\int d\Delta_r H = \Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$$

and we can adjust the reaction enthalpy for the new temperature