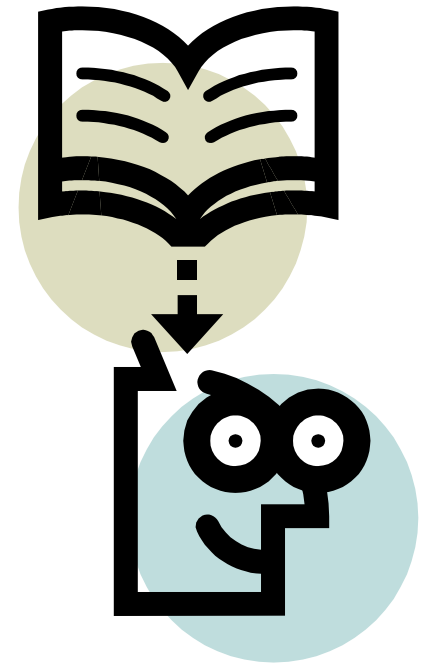


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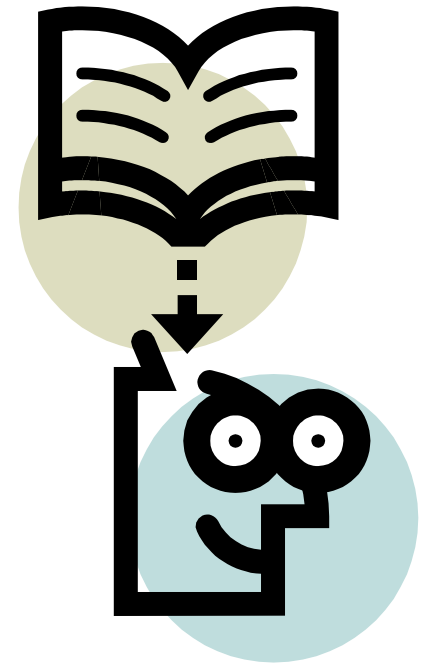
Introduction to Thermodynamics



Concepts and introduction to calculations

Part 1

The First Law: Energy is Conserved



Concepts and introduction to calculations

3 Laws of Thermodynamics

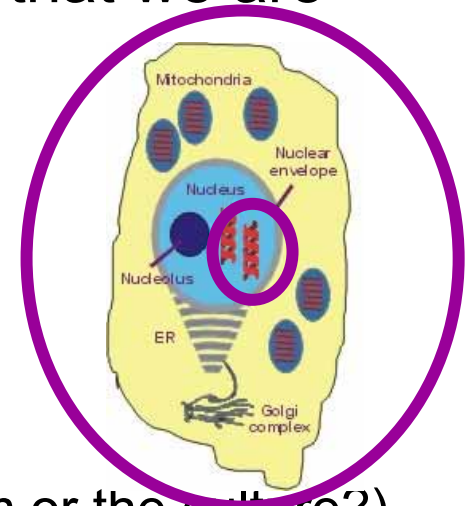
- Scientific "Law" - an attempt to describe one aspect of nature (always has exceptions or can be wrong).
 - We need to specify WHEN the laws are valid!
This is very important.
- Thermodynamics deals with **changes between forms of energy** : burning gas, absorbing light, substrate binding to an enzyme, formation of DNA duplex
- The laws summarize limits on how the transfer can occur and help us to derive equations to describe the process

3 Laws of Thermodynamics

- The **first law** of thermodynamics - **energy is conserved**; different form of energies can interconvert.
- The **second law** of thermodynamics - **the entropy of an isolated system always increases** during a spontaneous process.
- The **third law** of thermodynamics - the entropy of any pure, perfect crystal can be chosen as equal to 0 at 0 K absolute temperature (**defines zero for entropy**).

Using the laws


- Some definitions are needed to keep things straight!
- **System** vs. **surroundings**
- The **system** is the portion of the universe that we are interested in studying
- The **surroundings** are everything else
- The boundary is defined by the problem!
(is the system the enzyme, the cell, the organism or the culture?)



The first law and energy transfer

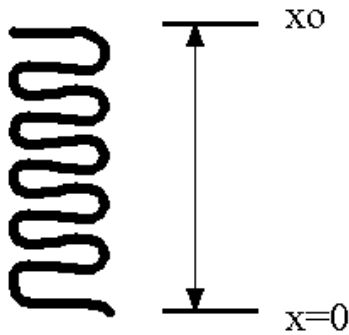
- *Energy is conserved – it is neither created nor destroyed, only transferred*
- The total energy of the system can change, but the total energy of system + surroundings does not!
- Can a particular system exchange energy?
 - **Isolated** system: no exchange of any kind with surroundings (like a sealed, rigid, perfect thermos)
 - **Closed** system: no exchange of matter, but it can exchange energy
 - **Open** system: can exchange matter and energy

Energy transfer: **Work** and **Heat**

- *Work*: a general form of energy exchange 
- **Work** = external (opposing) force * displacement
 - No ext. force → no work!! (sounds simple, but is important)
 - The external force could be wind, weights, friction, gravity, electrostatic field, etc
- **Work has a sign!** (shows the direction of the transfer)
 - **Work done ON the system is positive**, the energy of the system increases (examples: stirring, lifting)
 - **Work done BY the system is negative**, the energy of the system decreases (falling, pushing)
- The difference is just in the sign and what part we are calling the system

How do we calculate work?

- Work = external (opposing) force * displacement
- Imagine compressing or extending a spring (or a muscle fiber, or many other things that work this way)
- Hooke's law says that the force of a spring is directly proportional to the change in length of the spring.



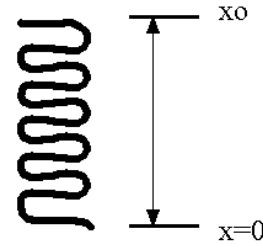
$$f = -k(X - X_0)$$

k is the force constant

- What opposes changing the spring length? **The spring force**: $F = -k(x - x_0)$ note that *the force is not a constant!*

Work = external (opposing) force * displacement

- What opposes changing the spring length? The spring force: $F = -k(x - x_0)$ note that the force is not a constant!
- The negative sign tells us that the direction of the force is opposite to the direction of displacement (opposes change away from X_0)



- If we decide that the spring is the system, the external force is the opposite of the internal force: $F = k(X - X_0)$
- Use our definition of work: $w = F * \text{distance}$
- We need an integral since force changes with distance!

Work = external (opposing) force * displacement

- More general form of work equation:

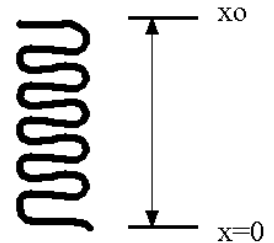
$$w = \int f dx \quad w \neq f \Delta x$$

- Using our definition of work and external force

$$f = k(X - X_0)$$

$$w = \int_{x_1}^{x_2} f d(x - x_0) = \int_{x_1}^{x_2} k(x - x_0) d(x - x_0)$$

$$= \int_{x_1 - x_0}^{x_2 - x_0} kx' dx' = \frac{1}{2} k[(x_2 - x_0)^2 - (x_1 - x_0)^2]$$



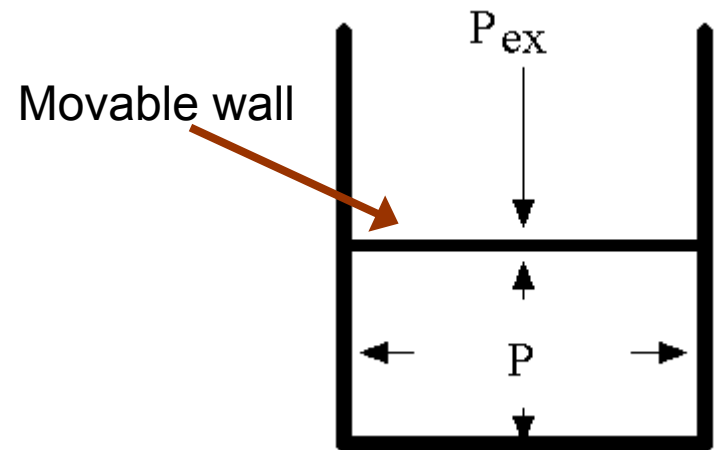
- Note that we used $dx = d(x - x_0)$ and a change of variable
- This equation gives us a general result, we need to put in the numbers to get an actual work value

Another example: PV work

- Work is involved in increasing or decreasing volume
- The system can expand and do work on the surroundings ($P_{\text{sys}} > P_{\text{ext}}$, work < 0)
- Negative work: means that the system **does** the work!
- The surroundings can do work on the system by compressing the system ($P_{\text{ext}} > P_{\text{sys}}$, work > 0)
- What is the work?

$$w = \int f dx = \int \frac{f}{A} (A dx) = - \int P_{\text{opposing}} dV$$

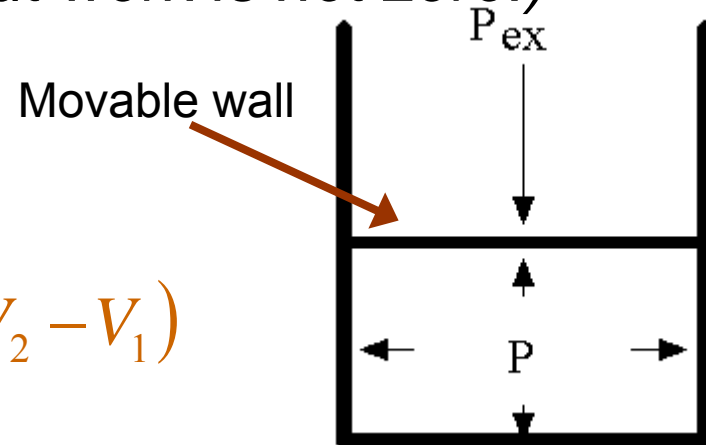
- We need the negative since the work is negative if the volume increases ($\Delta V > 0$) and $P \geq 0$ always



PV work: $w = \int f dx = \int \cancel{f/A} (A dx) = - \int P_{\text{opposing}} dV$

- Keep in mind that work is calculated using the **pressure opposing the volume change**
- For compression, this is the pressure of the system (and it often changes during compression!)
- For expansion, this is the external pressure (of the surroundings) and is usually constant
- If the pressure of the system and surroundings are nearly equal, the process is “*reversible*” (but work is not zero!)
- If the opposing pressure is **constant**, it can be factored out of the integral

$$w = - \int P_{\text{opp}} dV = -P_{\text{opp}} (V_2 - V_1)$$



PV work and the ideal gas law

- Ideal gas law: relates properties of the system:
P, V, T, n (and R)

$$PV = nRT$$

- Use only for (ideal) gases!!

$$V = \frac{nRT}{P}$$

- Rearrange equation to solve for what you need

$$P = \frac{nRT}{V}$$

- Sometimes P, V, T or n will be constant

- Remember: OK to factor constants out of integrals

$$T = \frac{PV}{nR}$$

$$w = -\int PdV = -P \int dV = -P(V_2 - V_1) \text{ (if P const)}$$

$$w = -\int PdV = -\int \frac{nRT}{V} dV = -nRT \int \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} \text{ (if n, T const)}$$

- Make sure that the integral uses P_{gas} (not P_{ext})
before using the ideal gas law to substitute!

Non-PV work

- PV work relates to volume changes (which usually require work)
- Work in a gravitational field
 - Falling objects can convert potential energy to kinetic energy
 - Water at the bottom of waterfall can be warmer
 - At constant velocity, the gravitational energy can be converted to work



$$F_{\text{grav}} = \text{mass} * g \quad : \quad w = \text{mass} * g * (h_2 - h_1)$$

- Or, work is required to lift objects!!
- Work in an electric field (gel electrophoresis, ion channels, etc.)
 - An electric field (from uneven electron distribution) produces force on other charges

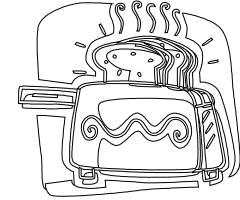
$$\text{work} = \text{voltage} * \text{current} * \text{time} \quad w = E / t$$



LIPA charges for their work : more current or longer time = more money



Energy transfer, again: *heat*



- Heat can *usually* be defined in terms of **temperature change**
- Like work, **the sign matters!** Skiing vs. sunbathing.
- **Heat added to the system is positive** (temperature usually \uparrow)
- **Heat removed from the system is negative** (temperature usually \downarrow)
- The key property for heat is called the *heat capacity*
- **How much heat is needed to change the system temperature?**
 - **What is the system?** (no complex no energy storage)
 - **How big is the system?** (big no energy storage)
 - **What is the current temperature of the system?**
 - **What is the heat energy?**
 - **Heat energy (temperature)**
 - **Vol (expansion or compression)**
 - **Phase changes?** (water at 0°C releases heat during melting)

Calculating energy transfer by heat



- For a closed system, q (the amount of heat transferred) is proportional to the temperature of the system before (T_1) and after (T_2) the heat exchange: $q = C \Delta T$ where the proportionality constant C is called the **heat capacity**
- Amount of heat required to increase system T by 1°C (1 K)
- Heat capacity is a property of the system
 - C depends on the **system size** (larger systems require more heat)
 - C depends on the **substance** (more complex systems require more heat)
 - C depends on the **phase**
 - C depends on the **temperature** And so on!
- C_p : heat capacity at constant P
- C_v : heat capacity at constant V (for solids/liquids, $C_p \approx C_v$)
- C_p^* : specific heat, or heat capacity per 1 kg of substance

System variables

- Each system will have certain properties, such as **temperature**, **pressure**, **volume**, etc.
- Some of these are special: they **depend only on the current state of the system**, not how it was prepared
- These are called **state variables**
- **P, V, T, are state variables (there are more)**
- **Energy is a state variable, q and w are not**
 - For travel, change in elevation does not depend on route but distance traveled (and gas used) DO
- **q and w depend on path: how system was prepared!**



New state variables

- Sometimes we find it useful to combine several state variables into a new state variable
- Enthalpy (H) is a combination that is very useful
- $H = E + PV$
- Why is this useful? We will see that when the pressure is constant, the enthalpy change of the system is equal to the heat transferred
- $\Delta H = q$ if P constant (more on this later)

Intensive vs. Extensive variables

- Variable can be classified into two groups
- Which group depends on whether the property depends on the *size* of the system
- **Extensive:** depend on system size (extent)
 - Volume, energy, enthalpy, heat capacity, mass, etc
- **Intensive:** do NOT depend on system size
 - Density, molar mass, pressure, temperature, etc.
- We can always convert an *extensive* variable to an *intensive* version by dividing by the system size
 - Volume → molar volume mass → density heat capacity → C_p

Equations of state

- Many of the state variables are determined by values of the other variables (they are not all independent)
- Equations that relate the variables of state are called **equations of state**
- Volume depends on other properties
 - Liquids and solids
 - volume is approximately constant! ($V=c$)
 - Better: volume depends slightly on T and P

$$\bar{V} = 18.07(1 - 45.9 \times 10^{-6} P) \quad \text{Isothermal compressibility of water}$$

- This equation relates **molar volume** (\bar{V} with bar over it, **the bar always mean quantity per mole**), **pressure** and **a constant** that depends on how easy it is to compress that substance

Equations of state: gas volumes

- While the volume of liquids and solids is nearly constant, the volume of gases depends greatly on conditions
- $PV=nRT$ (the ideal gas law or ideal gas equation)
- Notice that increasing pressure from 1 to 1000 atm decreases volume by 1000x (at constant n and T)
- This is good only at low pressures where gas molecules do not interact with each other. $\pm 10\%$ at 1 atm.
- For more accurate data, use the van der Waals equation

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad \text{note } a \text{ and } b \text{ are zero for an ideal gas}$$

Energy and Enthalpy changes

- We need equations to tell us how to calculate ΔE or ΔH
- Remember: change means final value minus initial value
- Since E and H are state variables, ΔE and ΔH depend only on initial and final states, not the path of the change!
- We can imagine ANY path between initial and final states and the values must not change
- Pick a path for which the calculation is easy!
- This will be the approach we take all semester
 - Often we can solve the problem many ways
 - Try to pick the easiest way
 - You must explain your work since “correct” solutions vary!

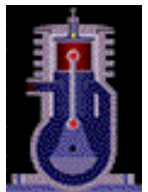


Heat and Work changes

- Transfer of heat and/or work will result in changes to the energy of the system (recall first law)
- For a **closed** system, the follow equation holds:

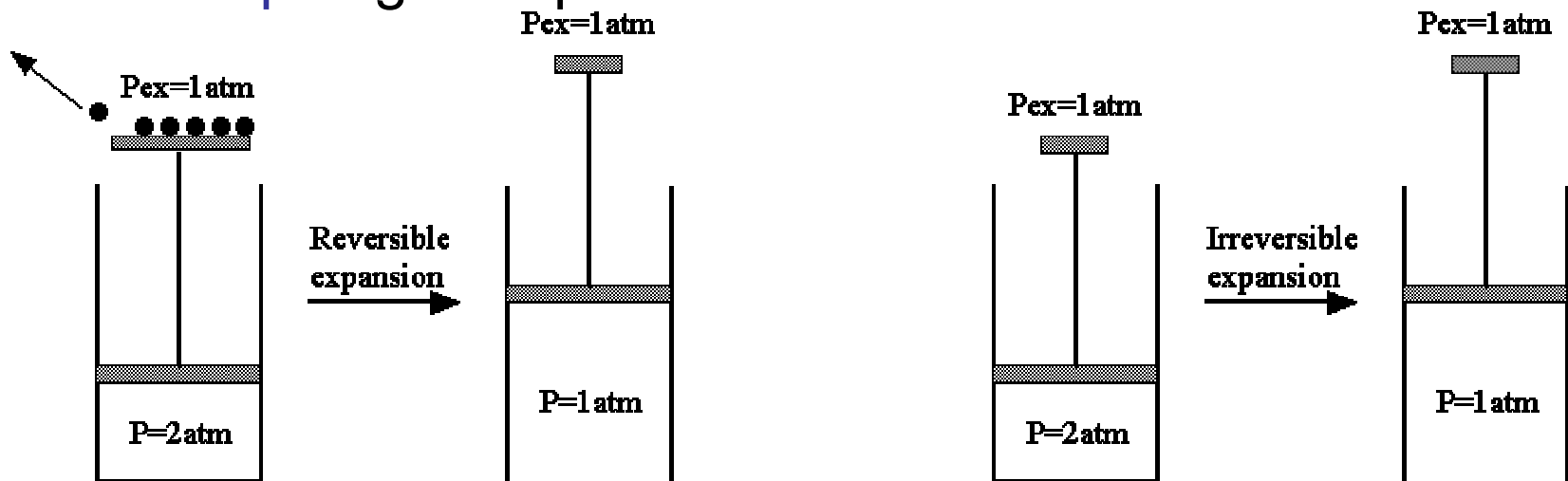
$$\Delta E = q + w \quad (\text{energy change equals sum of heat and work})$$

- Energy change is defined as $\text{energy}_{\text{final}} - \text{energy}_{\text{initial}}$
- All signs are from the point of view of the system
- q is net heat transfer into the system (heat in)
- w is the net work done on the system (work in)
- If we can calculate heat and work, we can find ΔE



Reversible paths

- There are an infinite number of ways to change a system from state A to state B
- A path where the system is kept **very close to equilibrium** is called a **reversible path**
- Other paths are called **irreversible paths**
- **The endpoints do not depend on the path!**
- **Example:** gas expansion can be **reversible** or **irreversible**



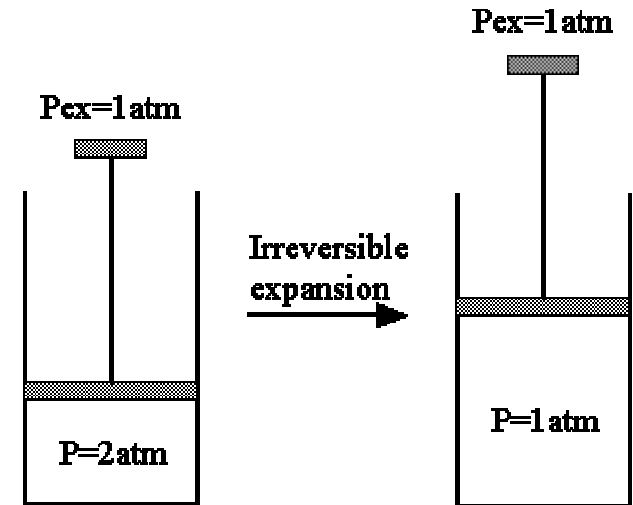
Example

- $P_1V_1T_1 \rightarrow P_2V_2T_2$

$$\Delta E = q + w$$

$$w = -\int P_{op} dV = -\int P_{ext} dV$$

$$= -1atm \int dV = -1atm \Delta V$$



- For q , we need heat capacity but P_{sys} and V both change!
- In general, we may find it necessary to consider a multi-step path in which something is kept constant during each step
- First change P , then V (or first T , then P , etc)

Multi-step paths

- $P_1V_1T_1 \rightarrow P_2V_2T_2$
- This can be much easier to calculate using an intermediate state:

$$P_1V_1T_1 \rightarrow P_1V_2 \rightarrow P_2V_2T_2$$

or

$$P_1V_1T_1 \rightarrow V_1T_2 \rightarrow P_2V_2T_2$$

$$P_1V_1T_1 \rightarrow P_1T_2 \rightarrow P_2V_2T_2$$

$$P_1V_1T_1 \rightarrow V_2T_1 \rightarrow P_2V_2T_2$$

Multi-step reversible path, example

- $P_1V_1T_1 \rightarrow P_2V_2T_2$

$$P_1V_1T_1 \xrightarrow{\text{(constant } P)} P_1V_2T \xrightarrow{\text{(constant } V)} P_2V_2T_2$$

$$\Delta E = \Delta E_1 + \Delta E_2 = q_1 + w_1 + q_2 + w_2$$

$$w_1 = -\int P_{op} dV = -\int P_{sys} dV = -P_1 \int dV$$

$$= -P_1 \Delta V$$

$$q_1 = -\int C_p dT = -C_p \Delta T_A$$

$$w_2 = -\int P_{op} dV = 0$$

$$q_2 = -\int C_v dT = -C_v \Delta T_B$$

$$\Delta E = -P_1 \Delta V - C_p \Delta T_A - C_v \Delta T_B$$

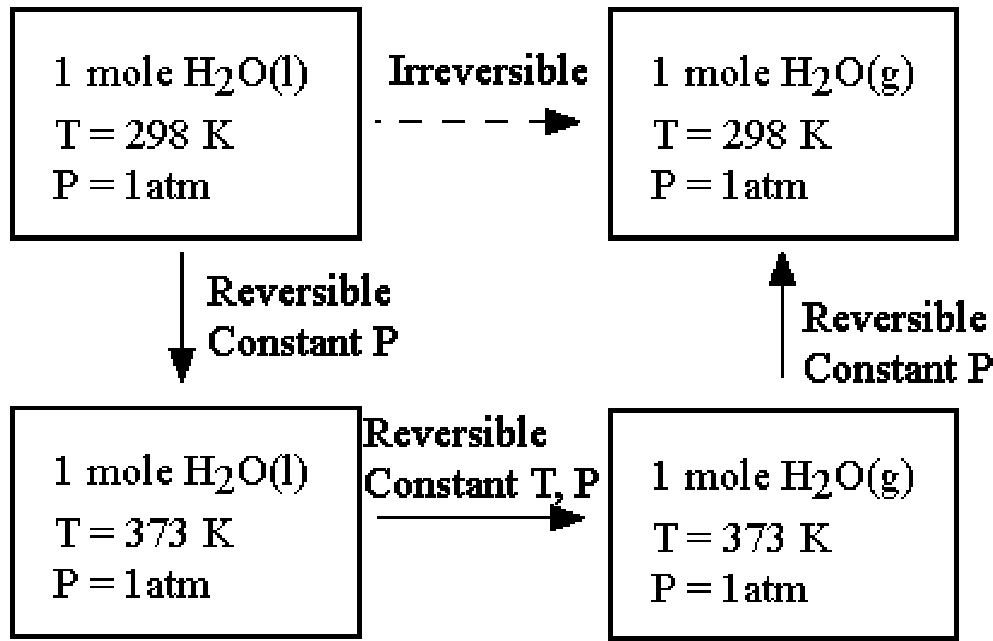


Multi-step paths, another example

- The change from gas to liquid H_2O at 100°C and 1atm is **reversible**
- What is the energy for this phase change at 25°C and 1atm (**not reversible**)?



- We use **several reversible steps** to calculate ΔE



Always explicitly
define your
intermediate states

Make an alternate
reversible path using
constant T steps

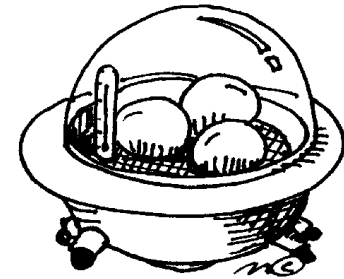
Common thermodynamic steps

- Some very useful restricted step have special names

- **Isobaric:** constant pressure, $\Delta P=0$



- **Isothermal:** constant temperature, $\Delta T=0$



- **Adiabatic:** no heat transfer, $q=0$



- **Isochoric:** constant volume, $\Delta V=0$



- **Cyclic:** final state is the same as initial state!



Key idea!



- The change in **ANY** variable of state of the system during a process depends **ONLY** on the initial and final states of the system, not on the paths taken.
- Changes in non-state variables such as q or w **DO** depend on the path
- For a cyclic path, there is **NO** change in any variable of state (this one is more useful than you might think)

T & P changes: liquids or solids



- Use a series of steps with something held constant
- n moles H_2O @ $P_1V_1T_1 \rightarrow P_2V_2T_2$ (all 3 change!)

1. Constant P $q_P = \int_{T_1}^{T_2} C_P dT = C_P(T_2 - T_1)$
 $w_P = -P_1(V_2 - V_1) \approx 0$ for liquid/solid

$$q = \int C dT$$
$$w = -\int P_{opp} dV$$

2. Constant V $q_V = \int_{T_1}^{T_2} C_V dT = C_V(T_2 - T_1)$
 $w_V = 0$

3. Constant T $q_T = 0$
 $w_T = 0$ (Since $dT=0$ and $dV \approx 0$)

4. $\Delta E = q + w$, $\Delta H = H_2 - H_1 = E_2 - E_1 + (P_2V_2 - P_1V_1)$

T & P changes: ideal gas



- Use a series of steps with something held constant
- n moles $\text{H}_2\text{O}(\text{g})$ @ $P_1V_1T_1 \rightarrow P_2V_2T_2$ (all 3 change!)

1. heat

- Constant P : $q_p = C_p(T_2 - T_1)$
 - Constant V : $q_v = C_v(T_2 - T_1)$
- recall $C = n\bar{C}$

$$q = \int C dT$$
$$w = -\int P_{\text{opp}} dV$$

2. Work ($\Delta V \neq 0$ for gas!)

- Constant P , expansion : $w_p = -P_{\text{ex}}(V_2 - V_1)$
- Constant P , **reversible** (expansion or compression):

$$w_p = -\int P_{\text{sys}} dV \quad (P_{\text{sys}} = P_{\text{ext}})$$

$$w_p = -P_{\text{gas}} \int dV = -P(V_2 - V_1) = -nR\Delta T$$

Ideal gas: work at variable pressure

- Pressure varies: keep either T or V constant
- Use reversible process
- Constant V (isochoric): $w=0$
- Constant T (isothermal):

$$w_T = -\int P_{\text{sys}} dV = -\int \frac{nRT}{V} dV$$

$$w = -nRT \int \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

$$w = -nRT \ln \frac{P_1}{P_2}$$

Note initial/final switch places
in change from V to P

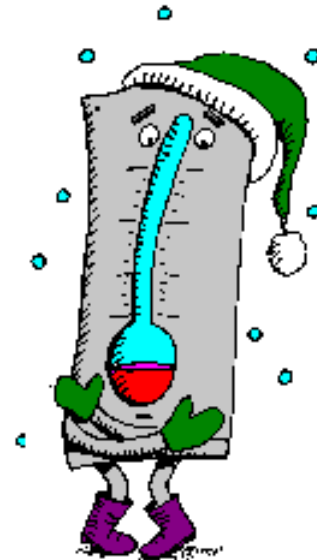
$$P_1 V_1 = P_2 V_2 \text{ or } V_2/V_1 = P_1/P_2$$

Key idea!



- The change in energy for an ideal gas depends only on temperature

$$\Delta E_{ideal\ gas} = f(T)$$



Ideal gas: work at variable pressure

- Pressure varies: keep either T or V constant
- Use reversible process
- Constant V (isochoric): $w=0$
- Constant T (isothermal):

$$w_T = -\int P_{\text{sys}} dV = -\int \frac{nRT}{V} dV$$

$$w = -nRT \int \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

$$w = -nRT \ln \frac{P_1}{P_2}$$

Note initial/final switch places
in change from V to P

$$P_1 V_1 = P_2 V_2 \text{ or } V_2/V_1 = P_1/P_2$$

Ideal gas: isothermal P change

$$w_T = -nRT \ln \frac{P_1}{P_2}$$

- Cannot calculate heat using heat capacity
- Recall that $\Delta E = 0$ for isothermal process (ideal gas)
- $\Delta E = q + w = 0$: $q = -w$
- remember this shortcut!

$$q_T = nRT \ln \frac{P_1}{P_2}$$

Ideal gas: $P_1V_1T_1 \rightarrow P_2V_2T_2$ example

- Remember we are free to choose any path
- One possibility: $(T_1, P_1) \rightarrow (T_1, P_2) \rightarrow (T_2, P_2)$ ($V = nRT/P$)

$$\Delta E = \Delta E_1 + \Delta E_2 = \left[q_T + w_T \right] + \left[q_p + w_p \right]$$

=0!

$$\Delta E = nRT_1 \ln \frac{P_1}{P_2} - nRT_1 \ln \frac{P_1}{P_2} + C_p(T_2 - T_1) - nR(T_2 - T_1)$$

$$\Delta E = (C_p - nR)(T_2 - T_1) = (C_p - nR)\Delta T$$

$$\Delta H = \Delta E + \Delta(PV) = (C_p - nR)\Delta T + \Delta(nRT) = (C_p - nR)\Delta T + nR\Delta T$$

$$\Delta H = C_p \Delta T$$

Ideal gas: $P_1V_1T_1 \rightarrow P_2V_2T_2$ example

- 2nd possibility: $(T_1, V_1) \rightarrow (T_1, V_2) \rightarrow (T_2, V_2)$ ($P = nRT/V$)
- ΔE , ΔH **must** be the same as 1st path (q , w may not be)

$$\Delta E = \Delta E_1 + \Delta E_2 = \left[q_T + w_T \right] + \left[q_V + w_V \right]$$

$\quad \quad \quad =0! \quad \quad \quad \quad \quad \quad =0!$

$$\Delta E = nRT_1 \ln \frac{P_1}{P_2} - nRT_1 \ln \frac{P_1}{P_2} + C_V (T_2 - T_1) + 0$$

$$\Delta E = (\mathbf{C_V})\Delta\mathbf{T}$$

$$\Delta H = \Delta E + \Delta(PV) = C_V \Delta T + \Delta(nRT) = C_V \Delta T + nR \Delta T$$

$$\Delta\mathbf{H} = (\mathbf{C_V} + nR)\Delta\mathbf{T}$$

Ideal gas: $P_1V_1T_1 \rightarrow P_2V_2T_2$ summary

- Our results show ΔE , ΔH depend only on T (not P, V)
- ΔE , ΔH **must** be the same as 1st path (q , w may not be)
- Path 1: $\Delta E = (C_p - nR)\Delta T$ $\Delta H = C_p\Delta T$
- Path 2: $\Delta E = C_v\Delta T$ $\Delta H = (C_v + nR)\Delta T$
- So, $C_p = C_v + nR$ for ideal gas
- C_p is larger, some heat goes to work instead of ΔT
- $\Delta E = C_v\Delta T$ always, not just at constant V
- $\Delta H = C_p\Delta T$ always, not just at constant P

Ideal
gas only!

Useful special cases

- For a closed system at constant volume, the heat absorbed is equal to the energy change ($w=0$ if $dV=0$)

$$\Delta E = q_v = C_v \Delta T$$

note that this is ALWAYS true for an ideal gas

- For a closed system at constant pressure, the heat absorbed is equal to the enthalpy change
($w_p = -P\Delta V$: $\Delta H = \Delta E + \Delta(PV) = q - P\Delta V + P\Delta V = q$)

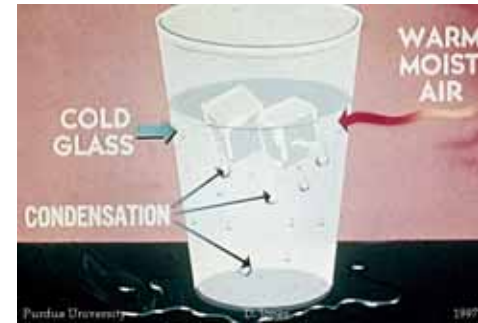
$$\Delta H = q_p = C_p \Delta T$$

note that this is ALWAYS true for an ideal gas

- These allow us to use heat to find ΔH and ΔE

Phase changes: names

- Gas \rightarrow liquid condensation
- Solid \rightarrow liquid fusion/melting
- Liquid \rightarrow solid freezing
- Liquid \rightarrow gas vaporization
- Solid \rightarrow gas sublimation



- Other phase changes possible:

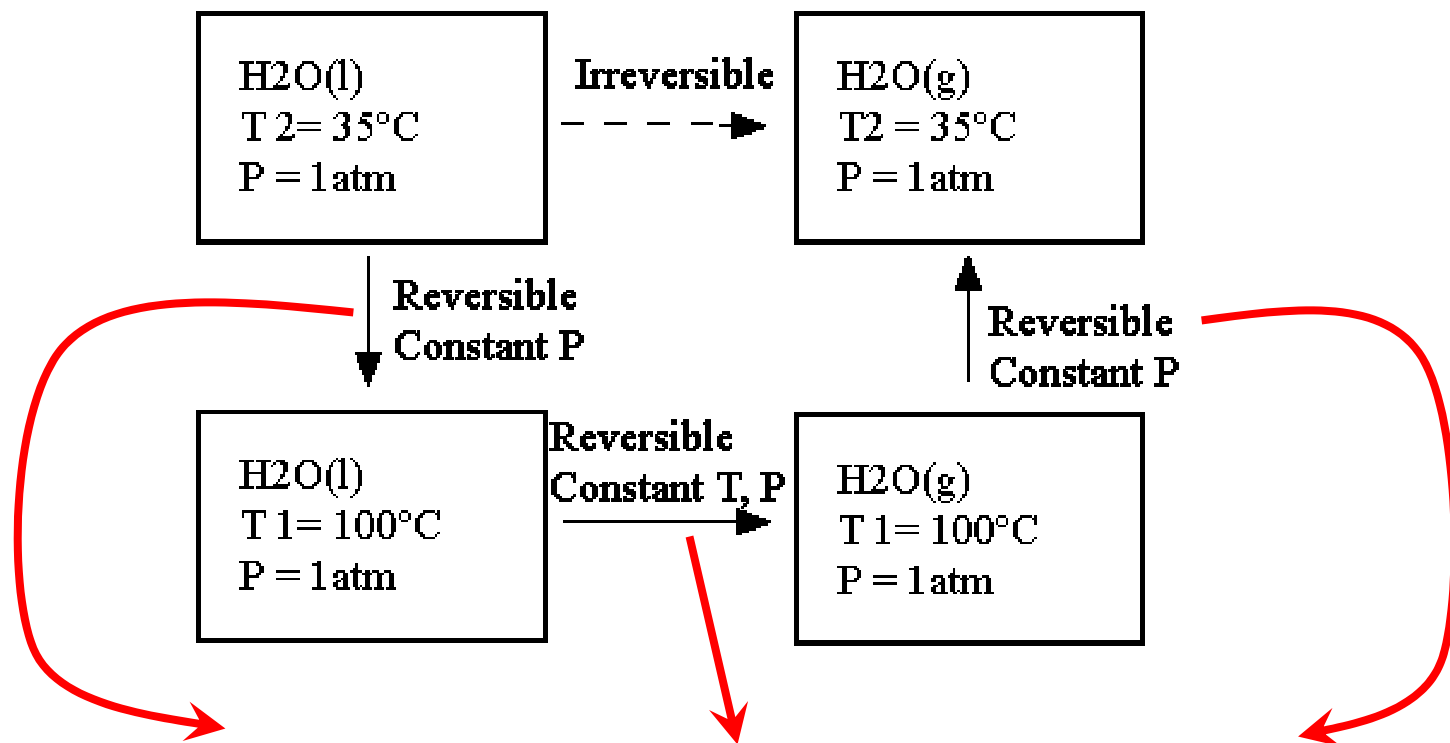
protein folding, lipid rearrangements, amyloid formation ...

Phase changes

沸水

- Consider a **reversible** phase change at constant T,P
- What is the work done on the system during the change?
$$w = -\int P_{op} dV = -\int P dV = -P \int dV = -P\Delta V$$
- If gas phases are not involved, ΔV is very small
- What is the heat for the phase change?
- At constant P, the **heat** $q_p = \Delta H$ (q is easy to measure here)
- The energy change for the phase change at constant P is
- $\Delta E = q + w = \Delta H - P\Delta V$ $\Delta E \approx \Delta H$ *if no gas: ΔV small!*
- Note that we previously calculated ΔE first, **here ΔH first**

What if the process is not near equilibrium?



$$\Delta H_{T_2} = C_p(liq)(T_1 - T_2) + \Delta H_{T_1} + C_p(gas)(T_2 - T_1)$$

$$\Delta H_{T_2} = \Delta H_{T_1} + (C_p(gas) - C_p(liq))(T_2 - T_1)$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p(T_2 - T_1)$$

Watch signs!
Lots of things change

Calculating ΔE for the phase change



- The energy of the isobaric phase change is always

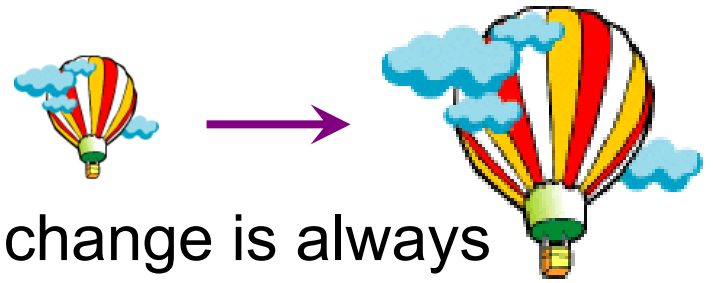
$$\Delta E = \Delta H - P\Delta V$$

- If all phases are condensed (liquid/solid), $\Delta V \approx 0$ & $\Delta E \approx \Delta H$
- If one phase is a gas, volume change is large!
- In this case we ignore the volume of the condensed phase in ΔV

$$\Delta E = \Delta H - P\Delta V_{\text{gas}} = \Delta H - \Delta n_{\text{gas}}RT$$

- Δn is the change in number of moles of gas (may be + or -)
- H_2O : $\Delta E_{\text{fusion}} = 333 \text{ kJ/kg}$ but $\Delta E_{\text{vap}} = 2367 \text{ kJ/kg}$

Volume changes

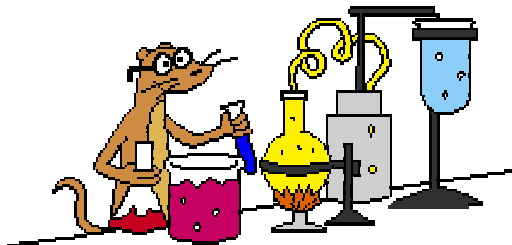


- The energy of the isobaric phase change is always

$$\Delta E = \Delta H - P\Delta V$$

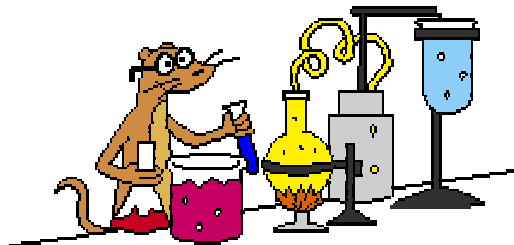
- ΔH values are found in tables (from q)
- Gas \rightarrow liquid $\quad \Delta V = V_{\text{liquid}} - V_{\text{gas}} \quad \approx -V_{\text{gas}}$
- Liquid \rightarrow gas $\quad \Delta V = V_{\text{gas}} - V_{\text{liquid}} \quad \approx V_{\text{gas}}$
- Solid \rightarrow liquid $\quad \Delta V = V_{\text{liquid}} - V_{\text{solid}} \quad \approx 0$
- Solid \rightarrow gas $\quad \Delta V = V_{\text{gas}} - V_{\text{solid}} \quad \approx V_{\text{gas}}$

Chemical reactions



- The change in the system is represented by the general reaction $n_A A + n_B B \rightarrow n_C C + n_D D$
- Heat transfer in chemical reactions
- If the reaction takes places at **constant P**, the heat transfer is equal to the change in **enthalpy** (just like before)
- Exothermic: negative ΔH , heat is released
- Endothermic: positive ΔH , heat is absorbed
- If the reaction takes places at **constant V**, the heat transfer is equal to the change in **energy** (just like before)

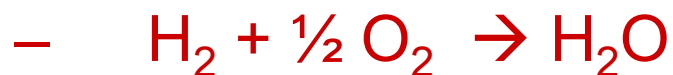
Chemical reactions



- Values for energy and enthalpy depend on the stoichiometric coefficients! (**even with per-mole units**)



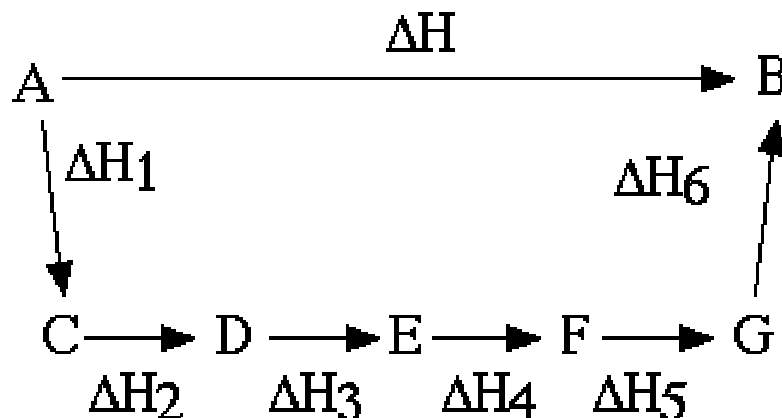
vs



- Energy per mole refers to a mole of **reaction**!

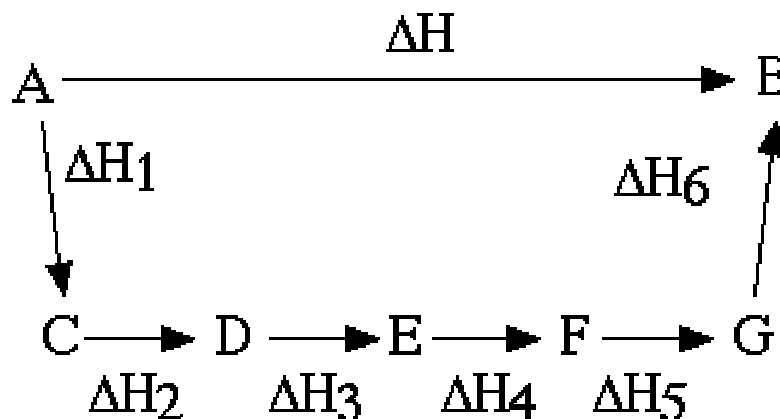
Chemical reactions and enthalpy

- Consider a reaction $A \rightarrow B$ containing a sum of many reactions ($E + S \rightarrow ES \rightarrow EP \rightarrow E + P$)
- Also consider a simple reaction that we can imagine taking place in many steps
- The overall ΔH is just the sum along the path
- As before, the **steps along the way do not affect the value** of ΔH (or ΔE , etc) between initial (reactants) and final (products) states



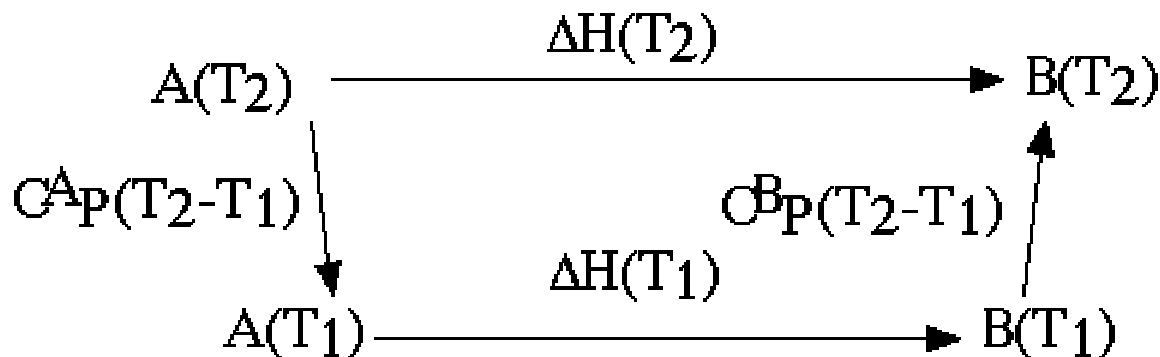
Chemical reactions and enthalpy

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Temperature dependence

- As with phase changes, ΔH values are often given for “standard” conditions and “typical” temperature
- Corrections for different conditions are done very similarly to the procedure shown for phase changes



- where $\Delta H = H(\text{products}) - H(\text{reactants})$
and $\Delta C_p = C_p(\text{products}) - C_p(\text{reactants})$ {or $C_p(B) - C_p(A)$ }

Energy changes of a reaction

- The **energy change** of a reaction at constant P is calculated AFTER the enthalpy (like for phase changes)

$$\Delta E = \Delta H - P(\Delta V)$$

- We still need the tables for ΔH
- If gases are involved, we can **ignore the volumes of solids and liquids**, and if the gas phase is close to an ideal gas

$$\Delta E = \Delta H - \Delta nRT$$

- Note that the number of moles of gas can change, so we use Δn ! **This differs somewhat from phase changes.**

So what is ΔH for a reaction?

- Values for ΔE , ΔH , etc. depend on the chemical substances
- For heating, we use heat capacity for the substance(s)
- For work, we use ideal gas volume changes (or zero for solid/liq)
- For phase changes, we need to get ΔH from a table
 - Phase changes are tabulated for many substances
 - Not tabulated for each temperature/pressure/etc
- For chemical reactions, we also need tables
 - It is not possible to tabulate all known reactions
 - New reactions would still not have entries in the tables
- We need a method that gives accurate ΔH for all reactions
- Create a thermodynamic cycle

So what is ΔH for a reaction?

- Consider the reaction $n_A A + n_B B \rightarrow n_C C + n_D D$
- $\Delta H = H(\text{products}) - H(\text{reactants})$

$$\Delta H = n_C \bar{H}_C + n_D \bar{H}_D - n_A \bar{H}_A - n_B \bar{H}_B$$

- This seems OK, but **what is the enthalpy of substance A?**
- Imagine a new path for this reaction



- Standard molar enthalpy of a compound**
 - **defined** to be equal to the enthalpy of formation of 1 mol of the compound at 1 atm pressure from elements at their **standard states** (T must be specified)
 - Enthalpies of formation for pure elements in their most stable form at 1 atm pressure are zero by definition

So what is ΔH for a reaction?

- Consider the reaction $n_A A + n_B B \rightarrow n_C C + n_D D$
- $\Delta H = H(\text{products}) - H(\text{reactants})$

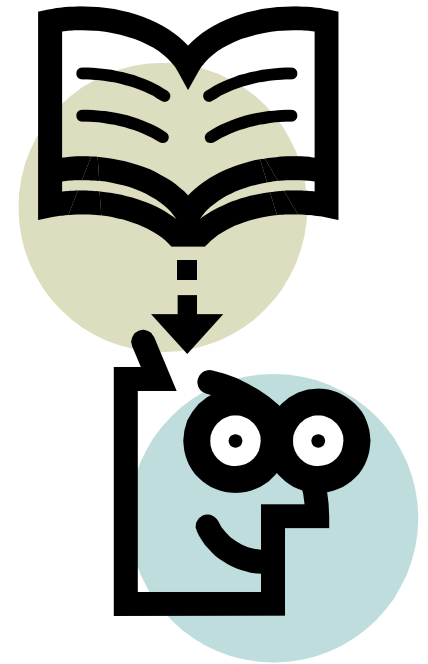
$$\Delta H(T) = n_C \Delta \overline{H}_{f,C}^0 + n_D \Delta \overline{H}_{f,D}^0 - n_A \Delta \overline{H}_{f,A}^0 - n_B \Delta \overline{H}_{f,B}^0$$

- Remember to use zero for any elements in most stable form (at 298K, $O_2(g)$, not $O_2(liq)$)
- The superscript zero denotes that the value corresponds to the standard state (more later: for now it is 1atm pressure)
- We can calculate the ΔH for other T as we did previously, using ΔC_p for all products and reactants **multiplied by their stoichiometric coefficients**

Molecular interpretation of energy and enthalpy

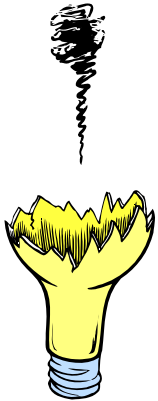
- For ideal gases, the increase in the internal energy (as a function of T) represents the gas molecules with higher translational, rotational and vibrational energies
- More complex molecules have more ways to store energy before T rises and hence higher heat capacities
- For real gases, liquids and solids, molecular interactions can also store energy, resulting in higher heat capacities
- Relative energy changes:
temperature < phase change < reaction

The Second Law:
The entropy of the
universe (always)
increases



Entropy : concepts

- Entropy (S) is a measure of disorder. The greater the disorder, the larger the entropy
- Entropy can also be related to information content and probabilities
- Disorder occurs spontaneously (“time’s arrow”)
- If the system is kept at constant energy and volume (isolated), every change increases the disorder of the system
- If S_{sys} does go down, the entropy of the universe always increases
- Any attempt to reduce disorder **must** be accompanied by an increase in disorder somewhere else!



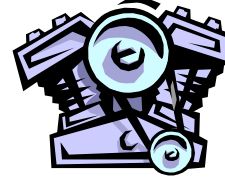
Gibbs free energy: concepts

- Gibbs free energy (G): a new state variable
- G is a useful combination of enthalpy and entropy (why?)

$$G = H - TS \quad \Delta G = \Delta H - \Delta(TS)$$

- At constant T and P, G_{system} **always decreases** for a spontaneous process
- Note constant T, P are required. There was no such restriction for entropy-based spontaneity
- G can tell us whether a process is possible (before we even try)
- G does not tell us how fast the process will occur

Carnot cycle



- Carnot's cycle led to the historical development of entropy as a state variable
- He showed that $\frac{q_{rev}}{T}$ is path-independent ($=\Delta S$)
- Working through this process can provide a useful review of energy, heat and work calculations
- He showed that it is not possible to convert heat to work with perfect efficiency
- Conversely, it takes work to move heat from a cold area to a warmer one (air conditioner)
- We will not focus on the derivation, but rather the applications
- How is a heat engine related to disorder??

Entropy: the 2nd law

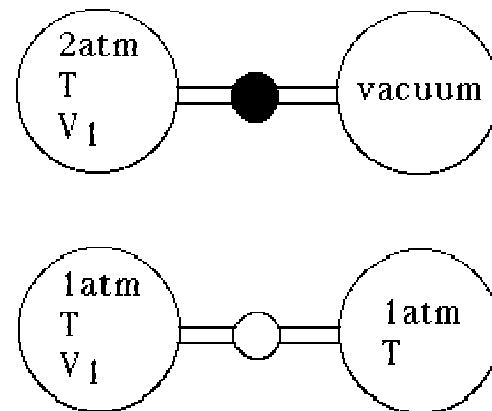


- Entropy is an extensive state variable
- The units are energy/temperature ($\Delta S = q_{\text{rev}}/T$)
- The sum of the entropy changes of the system and surroundings are always positive
- In special cases, the entropy change may be zero
- Entropy is NOT conserved
- The second law of thermodynamics:
 - Heat spontaneously flows from a hot body to a cooler body, but work must be done to transfer heat from the cooler to the hot body
 - $\Delta S(\text{system}) + \Delta S(\text{surroundings}) \geq 0$
 - $\Delta S(\text{isolated system}) \geq 0$

Equality is for
reversible changes

Entropy: an example

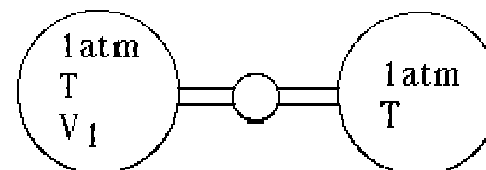
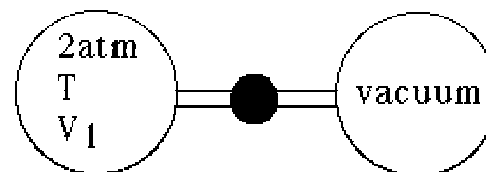
- Consider an ideal gas expansion with two possible paths
- Isolated system, $V_f = 2 \cdot V_i$
- $\Delta T = 0$ (remember why?)
- ΔS_{sys} must be same for all paths



- Irreversible expansion:
- $\Delta S_{\text{univ}} > 0$
- Reversible expansion:
- $\Delta S_{\text{univ}} = 0$

Entropy: an example

- Irreversible expansion:
- $\Delta E=0$, $w=0$ so $q_{\text{irrev}}=0$.
- we need q_{rev} to calculate ΔS !
- $\Delta S_{\text{surr}}=0$



- ΔS is independent of path, so consider an isothermal reversible path

$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln 2$$

$$q_{\text{rev}} = nRT \ln 2$$

- Thus for the irreversible process

$$\Delta S_{\text{sys}} = \Delta S_{\text{univ}} = \frac{q_{\text{rev}}}{T} = nR \ln 2 > 0$$

Entropy: an example

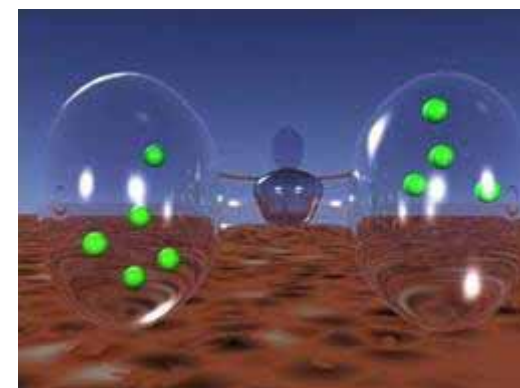
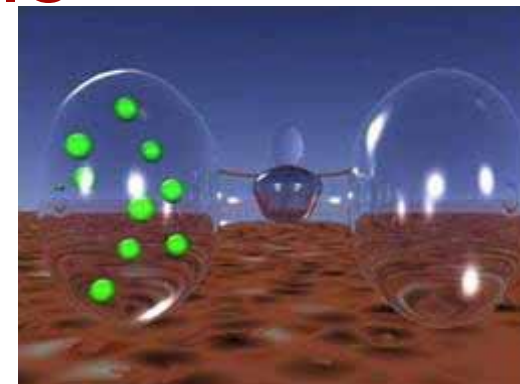
- Irreversible expansion:
- $\Delta E=0$ (why?), $w=0$ so $q_{\text{irrev}}=0$.
- we need q_{rev} to calculate ΔS !
- $\Delta S_{\text{surr}}=0$
- ΔS is independent of path, so consider an isothermal reversible path

$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln 2$$

$$q_{\text{rev}} = -w = nRT \ln 2$$

- Thus for the irreversible process

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} + 0 = nR \ln 2 > 0$$



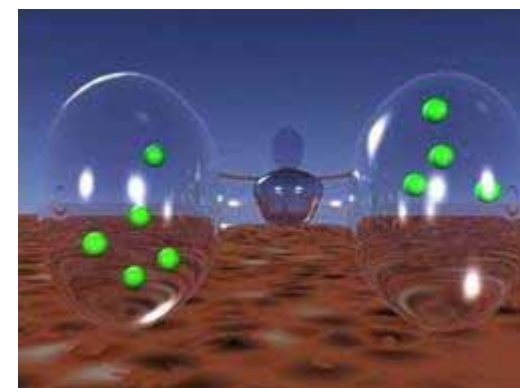
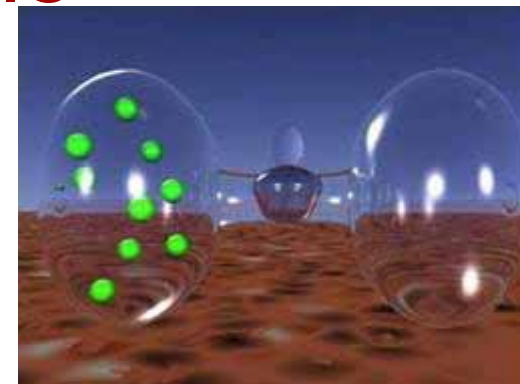
Entropy: an example

- **Reversible** expansion:
- Since it is reversible, $q = q_{\text{rev}}$
- What is q here? $q_{\text{rev}} = nRT \ln 2$
- Since the process actually IS reversible,

$$q_{\text{surr}} = -nRT \ln 2$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = nR \ln 2 - nR \ln 2 = 0$$

- ΔS_{sys} is the same for both paths, but ΔS_{univ} is not (??)
- Note that $\Delta S_{\text{univ}} = 0$ only for this special case.



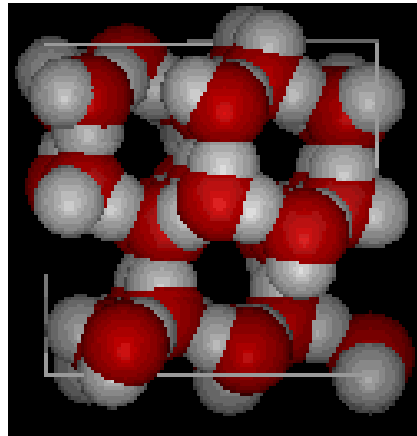
Entropy happens

- Entropy is a measure of disorder
- More disorder \equiv more entropy
- The total entropy of the universe increases with every spontaneous process
- A part of the universe may show a decrease in entropy and become more ordered
 - Biological organisms are complex
 - We can construct complex materials from simpler ones
 - Water can freeze, gases condense, etc.
- The entropy of the rest of the universe will increase even more than the partial universe decreased

Example: entropy of water

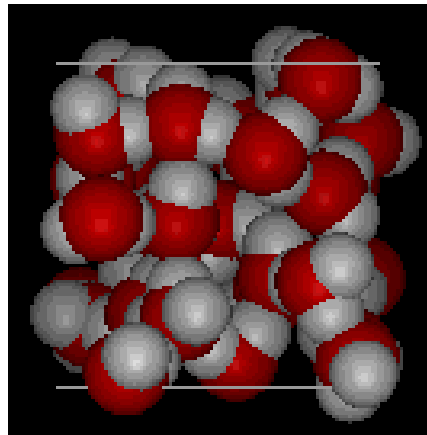
\overline{S} = molar entropy

- $\text{H}_2\text{O (s)}$: 41.0 J/K



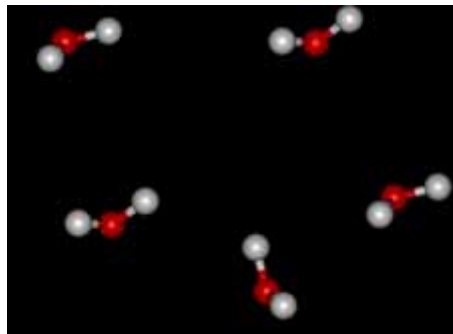
highly ordered

- $\text{H}_2\text{O (liq)}$: 63.2 J/K



partly ordered

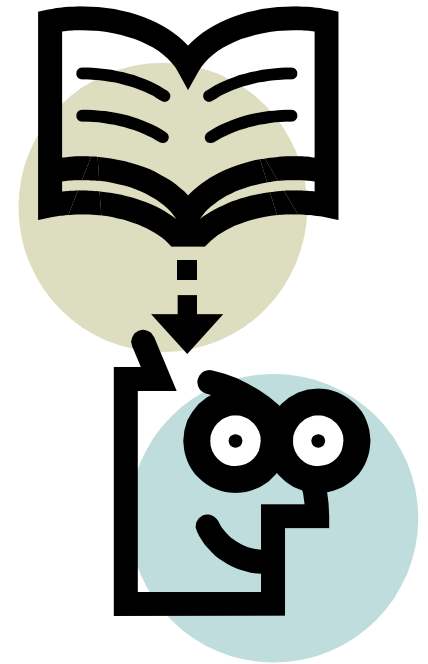
- $\text{H}_2\text{O (g)}$: 188.3 J/K



very disordered

The Third Law:

A pure, perfect crystal at
0 Kelvin has no entropy



What do entropy values *mean*?

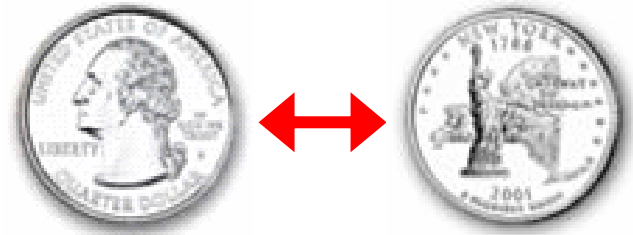


$$S = k_b \ln N \quad \text{Key equation!}$$

- k_b is Boltzmann's constant: $1.381 \times 10^{-23} \text{ J/K}$
- N is the number of states of the system
- Inversely, $N = e^{S/k_b}$
- We can use this to estimate N from measurement of S (or ΔN from ΔS)
- This provides a ZERO for entropy:
- For a pure, perfect crystal at 0K, there is one state and entropy $S = k \ln 1 = 0$



Example: coin flips



- The probability of getting a head or tail is 0.5 (50%)
- What happens if we flip a coin twice?
- HH, HT, TH, TT each have 0.25 probability
- **The number of possible states depends on how we define our system!**
- Two heads : 1 state
- Matching flips: 2 states
- A head and a tail (any order): 2 states
- A head THEN a tail: 1 state

Example: deck of playing cards

- There are 52 unique cards in a deck
- There is only 1 state with all cards in a specific order : $S=0$
- If we randomly shuffle the cards, there are $52!$ possible arrangements. $52! = 8 \times 10^{67}$
- $52 \times 51 \times 50 \times 49 \times 48 = 12 \text{ million}$ sequences of 5 cards
- Is $A_{\clubsuit} K_{\clubsuit} Q_{\clubsuit} J_{\clubsuit} 10_{\clubsuit}$ better than $J_{\clubsuit} 2_{\diamondsuit} 7_{\spadesuit} 9_{\heartsuit} 4_{\spadesuit}$?? Why??
- What is the entropy gain from shuffling the cards?
 - Note that the shuffled cards will still have 1 state, but it is not defined
- $\Delta S = S_{\text{shuffled}} - S_{\text{ordered}} = k \ln(52!) - k \ln(1) = 2.1 \times 10^{-21} \text{ J/K} > 0$



Other important examples of entropy

- Protein folding
 - chain entropy
 - hydrophobic effect
- mixing** of gases (or of any components)
- solvation** or desolvation of ions
- ligand **binding**, dimer formation, etc.

Reaction	ΔS^0 (J K ⁻¹ mol ⁻¹)	
$\text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq})$	+148.1	why??
$\text{NH}_4^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{HCO}_3^-(\text{aq})$	+146.0	less charge
$\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$	+80.7	
$\text{NH}_4^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{NH}_3(\text{aq})$	+94.2	less charge, more molec.
$\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq})$	+2.1	
$\text{HC}_2\text{O}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{C}_2\text{O}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	-23.1	charge more dense
$\text{CH}_4(\text{aq}) \rightarrow \text{CH}_4(\text{CCl}_4)$	+75	hydrophobic effect

Entropy of mixing

- Consider mixing of 2 ideal gases (mixing of other substances is *conceptually* similar: lipids, etc)

$$\Delta S(\text{mixing}) = -R[n_1 \ln X_1 + n_2 \ln X_2]$$

Where n_i are the number of moles and X_i are the mole fractions

$$X_1 = \frac{n_1}{n_1 + n_2}, X_2 = \frac{n_2}{n_1 + n_2}$$

- Since X_1 and X_2 are **always** less than 1, ΔS of mixing is always positive (why?), so the mixed state is less ordered.
- Shake a box of marbles with 2 colors
 - what happens?
 - what if you don't shake it?
- The mixture of gases in the air would not be expected to separate spontaneously!!

Entropy

- The **general** form that we will use to calculate entropy is

$$\Delta S = S_{final} - S_{initial} = \int_{initial}^{final} dS = \int_{initial}^{final} \frac{dq_{rev}}{T} \quad (\text{T may change, but what is } dq?)$$

- You **MUST** use a reversible path to calculate entropy with heat: q_{rev}
- Can the second law be violated?
 - Consider a box with 2 molecules
 - What happens if they both move to the same side? (0.5 probability)
- The second law is based on probabilities.
- For macroscopic systems, the probability of violation is **very** small (10^{-300} for 1000 molecules on same side)
- For microscopic systems, fluctuations do occur.

Entropy of chemical reactions

- For the general reaction $n_A A + n_B B \rightarrow n_C C + n_D D$

$$\Delta S = n_c \overline{S}_c + n_d \overline{S}_d - n_a \overline{S}_a - n_b \overline{S}_b$$

- Tables of standard molar entropies are available
- Watch T, P just like with molar enthalpies
- Important: standard entropies for elements in their most stable form are **NOT** zero. What is zero?
- Third law of thermodynamics:**
 - The entropy of a pure, perfect crystal at 0K is zero
 - Only one state: $S = k_b \ln(1) = 0$
 - Not all crystals are perfect!
 - defects
 - carbon monoxide

Temperature dependence of entropy

- Entropy values in tables are for a specific temperature
- Heating a substance should increase the entropy

$$S_2 - S_1 = \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C dT}{T}$$

- Note that we can NOT use $\Delta S = q_{\text{rev}}/T$ if T changes!
- If P is constant:

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

- If C_p is independent of T (watch out for phase changes)

$$S_2 - S_1 = C_p \ln \frac{T_2}{T_1}$$

- Do NOT use $\Delta S = C_p \Delta T / T$ (why not??)

Temperature dependence of entropy

$$S_2 - S_1 = \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C dT}{T}$$

- If P is constant:

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_P dT}{T}$$

- If C_P is independent of T (watch out for phase changes)

$$S_2 - S_1 = C_P \ln \frac{T_2}{T_1}$$

- If V is constant: $S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_V dT}{T}$

- If C_V is independent of T $S_2 - S_1 = C_V \ln \frac{T_2}{T_1}$

- Note that heating *always* increases S ($T_2 > T_1$, $\ln(T_2/T_1) > 0$)

Example: T dependence of entropy

- Calculate the entropy change at constant P when 1 mole of liquid water at 100°C is brought in contact with 1 mole of liquid water at 0°C. Assume $C_p(\text{H}_2\text{O}, \text{liq}) = 75 \text{ J/molK}$.
- What happens? What is the final temperature?
 - $(100\text{K} + 0\text{K})/2 = 50^\circ\text{C}$ (only since C_p is a constant here)

- The entropy change of the hot water is

$$S(50^\circ\text{C}) - S(100^\circ\text{C}) = \bar{C}_p \ln \frac{323}{373} = -10.7 \text{ J/K}^{-1} \quad <0 \text{ but 2nd law ok}$$

- The entropy change of the cold water is (using $q_{\text{cold}} = -q_{\text{hot}}$)

$$S(50^\circ\text{C}) - S(0^\circ\text{C}) = \bar{C}_p \ln \frac{323}{273} = 12.61 \text{ J/K}^{-1}$$

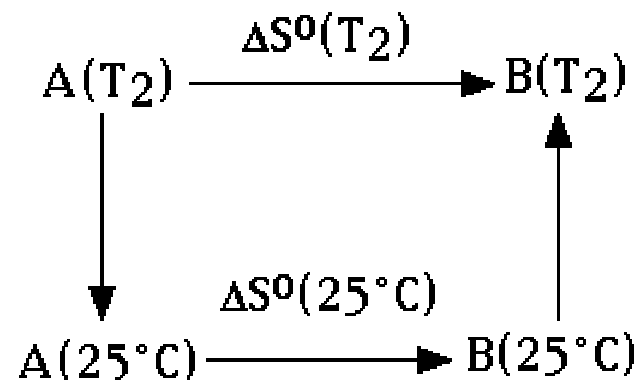
- Note that the entropy change is *larger* at lower T**

- $\Delta S_{\text{univ}} = 1.82 \text{ J/K} > 0$ so process is spontaneous

Note: for 1 mole each hot and cold water

Entropy of a chemical reaction at different T

- Consider a reaction $A \rightarrow B$ at constant P with a temperature T_2 not in the table (25°C in this case)



- Construct a new path using 25°C data
- Correction term involves entropy for changing temperatures of reactants and products

$$\Delta S^\circ(T_2) = \Delta S^\circ(25^\circ\text{C}) + \int_{T_2}^{298} C_P(A) \frac{dT}{T} + \int_{298}^{T_2} C_P(B) \frac{dT}{T} \quad \text{Watch initial/final T}$$

- General form of temperature correction

$$\Delta S^\circ(T_2) = \Delta S^\circ(T_1) + \int_{T_2}^{T_1} \Delta C_P \frac{dT}{T} \quad \Delta C_p = C_p(B) - C_p(A)$$

- Note that only the **difference** in heat capacity is important

Example: entropy of a chemical reaction

- Consider the reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
 - reaction is exothermic ($q < 0$), reaction is spontaneous ($\Delta S > 0$?)

- The entropy change at 25°C is

$$\Delta S(25^\circ\text{C}) = 2\bar{S}_{\text{H}_2\text{O}(\text{g})}^\circ - 2\bar{S}_{\text{H}_2(\text{g})}^\circ - \bar{S}_{\text{O}_2(\text{g})}^\circ$$

Note the use of stoichiometry

$$= 2(188.72) - 205.04 - 2(130.57) = -88.74 \text{ JK}^{-1}$$

- The heat capacity change is

$$\Delta C_P^\circ = 2\bar{C}_{\text{PH}_2\text{O}(\text{g})}^\circ - 2\bar{C}_{\text{PH}_2(\text{g})}^\circ - \bar{C}_{\text{PO}_2(\text{g})}^\circ$$

Note the use of real C_p values

$$= 2(33.6) - 29.4 - 2(28.8) = -19.8 \text{ JK}^{-1}$$

- Using data in table for S and C

$$|\Delta S_{\text{rxn}}| > |\Delta S_{\text{temperature}}|$$

$$\Delta S^\circ(100^\circ\text{C}) = \Delta S^\circ(25^\circ\text{C}) + \int_{298}^{373} \Delta C_P \frac{dT}{T} = -88.74 + \Delta C_P \ln \frac{373}{298} = -93.18 \text{ JK}^{-1}$$

- $\Delta S < 0$ yet the reaction DOES take place! Why? AMS691

Entropy of a phase change

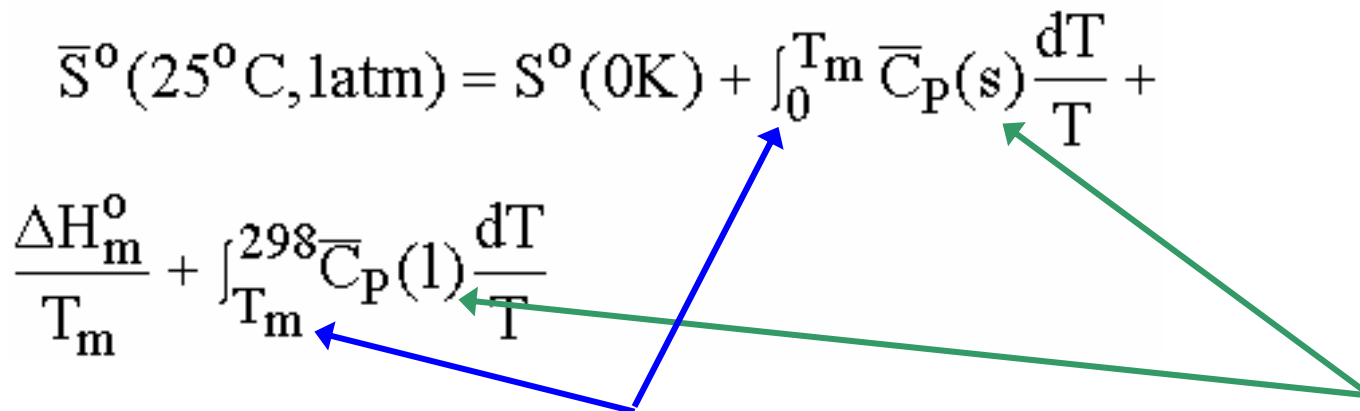
- Consider a reversible phase change
- The entropy is the heat absorbed by the system divided by the equilibrium temperature (q_{rev}/T)
- If P and T are constant during the phase change

$$\Delta S_{\text{tr}} = \frac{q_{\text{rev}}}{T_{\text{tr}}} = \frac{\Delta H_{\text{tr}}}{T_{\text{tr}}}$$

- If the phase change is not reversible, construct a new path
- Heat or cool each phase to get to the equilibrium T
- This is done in the same way as T corrections for reactions

Absolute (3rd law) entropies

- The 3rd law stated that the entropy of a **pure, perfect crystal** at 0K is zero
- The absolute entropy is the **sum all of the entropy** involved in getting from this state to the state of interest
- Residual entropy at 0K + heat until phase change + phase change entropy + heat until next phase change + etc...
- For a liquid compound at 25°C and 1atm

$$\bar{S}^{\circ}(25^{\circ}\text{C}, 1\text{atm}) = S^{\circ}(0\text{K}) + \int_0^{T_m} \bar{C}_P(\text{s}) \frac{dT}{T} +$$
$$\frac{\Delta H_m^{\circ}}{T_m} + \int_{T_m}^{298} \bar{C}_P(\text{l}) \frac{dT}{T}$$


- Note how the temperatures of the integrals and the C_p s change

Gibbs Free Energy

- Gibbs free energy is **defined** as $G = H - TS$ $\Delta G = \Delta H - \Delta(TS)$
memorize!
- G is an extensive variable of state
- The molar Gibbs free energy is intensive and has a special name: chemical potential or μ
- For an equilibrium system, $\Delta\mu=0$
- Recall that the 2nd law told us that any process would be spontaneous if (and only if) $\Delta S_{\text{univ}} > 0$
- **At constant T and P, we only need to consider ΔG_{system}**
- $\Delta G_{\text{system}} < 0$: process **will** occur spontaneously (when??)
- $\Delta G_{\text{system}} > 0$: process **will not** occur spontaneously (reverse will)
- $\Delta G_{\text{system}} = 0$: process is at equilibrium (no change)

Calculation of Gibbs free energy changes

- If the temperature is constant : $\Delta G = \Delta H - T\Delta S$
- Note that we care about ΔG for constant T process, but we may need to know the effect of T on G (for T corrections)
- If we know ΔH and ΔS , we can calculate ΔG from def'n
- Values are tabulated for \bar{H}^0 , \bar{S}^0 , and also \bar{G}^0
- Recall that these values relate to the *standard state*
- Standard states involve pressure but also concentration!
 - More on this extremely important topic later
- Zero free energy is arbitrary (like energy & enthalpy)
- G for elements in most stable form are zero

Example: Gibbs free energy changes

- Calculate ΔG° for the reaction $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$
will it occur spontaneously?

$$\begin{aligned}\Delta G^\circ(25^\circ\text{C}) &= \bar{G}_{\text{H}_2(\text{g})}^\circ + \frac{1}{2} \bar{G}_{\text{O}_2(\text{g})}^\circ - \bar{G}_{\text{H}_2\text{O}(\text{l})}^\circ \\ &= 0 + 0 - (-237.19) = 237.19 \text{ kJ mol}^{-1}\end{aligned}$$

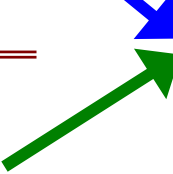
Since $\Delta G > 0$, the reaction will **not** occur spontaneously (but the reverse reaction will)

- Another approach:

$$\begin{aligned}\Delta H^\circ &= \bar{H}_{\text{H}_2(\text{g})}^\circ + \frac{1}{2} \bar{H}_{\text{O}_2(\text{g})}^\circ - \bar{H}_{\text{H}_2\text{O}(\text{l})}^\circ \\ &= 0 + 0 - (-285.83) = 285.83 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \bar{S}_{\text{H}_2(\text{g})}^\circ + \frac{1}{2} \bar{S}_{\text{O}_2(\text{g})}^\circ - \bar{S}_{\text{H}_2\text{O}(\text{l})}^\circ \\ &= 130.5 + \frac{205.04}{2} - 69.95 = 163.14 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$


$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$


$$\Delta G^\circ = 237.19 \text{ kJ / mol}$$

The **same** value of ΔG is obtained with either method

Example: Gibbs free energy changes

- Calculate ΔG° for the hydrolysis of proteins using Gly₂ as a model system, at 25°C and 1atm in dilute aqueous solution



- The table only has data for Gly(s), we assume that the ΔG for dissolution of Gly₂ is same as 2Gly

$$\begin{aligned}\Delta G^\circ(25^\circ\text{C}) &= 2\bar{G}^\circ(\text{glycine}, \text{s}) - \\ &\bar{G}^\circ(\text{glycylglycine}, \text{s}) - \bar{G}^\circ(\text{H}_2\text{O}, \text{l}) \\ &= 2(-377.69) - (-490.57) - (-237.19) \\ &= -27.62 \text{kJmol}^{-1}\end{aligned}$$

- This value is negative, thus **hydrolysis of the protein backbone is spontaneous** under these conditions
- We know that the process is slow (catalyzed by enzymes)

Gibbs free energy and temperature

- The Gibbs free energy can tell us whether a reaction will be spontaneous (or if the reverse is spontaneous)
- We *know* that temperature can influence whether a reaction goes forward or backward (not just the rate, but the direction!)
- Example: proteins can fold at intermediate temperature, but folded proteins can unfold at low or high temperatures
- Why does this change in direction occur? The “ ΔG sign rule” still holds, so ΔG itself must depend on T

$$\Delta G = \Delta H - T\Delta S \quad T \text{ is explicitly included in the } \Delta G \text{ definition}$$

ΔH and ΔS themselves depend on T !

- Which effect is dominant? Do we need to worry about both? *Usually not*

Gibbs free energy and temperature

- Very often, if the T does not change much, the following is a reasonable approximation:

$$\Delta G(T_2) = \Delta H(T_1) - T_2 \Delta S(T_1)$$

Note that we assumed ΔH and ΔS did not change from $T_1 \rightarrow T_2$

- Example: $\Delta G(37^\circ\text{C}) = \Delta H(25^\circ\text{C}) - 37^\circ\text{C} \Delta S(25^\circ\text{C})$
- In other words, the largest component of the temperature change usually comes from multiplying T times ΔS

$$\Delta G(T_2) = \Delta H(T_1) - T_2 \Delta S(T_1)$$

Subtract these equations

$$\underline{\Delta G(T_1) = \Delta H(T_1) - T_1 \Delta S(T_1)}$$

$$\Delta G(T_2) - \Delta G(T_1) = - (T_2 - T_1) \Delta S(T_1)$$

Note ΔH cancels

This can be useful to approximate how ΔG changes with T

Gibbs free energy and temperature

$$\{\Delta G(T_2) = \Delta H(T_1) - T_2 \Delta S(T_1)\} - \{\Delta G(T_1) = \Delta H(T_1) - T_1 \Delta S(T_1)\}$$

$$\Delta G(T_2) - \Delta G(T_1) = -(T_2 - T_1) \Delta S(T_1)$$

- Thus we can use ΔS to predict how ΔG changes
- We can also use ΔH to change ΔG (ΔH can be easier to measure)

$$\Delta G(T_2) \approx \Delta H(T_1) - T_2 \Delta S(T_1)$$

$$\frac{\Delta G(T_2)}{T_2} \approx \frac{\Delta H(T_1)}{T_2} - \Delta S(T_1)$$

Note ΔS cancels

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} \approx \frac{\Delta H(T_1)}{T_2} - \frac{\Delta H(T_1)}{T_1} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \Delta H(T_1)$$

- So, if we know ΔG and either ΔH or ΔS at T_1 , we can estimate ΔG at T_2

Example: peptide bond hydrolysis

- Calculate ΔG° for the hydrolysis of proteins using Gly₂ as a model system, at 37°C and 1atm in dilute aqueous solution



- Is the process more or less spontaneous than at 25°C?
- We'll discuss later what “more spontaneous” really means
- The table only has data for 37°C. What do we do?
- Let's take a quick review of what we did for this calculation at 25°C

Example: Gibbs free energy changes

- Calculate ΔG° for the hydrolysis of proteins using Gly₂ as a model system, at 25°C and 1atm in dilute aqueous solution



- The table only has data for Gly(s), we assume that the ΔG for dissolution of Gly₂ is same as 2Gly

$$\begin{aligned}\Delta G^\circ(25^\circ\text{C}) &= 2\bar{G}^\circ(\text{glycine}, \text{s}) - \\ &\bar{G}^\circ(\text{glycylglycine}, \text{s}) - \bar{G}^\circ(\text{H}_2\text{O}, \text{l}) \\ &= 2(-377.69) - (-490.57) - (-237.19) \\ &= -27.62 \text{kJmol}^{-1}\end{aligned}$$

- This value is negative, thus **hydrolysis of the protein backbone is spontaneous** under these conditions

Peptide hydrolysis at 37°C

- We need our ΔG value at 25°C and *either* ΔS or ΔH

$$\Delta G(25^\circ\text{C}) = -27.62 \text{ kJ/mol}$$

$$\Delta S^\circ(25^\circ\text{C}) = 2\bar{S}^\circ(\text{glycine}) - \bar{S}^\circ(\text{glycylglycine})$$

$$- \bar{S}^\circ(\text{H}_2\text{O}, l) = 2(103.51) - (190.0) - (69.95)$$

$$= -52.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note that entropy favors reactants, but rxn still happens

$$\Delta G^\circ(37^\circ\text{C}) = \Delta G^\circ(25^\circ\text{C}) - 12\Delta S^\circ(25^\circ\text{C}) \quad \text{using the eqn}$$

$$= -27.62 - 12(-0.0529) = -26.98 \text{ kJ mol}^{-1} \quad \Delta G(T_2) = \Delta G(T_1) - (T_2 - T_1)\Delta S(T_1)$$

$$\Delta G(37^\circ\text{C}) = -26.98 \text{ kJ/mol}$$

- The value is *less negative*: less spontaneous at 37°C (but it is still spontaneous!)

Peptide hydrolysis at 37°C using ΔH

$$\Delta G(25^\circ\text{C}) = -27.62 \text{ kJ/mol}$$

$$\Delta H^\circ(25^\circ\text{C}) = 2\bar{H}^\circ(\text{glycine}) - \bar{H}^\circ(\text{glycylglycine})$$

$$- \bar{H}^\circ(\text{H}_2\text{O}, l) = 2(-537.2) - (-745.25) - (-285.83)$$

$$= -43.32 \text{ kJmol}^{-1}$$

Note: exothermic, enthalpy favors products

$$\frac{\Delta G(37^\circ\text{C})}{310} - \frac{\Delta G(25^\circ\text{C})}{298} \cong \left(\frac{1}{310} - \frac{1}{298} \right) \Delta H(25^\circ\text{C})$$

$$\frac{\Delta G(37^\circ\text{C})}{310} = \frac{-27.62}{298} + (-1.299 \times 10^{-4})(-43.32)$$

$$= -0.0871$$

$$\frac{\Delta G(T_2)}{T_2} \approx \frac{\Delta G(T_1)}{T_1} + \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \Delta H(T_1)$$

$$\Delta G(37^\circ\text{C}) = 310(-0.0871) = -26.99 \text{ kJmol}^{-1}$$

Value obtained using ΔS : -26.98 kJ/mol

- Using either ΔH or ΔS to correct ΔG gives the same answer

What *external* conditions affect ΔG ?

- ΔG determines whether a reaction is spontaneous
- We *know* that the environment can affect this
- Environmental effect #1 : how does pressure affect ΔG ?

$$G(P_2) - G(P_1) = \int P dV$$

- Why? $G = H - TS$: $dG = d(E + PV) - d(TS)$
- $dG = dE + d(PV) - d(TS) = dE + PdV + VdP - TdS - SdT$
- For a reversible path with PV work only,
 $dE = dq_{\text{rev}} + dw = TdS - PdV$ (cancels)
 $dG = TdS - PdV + PdV + VdP - TdS - SdT$
so $dG = VdP - SdT$ **at constant T, $dG = VdP$**

Pressure dependence of ΔG

- $dG = VdP$

$$\Delta G = \int VdP \quad \text{if } V \text{ independent of } P \text{ (liquid or solid!)},$$

$$\Delta G = V \int dP = V(P_2 - P_1)$$

$$\Delta G = \int VdP \quad \text{for ideal gas,}$$

$$\Delta G = \int \frac{nRT}{P} dP = nRT \ln \frac{P_2}{P_1}$$

Note difference!



How will pressure change ΔG for a process?

- We have $\Delta G(P_1)$ and need $\Delta G(P_2)$

$$\Delta\Delta G = \Delta G(P_2) - \Delta G(P_1)$$

$$\Delta\Delta G = \Delta V(P_2 - P_1) \quad \text{Reactant and product are solids/liquids only}$$

- Where ΔV is the volume change $V(\text{products}) - V(\text{reactants})$
- *If the volume does not change, pressure has no effect*
- *Increase P : favor lower volumes (and vice versa)*

$$\Delta\Delta G = \Delta n RT \ln \frac{P_2}{P_1} \quad \begin{array}{l} \text{Reactant and product include gases: we} \\ \text{Ignore volumes of solids and liquids} \end{array}$$

- *Reactions that increase n_{gas} are favored by reducing P*
- *Reactions that decrease n_{gas} are favored by increasing P*

Example: P,T dependence of ΔG

- Can diamond be spontaneously converted to graphite at 25°C and 1atm?
- Use the table to find ΔG° from molar G° for each phase
- $\text{C}(\text{graphite, s}) \rightarrow \text{C}(\text{diamond, s}) \quad \Delta G^\circ = 2.84 \text{ kJ/mol}$
- *This is positive, so the reaction is not spontaneous*
- **rEVERSE** reaction is spontaneous! (diamond \rightarrow graphite)
- Reverse reaction is VERY SLOW!
- ΔG° doesn't tell us about how fast reaction happens

Example: P,T dependence of ΔG

- Can diamond be spontaneously converted to graphite at higher pressures or temperatures? If so, what is the minimum value required? \$\$\$\$\$\$

- Pressure: we know $\Delta G(P_2) = \Delta G(P_1) + \Delta V(P_2 - P_1)$

- We need the volume change for the reaction


	Density g/cm ₃	Molar volume cm ³ /mol
C(graphite)	2.25	5.33
C(diamond)	3.51 (50% higher!)	3.42

Guess what
higher P will do!

•

$$\Delta G(P_2) = 2.84 \text{ kJ/mol} + (5.33 - 3.42) \text{ cm}^3/\text{mol} * (P_2 - 1 \text{ atm})$$

- ΔG will be zero when $P_2 = 15,000 \text{ atm}$

- Temperature: $\Delta G^0 = \Delta H^0 - T\Delta S^0$  T trend determined by sign of ΔS

- $\Delta S^0 = -3.31 \text{ J/(K mol)} < 0$ so increased T will NOT help

Gibbs free energy and temperature

$$\{\Delta G(T_2) = \Delta H(T_1) - T_2 \Delta S(T_1)\} - \{\Delta G(T_1) = \Delta H(T_1) - T_1 \Delta S(T_1)\}$$

$$\Delta G(T_2) - \Delta G(T_1) = -(T_2 - T_1) \Delta S(T_1)$$

- Thus we can use ΔS to predict how ΔG changes
- We can also use ΔH to change ΔG (ΔH can be easier to measure)

$$\Delta G(T_2) \approx \Delta H(T_1) - T_2 \Delta S(T_1)$$

$$\frac{\Delta G(T_2)}{T_2} \approx \frac{\Delta H(T_1)}{T_2} - \Delta S(T_1)$$

Note ΔS cancels

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} \approx \frac{\Delta H(T_1)}{T_2} - \frac{\Delta H(T_1)}{T_1} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \Delta H(T_1)$$

- So, if we know ΔG and either ΔH or ΔS at T_1 , we can estimate ΔG at T_2

Free energy of phase changes

- We often consider a phase change under equilibrium conditions
 - Melting point or boiling point of water
- Under equilibrium conditions, what is ΔG ?

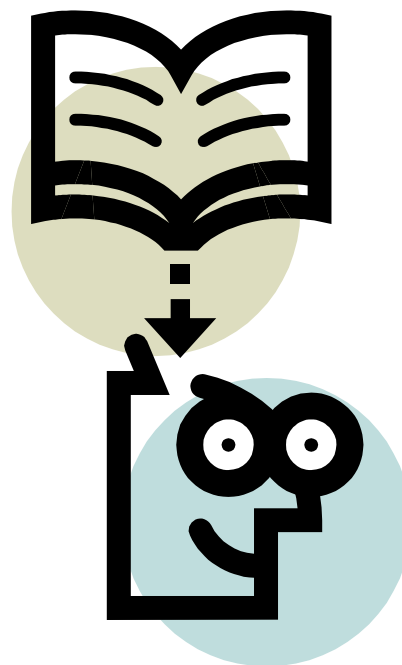
$$\Delta G = 0$$

- What if conditions are not at equilibrium?
 - Protein unfolding under native conditions
 - Changes to lipid bilayer structure
- In these cases, we still correct ΔG for temperature or pressure, but $\Delta G(T, P_{eq}) = 0$

Non-covalent reactions

- Most of our examples have involved making breaking chemical bonds
- These process are very important in biology
 - Enzymatic reactions - ATP hydrolysis
 - Protein/nucleic acid synthesis and polymerization
- **Many other important reactions do not change chemical bonds**
 - **Formation of duplex DNA** - **Protein folding**
 - **Hydrophobic effect** - **Ion transport**
 - **Ligand binding** - **Hydrogen bonding**
- **The same principles apply to all of these processes**

Free energy and chemical equilibria



Chemical equilibrium

energy

Many structures:
entropy favors

Few structures:
energy favors

“order parameter” (length, % native, etc)

Equilibrium, like free energy, is a (temperature-dependent) *balance* between energy and entropy

What is equilibrium?

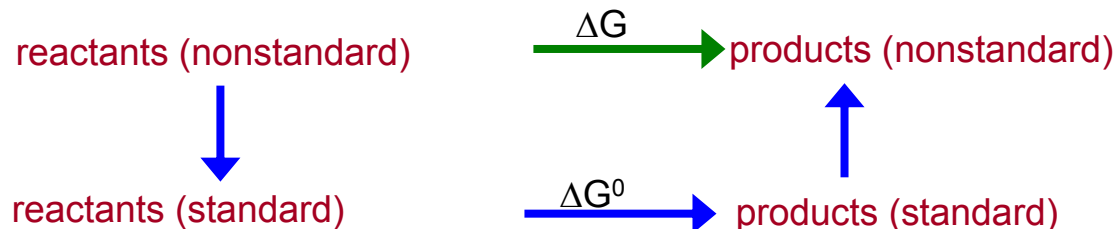
- We have been treating processes as “spontaneous” or not based on the sign of ΔG°
- What meaning does the *magnitude* of ΔG° have?
- How can we say that a reaction will be spontaneous or not based only on ΔG° , when we *know* that it depends on concentrations?
 - All reactant and no product \rightarrow form at least some product
 - All product and no reactant \rightarrow form at least some reactant
 - All reactions will have an **equilibrium mixture** of reactants and products
- The values of ΔG , ΔH , etc. in table refer to the substances in their standard state: ΔG^0 , ΔH^0 , etc.

Equilibrium and standard states

- Once equilibrium is reached, concentrations no longer change over time (but reactions still occur, more later)
- Associated with equilibrium is a **fixed ratio of reactants and products** (not necessarily referring to changes in chemical bonds)
- This ratio is known as the **equilibrium constant** : K_{eq}
- This constant is the same regardless of who prepared the system, or how it was prepared
- Living organisms are NOT at equilibrium (until they die), but in a **steady state**
- Many processes in organisms **are** at equilibrium, such as ligand binding, protein folding and more

Equilibrium and standard states

- Metabolic processes involve an enormous number of complex biological reactions operating together
- These reactions are controlled by the factors we have been studying
- We have seen that T , P and V influence ΔG , but a very important factor is also concentration
 - If $[\text{reactant}] = 0$, how could a reaction be spontaneous??
- Since we need to have some numbers in tables, we choose a “standard state” for the reactions in the table
- All reactions not in the standard state need a correction



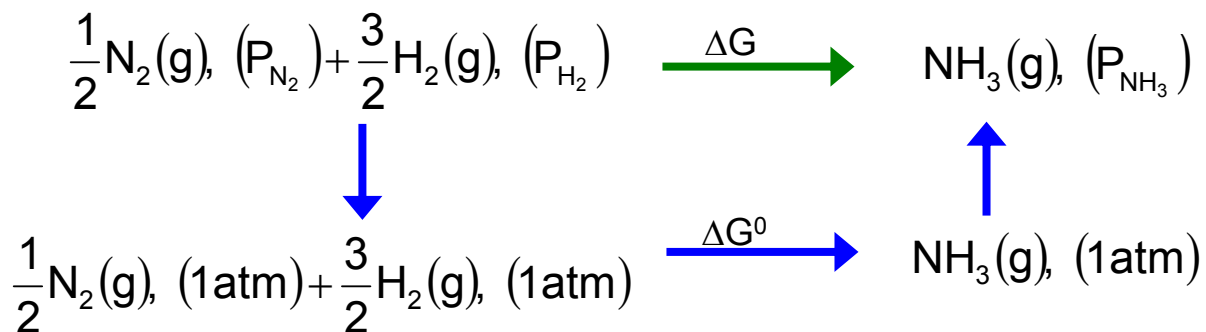
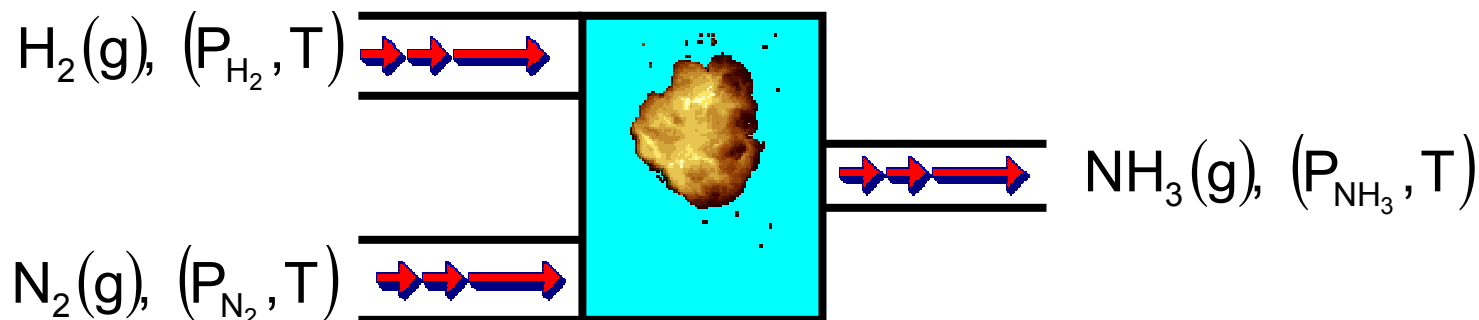
Ideal and non-ideal behavior

- One factor that influences behavior is concentration
- Another important factor is whether the system is ideal
 - Presence of some molecules may change the behavior of others
 - Ideal vs non-ideal gases
 - Ideal vs non-ideal solutions
- Example: the behavior of a certain amount of DNA is very different in pure water and in solution with ions (salt)
- We have 2 choices:
 1. Change all of our equations to handle all possible neighboring molecules that can influence behavior
 2. Use the same equations but introduce a way that the results can be corrected

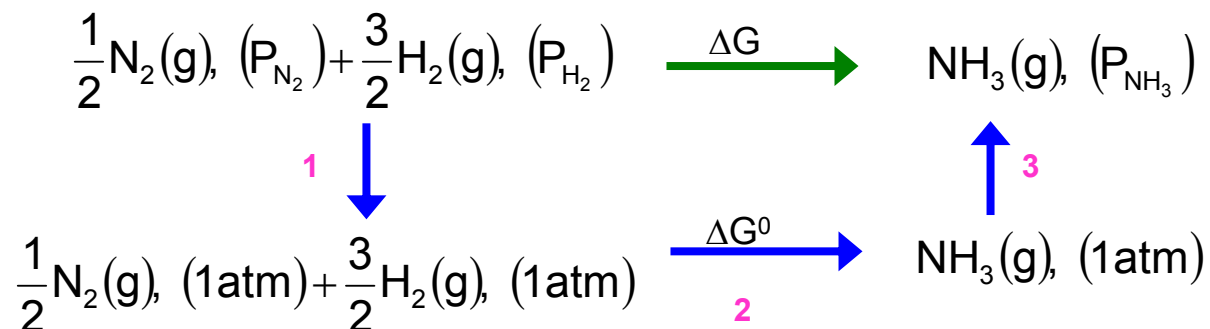


Free energy and non-standard states

- Consider a flow reaction chamber (details not important)
- $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ flow into the chamber at P_{H_2} and P_{N_2}
- $\text{NH}_3(\text{g})$ comes out of the chamber at P_{NH_3}
- T is constant



What is the overall ΔG ?



recall $G(P_2) - G(P_1) = nRT \ln \frac{P_2}{P_1}$

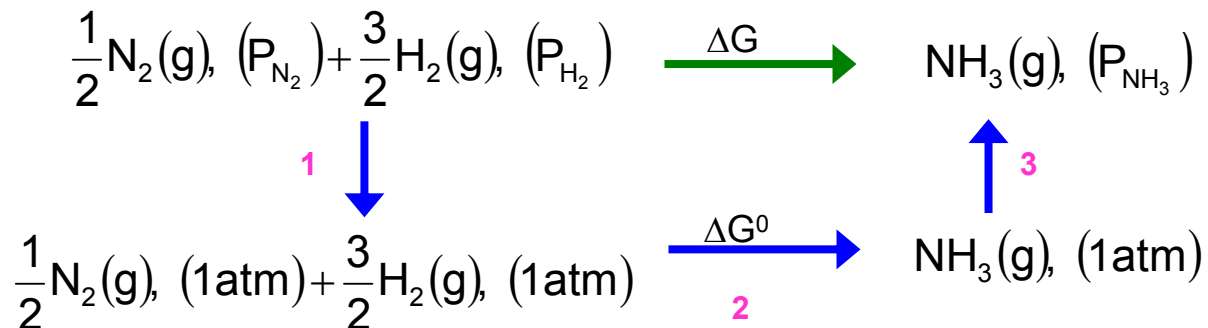
$$\Delta G_1 = \frac{1}{2}RT \ln \frac{1}{P_{\text{N}_2}} + \frac{3}{2}RT \ln \frac{1}{P_{\text{H}_2}} = RT \ln \left(\frac{1}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}} \right)$$

where we used $a \ln x = \ln x^a$ and $\ln a + \ln b = \ln(ab)$

$$\Delta G_2 = \Delta G^0 \quad \Delta G_3 = RT \ln P_{\text{NH}_3}$$

$$\Delta G_{\text{total}} = \Delta G^0 + RT \ln \left(\frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}} \right)$$

What is the overall ΔG ?



recall $G(P_2) - G(P_1) = nRT \ln \frac{P_2}{P_1}$

$$\Delta G_1 = \frac{1}{2}RT \ln \frac{1}{P_{\text{N}_2}} + \frac{3}{2}RT \ln \frac{1}{P_{\text{H}_2}} = RT \ln \left(\frac{1}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}} \right)$$

where we used $a \ln x = \ln x^a$ and $\ln a + \ln b = \ln(ab)$

$$\Delta G_2 = \Delta G^0 \quad \Delta G_3 = RT \ln P_{\text{NH}_3}$$

$$\Delta G_{\text{total}} = \Delta G^0 + RT \ln \left(\frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}} \right)$$

Correction to ΔG° for non-standard states

$$\Delta G_{total} = \Delta G^0 + RT \ln \left(\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} \right)$$

- Recall that we cannot take the log of a number with units
- The true equation should really be:

$$\Delta G_{total} = \Delta G^0 + RT \ln \left(\frac{\left(\frac{P_{NH_3}}{P^0} \right)}{\left(\frac{P_{N_2}}{P^0} \right)^{1/2} \left(\frac{P_{H_2}}{P^0} \right)^{3/2}} \right)$$

- The standard state is usually left out (value usually 1)

Example

$$\Delta G_{total} - \Delta G^0 = RT \ln \left(\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} \right)$$

- Calculate the Gibbs free energy *relative to that under standard conditions* for forming 1 mole of NH_3 at 298K if
 - 10 atm of N_2 and 10 atm of H_2 were used to form 0.01 atm of NH_3
 - 0.01 atm of N_2 and 0.01 atm of H_2 were used to form 10 atm of NH_3

a)

$$\Delta G_{298K} - \Delta G_{298K}^0 = RT \ln \left(\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} \right)$$

$$= 8.314 \text{ J/molK} \cdot 298K \ln \left(\frac{0.01}{3.16 \cdot 31.6} \right)$$

$$= -2.28 \times 10^4 \text{ J/mol}$$

Note that we don't need values for ΔG^0 to know which direction ΔG will change

More favorable than at std. state

b)

$$\Delta G_{298K} - \Delta G_{298K}^0 = 8.314 \text{ J/molK} \cdot 298K \ln \left(\frac{10}{0.1 \cdot 0.001} \right) = 2.85 \times 10^4 \text{ J/mol}$$

Less favorable than at std. state

Doesn't give overall ΔG !

Generalized equations for ideal gases



$$\Delta G_{total} = \Delta G^0 + RT \ln Q$$

$$Q = \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$$

- Where P_i are the partial pressures of the gases
- Q is the **reaction quotient** ***not the equilibrium constant!***
- *Note that we add the LN of Q*
- $Q < 1$: more favorable than system at standard state
- $Q > 1$: less favorable than system at standard state
- This does not tell us if it is favorable overall! (need ΔG° too)

General approach

- Consider the reaction $A \rightarrow 2B$
- Assume that the table tells us that $\Delta G^\circ = 10 \text{ kJ/mol}$
- Equal mixture of both gases: each has $0.5 \text{ atm } P_i$

$$Q = \left[\frac{\left(\frac{[B]}{1 \text{ mol/L}} \right)^2}{\frac{[A]}{1 \text{ mol/L}}} \right]$$

Due to reaction

$$\Delta G_{total} = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln \left[\frac{\left(\frac{[B]}{1 \text{ mol/L}} \right)^2}{\frac{[A]}{1 \text{ mol/L}}} \right]$$

Due to conditions

$$\Delta G_{total} = \Delta G^\circ + RT \ln Q = 10 \text{ kJ/mol} + RT \ln \frac{0.5^2}{0.5} = 8.3 \text{ kJ/mol}$$

Equilibrium constant K_{eq}

- Consider a reaction that has reached equilibrium ($\Delta G=0$)
- The previous equation still holds, but we can replace Q with K

$$K_{eq} = \left(\frac{(P_C^{eq})^c (P_D^{eq})^d}{(P_A^{eq})^a (P_B^{eq})^b} \right)$$

K is Q at equilibrium

- Since $\Delta G=0$ at equilibrium,

KEY EQUATIONS!

$$\Delta G_{eq} = 0 = \Delta G^0 + RT \ln K \Rightarrow \Delta G^0 = -RT \ln K \quad \text{or} \quad K = e^{-\Delta G^0 / RT}$$

$$\Delta G_{total} = \Delta G^0 + RT \ln Q = -RT \ln K + RT \ln Q = RT \ln \left(\frac{Q}{K} \right)$$

- So, what matters is the **actual** ratio of product/reactant compared to the ratio at equilibrium

K_{eq} , entropy and enthalpy

$$K = e^{-\Delta G^0/RT} = e^{-\left(\frac{\Delta H^0 - T\Delta S^0}{RT}\right)} = e^{-\left(\frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R}\right)} = e^{-\frac{\Delta H^0}{RT}} e^{\frac{\Delta S^0}{R}}$$

- Thus the equilibrium constant is related to ΔH and ΔS too
- The value of the equilibrium constant will certainly **depend on the temperature**
- We will see later that knowing the values K_{eq} as a function of temperature can be used to determine ΔH° and ΔS° (as well as ΔG°)

Example

$$K = e^{-\Delta G^0 / RT}$$

- Calculate the equilibrium constant at 25°C for the decarboxylation of liquid pyruvic acid to form gaseous acetaldehyde and CO₂
- $\Delta G^0 = \Delta G_f^0(\text{acetaldehyde}) + \Delta G_f^0(\text{CO}_2) - \Delta G_f^0(\text{pyruvic acid})$
- $\Delta G^0 = (-33.3 \text{ kJ/mol}) + (-394.36 \text{ kJ/mol}) - (-463.38 \text{ kJ/mol}) = -64.28 \text{ kJ/mol}$
- So, $K = e^{-\left(\frac{-64.28 \text{ kJ/mol}}{RT}\right)} = 1.85 \times 10^{11}$ no units!
- Calculate the ***fraction of folded conformation*** for a protein with a free energy of folding of a) -0.5 kJ/mol b) -5 kJ/mol

$$K = \frac{[\text{folded}]}{[\text{unfolded}]} = \frac{X}{1-X} = e^{-\left(\frac{-0.5 \times 10^3}{8.314 \cdot 298 K}\right)} = 1.22$$

$$X = 1.22(1-X) \quad X = \frac{1.22}{2.22} = 0.55 = 55\%$$

$$K = \frac{[\text{folded}]}{[\text{unfolded}]} = \frac{X}{1-X} = e^{-\left(\frac{-5 \times 10^3}{8.314 \cdot 298 K}\right)} = 7.5$$

$$X = 7.5(1-X) \quad X = \frac{7.5}{8.5} = 0.88 = 88\%$$

Example

$$K = e^{-\Delta G^0 / RT}$$

- Let's say you want to design a “picomolar” inhibitor of HIV reverse transcriptase (RT) at 37°C. What does the (standard) free energy of binding need to be?



$$K_d = \left(\frac{[free\ inhibitor][RT]}{[bound\ inhibitor]} \right) = 1 \times 10^{-12}$$

- Note that K_{eq} is the concentration of inhibitor needed to form a complex with $\frac{1}{2}$ of the enzyme

$$\Delta G^0 = -RT \ln K = -8.314 \frac{J}{mol \cdot K} 325 K \ln(1 \times 10^{-12}) = -74.6 \frac{kJ}{mol}$$

- Compare this very large binding energy to the protein stability energies discussed previously