

LECTURE 5

Entropy in Chemistry

Can we predict:

- If a reaction or process can occur?
- How will it proceed?
- How fast will it go?

Thermodynamics tells us nothing about rates tells everything about the rest

So what determines whether things happen?

Systems generally try to minimise the energy but that isn't the whole story

Consider:

- isothermal expansion of an ideal gas $\Delta U = 0$
- gas flows from high pressure to low
- heat flows from hot to cold
- gases, fluids diffuse into each other
- $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$

All these processes are SPONTANEOUS

Another factor plays a part in determining whether reactions happen

The *entropy*, S .

The easiest way to consider entropy is to consider the molecular state of the system.

Each physical situation (water later) results in a more random distribution of matter.

We describe the entropy as a measure of this randomness or *disorder* of the system.
A fundamental definition of entropy is given by *the Boltzmann equation*.

$$S = k_B \ln \omega$$

where ω is the number of ways of arranging the molecules of the system and k_B is the *Boltzmann constant*.

The larger the number of arrangements, or the less organised the system, the larger the entropy.

The Second Law of Thermodynamics

The usefulness of entropy is embodied in *the Second Law of Thermodynamics*.

Spontaneous processes are those which increase the entropy of the Universe

Thus, if we can calculate the entropy of a process, we can tell whether it is spontaneous.

Entropy \Rightarrow related to order \therefore spontaneous processes are those which lead to an increase in disorder.

A Quantitative Measure of Entropy

First treatments of S considered heat - work cycles and the efficiency of heat engines.

We will simply use the result

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

ΔS is the entropy *change* when an amount of heat q_{rev} is added in a reversible manner at temperature T.

q_{rev} is the maximum heat change available so that the entropy is associated with the maximum energy change which a system can undergo.

This is consistent with our ideas on entropy. Heating leads to faster molecular motion, increased bond vibration and larger population of higher energy levels i.e. greater disorder.

Entropy is a state function so:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Entropy changes during a change of phase

A straightforward application.

At the temperature of the phase change, the heat change is reversible at constant pressure.

$$\Delta S^{\text{vap}} = \frac{\Delta H^{\text{vap}}}{T_b} \quad ; \quad \Delta S^{\text{fus}} = \frac{\Delta H^{\text{fus}}}{T_m}$$

ΔS for the reverse changes - condensation or freezing - are given by the negative of these values

ΔH^{vap} and ΔH^{fus} are endothermic so ΔS must be positive - vapour is more disordered so higher entropy than a liquid:

ΔS^{vap} is positive.

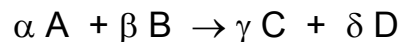
Entropy changes in chemical reactions

As with ΔH° ,

the standard entropy of reaction as the difference in standard entropy of the products from that of the reactants

$$\Delta S^\circ_{298} (\text{reaction}) = \sum v_i S^\circ_{298} (\text{products}) - \sum v_i S^\circ_{298} (\text{reactants})$$

v_i is the stoichiometry. So, applying this to our general reaction,



$$\Delta S^\circ_{298} = [\gamma S^\circ_{298}(\text{C}) + \delta S^\circ_{298}(\text{D})] - [\alpha S^\circ_{298}(\text{A}) + \beta S^\circ_{298}(\text{B})]$$

This is the entropy change for converting 1 mole of reactants into 1 mole of products (or whatever the stoichiometry is) under standard pressure at 298 K.

The entropy change at other temperatures can be calculated by $\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \frac{\Delta c_p}{T} dT$

Using mean heat capacities, this leads to

$$\Delta S_{T_2} = \Delta S_{T_1} + \Delta c_p \int_{T_1}^{T_2} \frac{1}{T} dT = \Delta S_{T_1} + \Delta c_p \ln\left(\frac{T_2}{T_1}\right)$$

This allows us to calculate entropy changes during reactions at any temperature.

Note: S°_{298} or S_T , *must* be positive - it must have greater disorder than a perfect crystal at 0 K.

However, ΔS°_{298} or ΔS_T can be positive or negative since they refer to *differences* in entropy between sets of conditions.

Entropy as a predictor of chemical reactivity

Consider a familiar reaction: $2 \text{ H}_2(\text{g}) + \text{ O}_2(\text{g}) \rightarrow 2 \text{ H}_2\text{O}(\text{l})$

$$\begin{aligned} \Delta S^\circ_{298} &= [2 \times S^\circ_{298}(\text{H}_2\text{O})] - [2 \times S^\circ_{298}(\text{H}_2) + S^\circ_{298}(\text{O}_2)] \\ &= [2 \times 70] - [2 \times 131 + 205] \\ &= -327 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

There is a large loss of entropy on forming water.
3 moles of high entropy gas form 2 moles of lower entropy liquid.

But, isn't this a problem ? :

Doesn't the negative entropy change contravene the 2nd law which states that spontaneous processes *increase* entropy?

We have only calculated the entropy change for the H₂ / O₂ / H₂O *system*. The 2nd Law refers to the entropy of *the Universe* increasing as a requirement for spontaneity.

$\Delta H_{f,298}^\circ$ for water is -285.8 kJ mol⁻¹ so ΔH for the above reaction (*i.e.* the system) is -571.6 kJ.

We know: $\Delta H^\circ(\text{surroundings}) = -\Delta H^\circ(\text{system})$

and: $\Delta S(\text{surroundings}) = \Delta H^\circ(\text{surroundings}) / T = -\Delta H^\circ(\text{system}) / T$
 $= + 571.6 \times 10^3 / 298$
 $= + 1920 \text{ J K}^{-1} \text{ mol}^{-1}$

Considering the total entropy change,

$$\begin{aligned}\Delta S(\text{Universe}) &= \Delta S(\text{system}) + \Delta S(\text{surroundings}) \\ &= -327 + 1920 = +1593 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Hence, there is an overall *increase* in the total entropy of the Universe, in accord with that expected from the second law.

Free Energy and Equilibrium

Most (but not all) chemical reactions are exothermic with negative ΔH . Most reactions (but not all) lead to an increase in disorder - positive ΔS

The *free energy* function allows us to combine these factors

From earlier, for a spontaneous process at constant T, p :

$$\Delta S(\text{Universe}) = \Delta S(\text{System}) + \Delta S(\text{Surroundings}) > 0$$

or

$$\Delta S(\text{Universe}) = \Delta S(\text{System}) + \{\Delta H(\text{Surroundings}) / T\} > 0$$

We don't want to focus on the Universe every time: Since,

$$\Delta H(\text{Surroundings}) = -\Delta H(\text{System}).$$

$$\Delta S(\text{System}) + (-\Delta H(\text{System}) / T) > 0$$

referring only to the system, we can write

$$\Delta H - T \Delta S < 0$$

The value of $\Delta H - T \Delta S$ has its own name, the *Gibbs function or Gibbs free energy*, G . An exact definition of G is therefore given by:

$$G = H - TS \quad \text{or} \quad \Delta G = \Delta H - T \Delta S$$

For a spontaneous process at constant T, p there must be a lowering of the Gibbs free energy or

$$(\Delta G)_{p, T} < 0$$

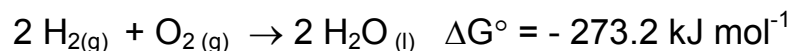
This refers to ΔH *i.e.* at constant pressure. The same argument can be made in terms of ΔU at constant volume.

We define the *Helmholtz free energy*, A ,: $A = U - TS$.

Spontaneous changes at constant volume have $\Delta A < 0$.

In general, we can conclude that *if a process or reaction results in a lowering of the free energy, it will be spontaneous i.e. that it will be favourable and CAN happen. It does not mean that it WILL happen.*

e.g. at 1 bar and 25 °C



However, a mixture of hydrogen and oxygen gases in a container will not react until started by a catalyst or source of ignition.

The reaction is *thermodynamically* very favourable but occurs extremely slowly. It is *kinetically* unfavourable as it has a high activation energy.

General observations on reactions:

Low temperatures: $T\Delta S$ will be small compared with ΔH so that ΔG is insensitive to the sign of the entropy change. The sign of ΔG is therefore determined by the sign of ΔH .

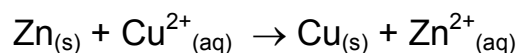
Hence for a spontaneous reaction, we need to have negative ΔH or an exothermic reaction.

At high temperatures the $(-T\Delta S)$ term will be dominant so that a positive ΔS , hence a disordering process, is needed to give a negative ΔG .

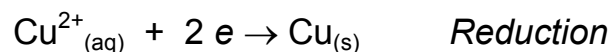
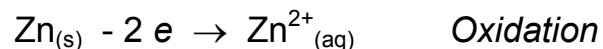
Electrochemical cells

An important class of reaction not so far discussed is that of electron transfer or **redox** reactions.

If pure Zn metal is placed in a solution of $\text{CuSO}_4(\text{aq})$, the zinc rapidly coats with a brown deposit of Cu metal. The chemical reaction taking place is



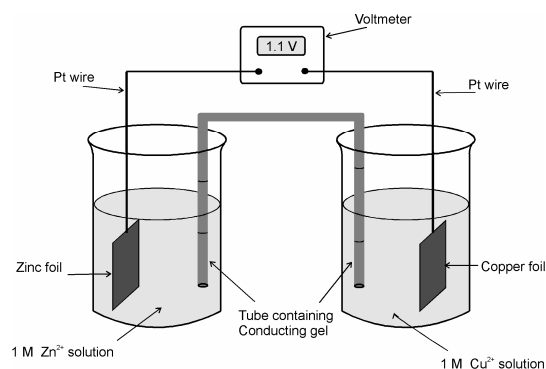
This can be split into two *half-reactions*



Reactions involving electron gain - **reductions**
Reactions involving electron loss - **oxidations**.

There must be a net balance of electrons and so both must take place concurrently, hence the name *redox* reaction.

If we keep the two half reactions separate (but linked together) electrons can be made to flow around an external circuit.



The *potential difference* between the electrodes provides the “driving force” for the electron flow.

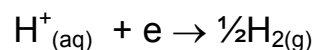
If we use a voltmeter with a very high resistance, no electrons can flow so we just measure the e.m.f. (*or potential or voltage*) of the cell. Under these conditions, the cell acts reversibly.

There are many types of half-cell and electrochemical reaction – we will only consider a short introduction to the topic from a thermodynamic point of view.

Standard electrode potentials

The voltage generated clearly depends on the nature of the two half cells. Again, we need to fix a *standard*.

We set to zero, the potential for a half-cell involving the reaction



at 298 K, 1 bar of hydrogen pressure and 1 mol dm⁻³ concentration of H⁺.

Construction of a cell in which one half consists of this *Standard Hydrogen Electrode, S.H.E.* allows the potential for any other half-cell to be determined.

Note: Again the definition of 1 mol dm⁻³ as the standard concentration is an approximation and it should be defined as *unit activity*.

Extensive lists of these values have been published.

(For example, see your Inorganic textbook and Atkins)

Electrode potentials measured under these standard conditions are given the symbol E° while E represents the voltage generated when the cell operates under conditions other than those specified above.

The e.m.f. of the cell, E, tells us about the tendency for electrons to flow around the circuit - the same as the tendency for the redox reaction to occur - so it must be related to the reaction free energy

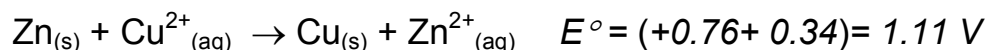
e.g. higher E = more tendency to happen

Higher E will oxidise lower E (or lower E will reduce higher)

For the two *half-reactions*



For the overall reaction, we add these together



Note: In texts, the E° values are always listed as standard **reduction** potentials so that you will see $\text{Zn}^{2+}_{(aq)} + 2 e \rightarrow \text{Zn}_{(s)}$ $E^\circ = -0.76 \text{ V}$. For the opposite reaction, we switch the sign of the potential.

The same principles hold if conditions other than standard are used.

Electrode Potentials and free energy changes

The tendency for a reaction to happen is correlated by ΔG so there must then be a direct connection between E and ΔG .

If n electrons are transferred in a reaction, then the total charge per mole, Q, is nF. F is the **Faraday constant** which is the total charge on 1 mole of electrons - 96485 C mol⁻¹.

When a charge Q moves through a potential difference E, the work done is given by

$$w_{\text{elec}} = \int_{Q_{\text{initial}}}^{Q_{\text{final}}} -E \, dQ$$

If the potential difference, or voltage, is constant, the work done in transferring a charge nF is simply $w_{\text{elec}} = -nFE$

At constant T, p, this work is done as a result of the lowering of the system free energy Thus, we can write

$$\Delta G = - n F E$$

In the particular case of standard conditions and all components in their standard states, then

$$\Delta G^\circ = - n F E^\circ$$

Since E and ΔG , have opposite sign, if a cell has a positive potential the reaction taking place will be spontaneous.

Thermodynamic measurements by electrochemistry

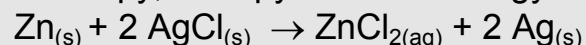
Electrochemistry allows us to make thermodynamic measurements on systems which would be difficult to perform calorimetry e.g. biochemical systems.

We already know that $\left(\frac{dG}{dT}\right)_p = -S$ or $\Delta S^\circ = -\left(\frac{d\Delta G^\circ}{dT}\right)_p$

so
$$\Delta S^\circ = nF \left(\frac{dE^\circ}{dT}\right)_p$$

so that, as long as we are operating at constant p, the temperature variation of the cell voltage allows us to measure the entropy change for the reaction. Once $\Delta G^\circ (= -n \mathfrak{z} E^\circ)$ and ΔS° are known, ΔH° can be calculated.

An electrochemical cell with the following reaction generates a standard electrode potential of 1.055 V at 25 °C and 1.015 V at 0°C. Calculate the standard enthalpy, entropy and free energy changes for the reaction at 25 °C.



The standard free energy change at 298 K follows directly from

$$\Delta G^\circ = - n \mathfrak{z} E^\circ = -(2) (96485) (1.055) = -203.58 \text{ kJ mol}^{-1}$$

We will make the approximation that the voltage is a linear function of temperature. The standard entropy arises

from the temperature dependence $\Delta S^\circ = n\mathfrak{F} \left(\frac{dE^\circ}{dT} \right)_p = (2) (96485) \left(\frac{1.055 - 1.015}{298.15 - 273.15} \right) = 308.75 \text{ J K}^{-1} \text{ mol}^{-1}$

ΔH° can then be found

$$\begin{aligned} \Delta H^\circ &= \Delta G^\circ - T\Delta S^\circ = (-203.58 \times 10^3) - (298.15)(308.75) \\ &= -295.63 \text{ kJ mol}^{-1} \end{aligned}$$