Lecture 14
Black's Explanations of Known Facts

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Introduction

We've seen:

- Lime is produced by putting calcareous earth in a fire.
- The fire theory said fire is being added to calcareous earth to make lime.
- Black said nothing is added. Air and water are driven off and what remains is lime.

Today:

- We'll learn some facts and concepts that were known to 18th century chemists. I'll use 18th century terminology because modern terminology is based on theories that weren't always accepted by 18th century chemists.
- Then we'll look at how Black explained some known properties of lime using his theory.

Salt

In the 18th century, the term "salt" covered acids, alkalis, and neutral salts.

Acids

- Turn syrup of violets from blue to red. (Robert Boyle discovered this in the 17th century.)
- Taste sharp or sour. Examples are lemon juice and vinegar. The word "acid" comes from Latin "acidus" meaning sharp or sour.

Alkalis

- Turn syrup of violets from blue to green.
- How obtained: burn a plant, put the ashes in water, pour off the liquid, and evaporate it. What remains is a white powder; this is the alkali.
- The reason for the name "alkali" is said to be that the Arabs made it by burning a plant called kali.
- Examples: soda and potash.
- Have a burning (acrid) taste.
- Effervesce with acids. (Soda drinks are called that because the gas in them was produced from soda and acid.)

Neutral salts

- Don't change syrup of violets to red or green but leave it blue.
- Obtained by mixing an acid and an alkali until the mixture is neutral.
- Don't taste either sour or burning but "salty."
- Today only neutral salts are called salt.
- Table salt is one of the neutral salts.

Why lime is more active than calcareous earth

Black's basic idea (185–86)

I . . . imagined that, when the calcarious earths are exposed to the action of a violent fire, and are thereby converted into quick-lime, they suffer no other change in their composition than the loss of a small quantity of water and of their fixed air. The remarkable acrimony which we perceive in them after this process, was not supposed to proceed from any additional matter received in the fire, but seemed to be an essential property of the pure earth, depending on an attraction for those several substances which it then became capable of corroding or dissolving, which attraction had been insensible as long as the air adhered to the earth, but discovered itself upon the separation.

Analogy with acids and alkalis (186–87)

This supposition was founded upon an observation of the most frequent consequences of combining bodies in chemistry. Commonly when we join two bodies together, their acrimony or attraction for other substances becomes immediately either less perceivable or entirely insensible; altho' it was sufficiently strong and remarkable before their union, and may be rendered evident again by disjoining them. A neutral salt, which is composed of an acid and alkali, does not possess the acrimony of either of its constituent parts. It can easily be separated from water, has little or no effect upon metals, is incapable of being joined to inflammable bodies, and of corroding and dissolving animals and vegetables; so that the attraction both of the acid and alkali for these several substances seems to be suspended till they are again separated from one other.

Restatement (187)

Crude lime [calcareous earth] was therefore considered as a peculiar acrid earth rendered mild by its union with fixed air: and quick-lime as the same earth, in which, by having separated the air, we discover that acrimony or attraction for water, for animal, vegetable, and for inflammable substances.

Attraction

- Suppose two substances, A and B combine to form a compound AB.
- Sometimes there is another substance C that will displace B from its combination with A.

$$AB + C \longrightarrow AC + B.$$

- Newton, in a query in his *Opticks*, suggested that the explanation for this is that A has a stronger attraction for C than for B and it cannot combine with both. His explanation was accepted by chemists in the 18th century.

Why calcareous earth effervesces in acids

When calcareous earth is put in acid, lots of little bubbles rise up; this is *effervescence*.

Black's explanation (185)

When we mix an acid with [calcareous earth] the air is then set at liberty and breaks out with violence; because the [calcareous earth] attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time.

$$(\text{lime} + \text{air}) + \text{acid} \longrightarrow (\text{lime} + \text{acid}) + \text{air} \uparrow$$

Why lime is soluble in water and calcareous earth isn't

Calcareous earth isn't soluble in water, e.g., when chalk is put it water, none dissolves. Lime is slightly soluble; when put in water it gives the water an acrid taste.

Black's explanation (188)

- Solubility is due to a substance's attraction for water.
- Lime is soluble in water because it has an attraction for water.
- Lime has a greater attraction for air than for water so, when combined with air it won't combine with water.

$$(\text{lime} + \text{air}) + \text{water} \longrightarrow (\text{lime} + \text{air}) + \text{water}$$

It follows that calcareous earth (= lime + air) won't combine with water.

Why a crust forms on lime water

Water in which lime has been dissolved is called lime water. When lime water is exposed to the atmosphere for a few minutes a crust appears on the surface. Examination of this crust shows that it is calcareous earth. If the crust is scraped off, a new crust replaces it.

Black's explanation

Black found that the air fixed in calcareous earth isn't the same as atmospheric air but there is some of it distributed in the atmosphere. He called it "fixed air" even when it isn't fixed but free in the atmosphere. He said particles of lime at the surface of the lime water combine with fixed air in the atmosphere to form calcareous earth at the surface of the water.

Quotation (189)

If [lime water] be exposed to the open air, the particles of quick-lime which are nearest the surface gradually attract the particles of fixed air which float in the atmosphere. But at the same time that a particle of lime is thus saturated with air, it is also restored to its native state of mildness and insolubility; and as the whole of this change must happen at the surface, the whole of the lime is successively collected there under its original form of an insipid calcarious earth, called the cream or crusts of lime-water.

Why lime makes alkalis caustic

Alkalis are fairly caustic but they can be made *more* caustic by mixing them with lime. Alkali made more caustic this way is called "caustic lye"; it is sold in stores for cleaning blocked drains.

Black's explanation

- Ordinary alkali = caustic alkali + fixed air.
- Lime has greater attraction for fixed air than caustic alkali does. So when lime is mixed with ordinary alkali, the fixed air in the alkali goes to the lime, leaving caustic alkali.

$$(\text{caustic alkali}+\text{fixed air})+\text{lime} \longrightarrow \text{caustic alkali}+(\text{lime}+\text{fixed air})$$

Quotation (190)

If quick-lime be mixed with a dissolved alkali, it likeways shews an attraction for fixed air superior to that of the alkali. It robs this salt of its air, and thereby becomes mild itself, while the alkali is consequently rendered more corrosive, or discovers its natural degree of acrimony or strong attraction for water, and for bodies of the inflammable, and of the animal and vegetable kind; which attraction was less perceivable as long as it was saturated with air.

Question

1. State Black's explanation for the following:
   (a) Lime is more active than calcareous earth.
   (b) Calcareous earth effervesces in acids.
   (c) Lime is soluble in water and calcareous earth is not.
   (d) A crust forms on lime water.
   (e) Lime makes alkalis caustic.

Modern terminology

18th century	**modern chemistry**
calcareous earth	calcium carbonate, $CaCO_3$
fixed air	carbon dioxide, CO_2
quicklime	calcium oxide, CaO
soda	sodium carbonate, $NaCO_3$
potash	potassium carbonate, KCO_3
caustic alkali	sodium or potassium oxide, NaO or KO

Video of calcareous earth dissolving in acid

References

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