

Issue #2: Lead

- Known since ancient times: used for plumbing systems (Roman Empire), roofing (medieval cathedrals)
 - Modern uses:
 - household plumbing
 - solder: Pb-Sn alloy (Franklin & the NW passage ^{1845 died cos of Pb as a solder in tinned food.})
 - paints (white lead, $2PbCO_3 \cdot Pb(OH)_2$; red lead, Pb_3O_4 ; lead chromate $PbCrO_4$)
 - lead-acid batteries
 - gasoline anti-knock agents tetramethyl- and tetraethyl-lead [no longer used in Europe or North America]
 - crystal glass ($PbO \rightarrow$ high refractive index)
 - lead shot (shooting ranges; waterfowl)
 - Radiation shielding
 - Historical production of lead: see text, Figures 10.4 and 10.5 (and next page)
 - Toxicity of lead:
 - Pb^{2+} substitutes for Ca^{2+} in bone; depuration is very slow so that Pb accumulates with age ^($\frac{1}{2}$ life ~ 6 years whole body)
 - as with mercury, organoleads are more toxic than inorganic lead; even inorganic salts are partly covalent e.g., $PbBr_2$ ^{↓ 15-20yr skeleton (so, cumulative)}
 - hence Pb can cross blood-brain barrier → neurotoxicity in adults and children; mental deficits in children (lead paint) ← they like to chew objects covered in lead paint.
 - lead recycling ("secondary lead smelters") → air pollution since Pb has m.p. $327^\circ C$; b.p. $1740^\circ C$
- like mercury, and also, organolead compounds (more toxic) are lipid soluble, hence.
- Irritability, sleeplessness, mental retardation, irrational behaviour, depressed appetite ⇒ starvation.

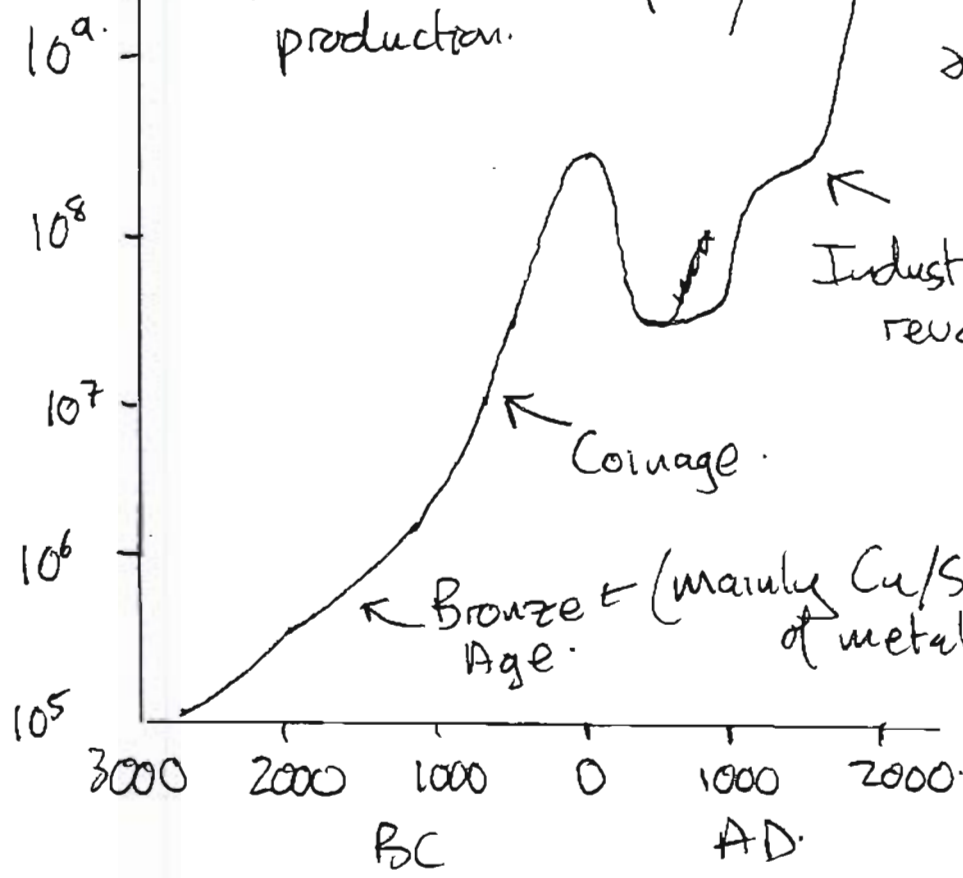
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Plumbum

Fig 10.4

Historical consumption/production.

Lead production, kg



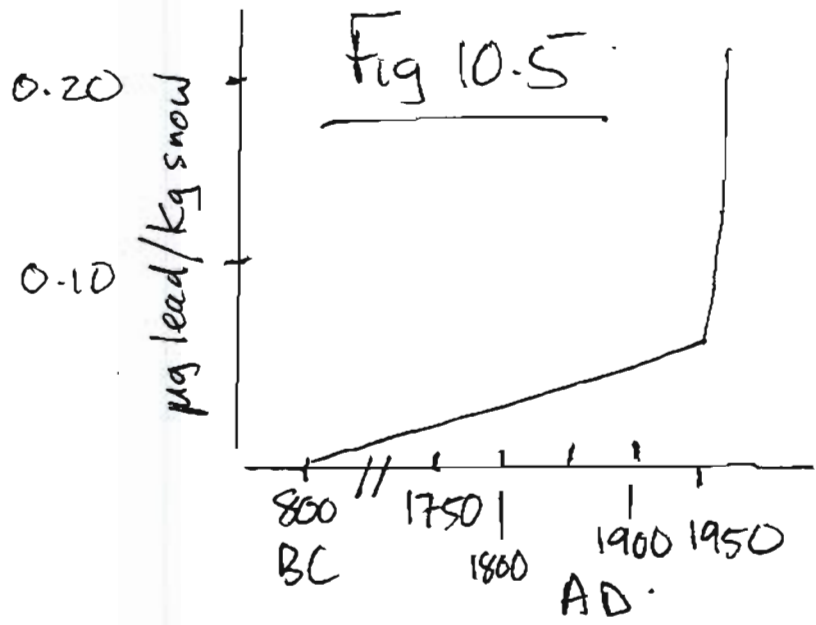
gasoline additives & batteries (auto)

Industrial revolution

Coinage

Bronze Age (mainly Cu/Sn ... but lots of metal working going on)

Fig 10.5

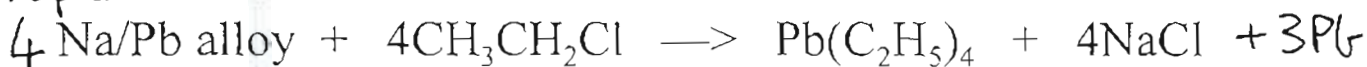


Increase of lead in Greenland snow.

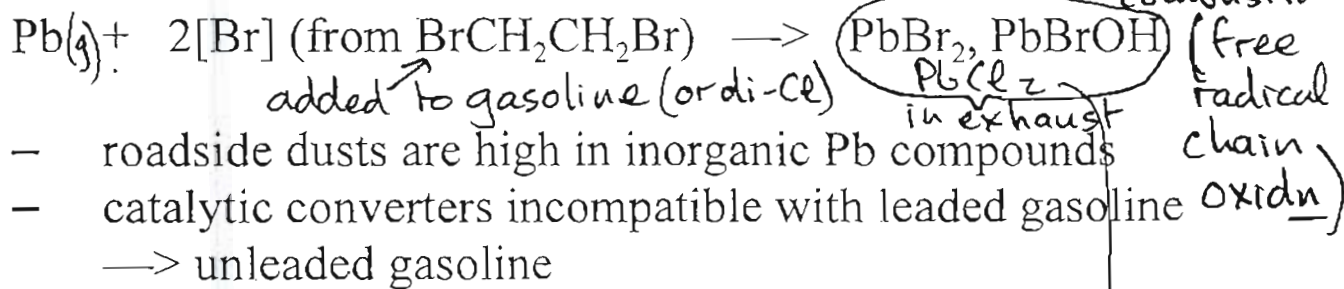
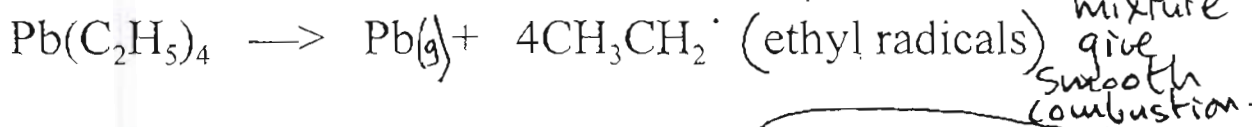
Lead in gasoline

- petroleum is mostly straight chain alkanes
- branched chain alkanes burn more smoothly
- petroleum distillation → "straight run" gasoline – a poor fuel with tendency to knocking/pinging (details in text)
- options to increase the **octane rating** are:
 - more complex refining processes → more branched chain and aromatic hydrocarbons → e.g. tetraethyllead (TEL)
 - addition of tetraalkyl lead compounds as "anti-knock agents": Ethyl Corp, founded 1920s

Preparation of TEL:



in the engine: promotes smooth combustion



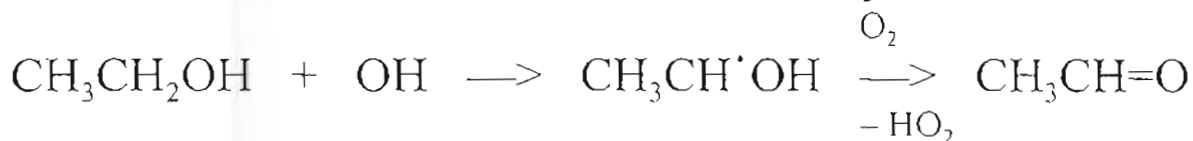
need to remove the Pb from inside the engine.

chloro-compounds can lead to TCDD in the environment.

North America legislated elimination of lead compounds from gas in 1990 ... it was already diminished by the intro. of unleaded gas and the incompatibility with catalytic converters.

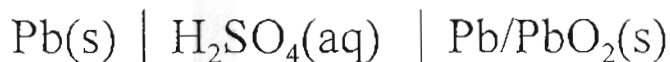
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- MTBE now found to be a ground water pollutant
 - recalcitrant \swarrow dense non-aqueous phase liquid (P150)
 - DNAPL source from leaking gas tanks
 - possible carcinogenicity
- alternative oxygenate = ethanol \rightarrow the "gasohol" movement.
 - from corn starch by fermentation and distillation
 - concern that ethanol increases aldehyde levels



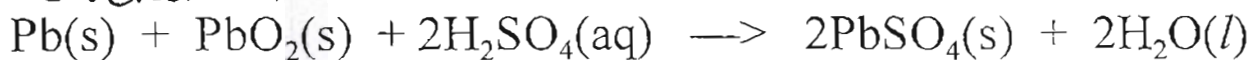
- recall that $\text{CH}_3\text{CH}=\text{O}$ is a precursor of peroxyacetyl nitrate, PAN

Lead-acid battery (in cars) (rechargeable
(can be discharged & charged)
 \therefore good storage cell)



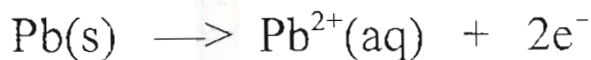
galvanic cell (when you start your car):

Overall rx:

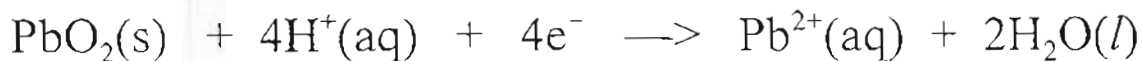


- note: H_2SO_4 consumed

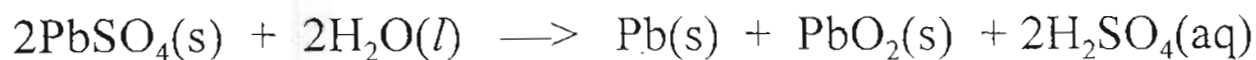
anode reaction:



cathode reaction:



electrolytic cell (when the battery charges):



- note H_2SO_4
reappears

For E_{cell} during discharge:

$$E = E^\circ - \frac{RT}{nF} \cdot \ln \left(\frac{1}{[H_2SO_4]} \right)^2$$

$$\approx E^\circ + \frac{RT}{nF} \{ 2 \ln [H^+] + 2 \ln [HSO_4^-] \}$$

This is why the charge of a battery can be determined by measuring the *density* of the electrolyte (H_2SO_4 is denser than H_2O)

↑
charged condition

↑
when battery is discharged

Problems with lead-acid batteries:

- technical problem of low energy density
- recycling – secondary lead smelters (Junction Triangle, Toronto) (old electrodes re-distilled)
- improper disposal: - nasty emissions
 - landfill leachate
 - poisoning of cattle

batteries
~~it~~ major source of lead in municipal waste

means that ratio of energy to the mass (they are heavy!!) is low.

Hence alternatives are being researched using lighter metals like titanium or aluminium