Titrations

H Ch 11

FIND EQUIVALENCE POINT FIRST

CORRECT MOLARITY AS TITRANT IS ADDED

H 11-4 Polyprotic Titrations

homework for week 14,15
due dates this Wednesday and Friday

Titrations

Titration of a Strong Base with a Strong Acid

EX: 50.00 mL of 0.02000 M KOH titrated with 0.1000 M HBr.

chemical equation (why reaction arrow?)

KOH(*aq*) + HBr(*aq*) –> KBr(*aq*) + H_2O(*l*)

net ionic equation

H^+(*aq*) + OH^-(*aq*) –> H_2O(*l*)

Titration of a Weak Acid with a Strong Base

EX: 50.00 mL of 0.02000 M MES, pK_a = 6. 27, titrated with 0.1000 M NaOH.

chemical equation (why reaction arrow?)

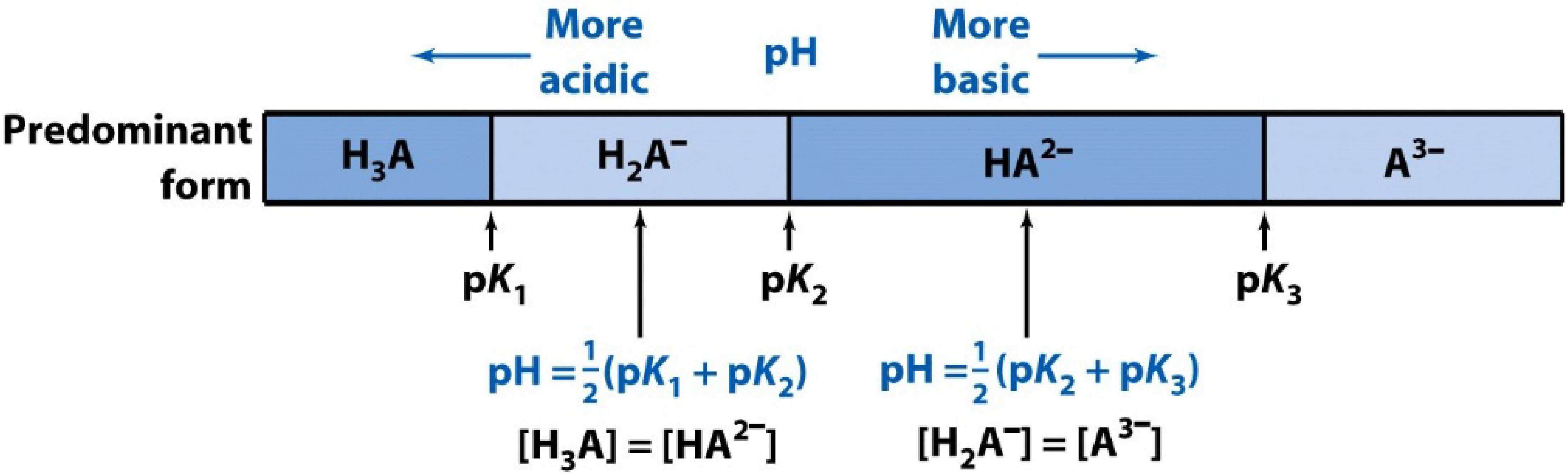
NaOH(*aq*) + HA(*aq*) –> NaA(*aq*) + H_2O(*l*)

net ionic equation

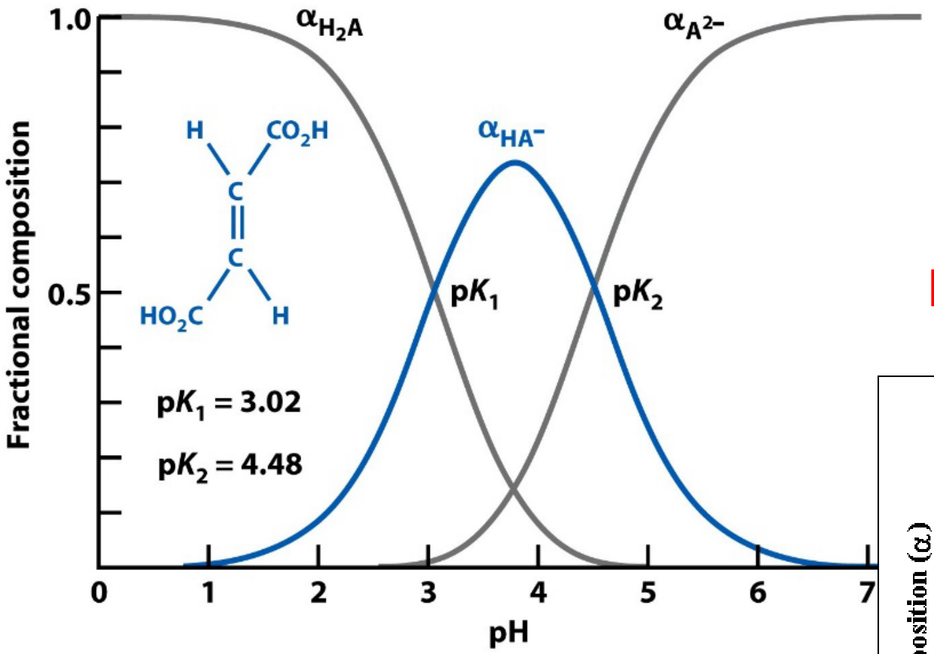
HA(*aq*) + OH^-(*aq*) –> A^-(*aq*) + H_2O(*l*)

Finding the Principal Species at a Given pH

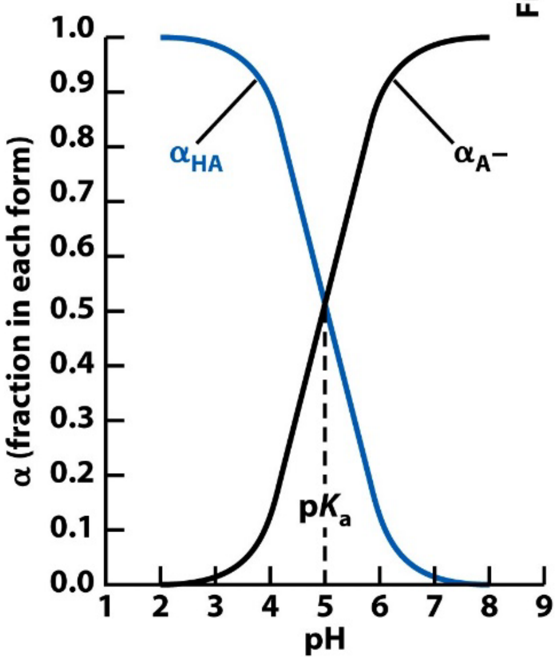
$pH = pK_a + \log [\text{base}] / [\text{acid}]$



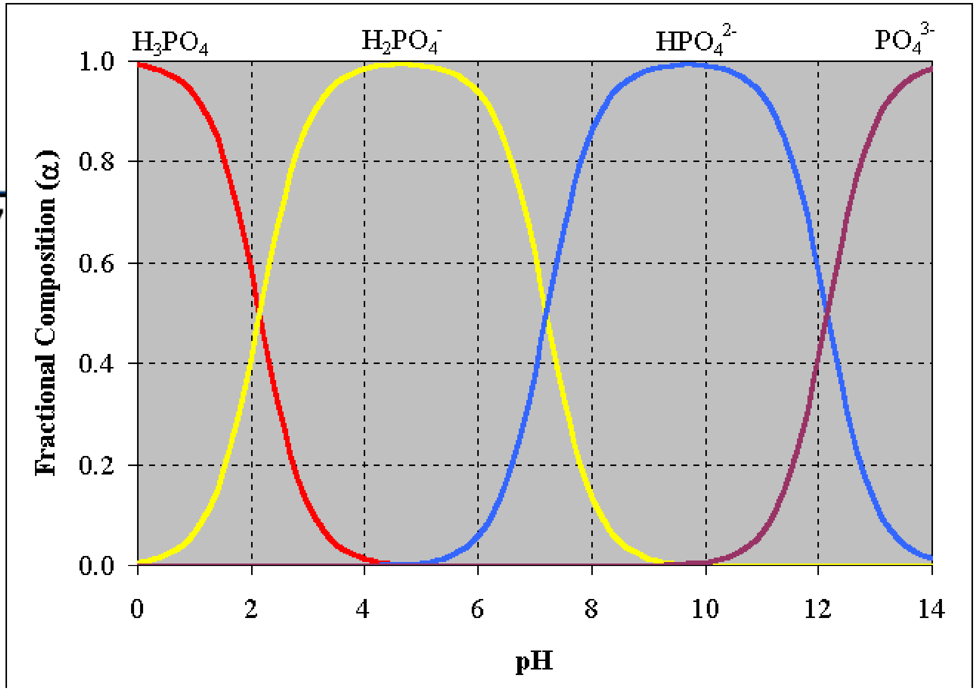
Finding the Fraction Dissociated at a Given pH



$H_3A \rightarrow H_2A^- \rightarrow HA^{2-} \rightarrow A^{3-}$



$pH = pK_a + \log [base] / [acid]$



Leveling Effect: $2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

Strongest acid (base) that can exist in a solvent is the **acidic** (**basic**) autoionization species of the solvent.

acids stronger than H_3O^+

Acidity Constants in Water at 25°C

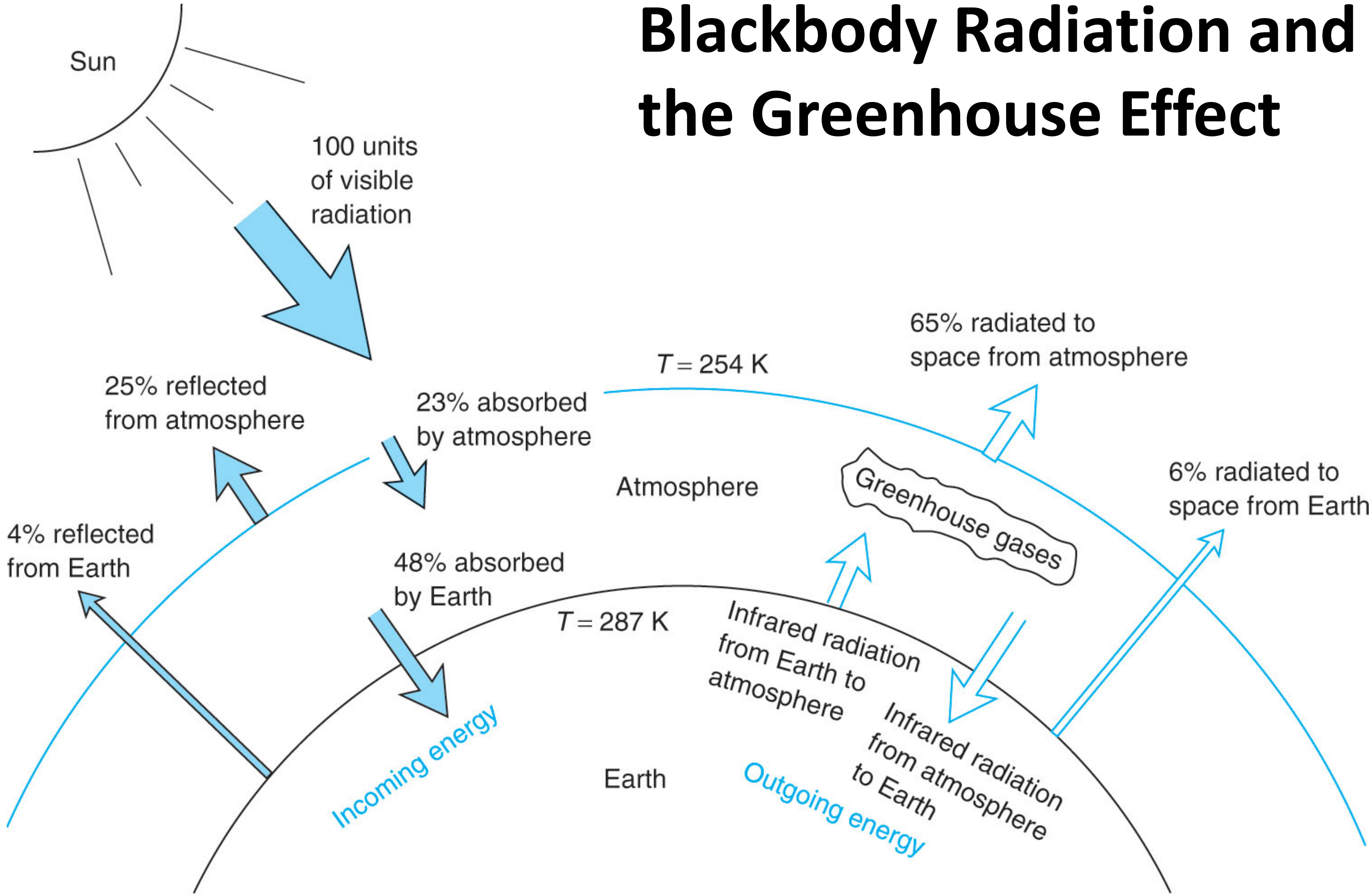
Acid	Formula	Conjugate Base	K_a	pK_a
Hydriodic	HI	I^-	$\approx 10^{11}$	≈ -11
Hydrobromic	HBr	Br^-	$\approx 10^9$	≈ -9
Perchloric	$HClO_4$	ClO_4^-	$\approx 10^7$	≈ -7
Hydrochloric	HCl	Cl^-	$\approx 10^7$	≈ -7
Chloric	$HClO_3$	ClO_3^-	$\approx 10^3$	≈ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\approx 10^2$	≈ -2
Nitric	HNO_3	NO_3^-	≈ 20	≈ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Urea acidium ion	$(NH_2)CONH_3^+$	$(NH_2)_2CO$ (urea)	6.6×10^{-1}	0.18
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.5×10^{-2}	1.82
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.5×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic	$ClCH_2COOH$	$ClCH_2COO^-$	1.4×10^{-3}	2.85
Hydrofluoric	HF	F^-	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	$HCOOH$	$HCOO^-$	1.8×10^{-4}	3.74
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.5×10^{-5}	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19

Acidity Constants in Water at 25°C

Acid	Formula	Conjugate Base	K_a	pK_a
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72
Acetic	CH_3COOH	CH_3COO^-	1.8×10^{-5}	4.74
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.3×10^{-5}	4.89
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N (pyridine)	5.6×10^{-6}	5.25
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.0×10^{-7}	7.00
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.2×10^{-8}	7.21
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}	7.52
Hydrocyanic	HCN	CN^-	6.2×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	2.3×10^{-11}	10.64
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	3.0×10^{-12}	11.52
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.66
Water	H_2O	OH^-	1.0×10^{-14}	14.00
Hydrogen sulfide ion	HS^-	S^{2-}	1.0×10^{-19}	19.00
Hydrogen	H_2	H^-	1.0×10^{-33}	33.00
Ammonia	NH_3	NH_2^-	1.0×10^{-38}	38.00
Hydroxide ion	OH^-	O^{2-}		

conjugate bases stronger than OH^-

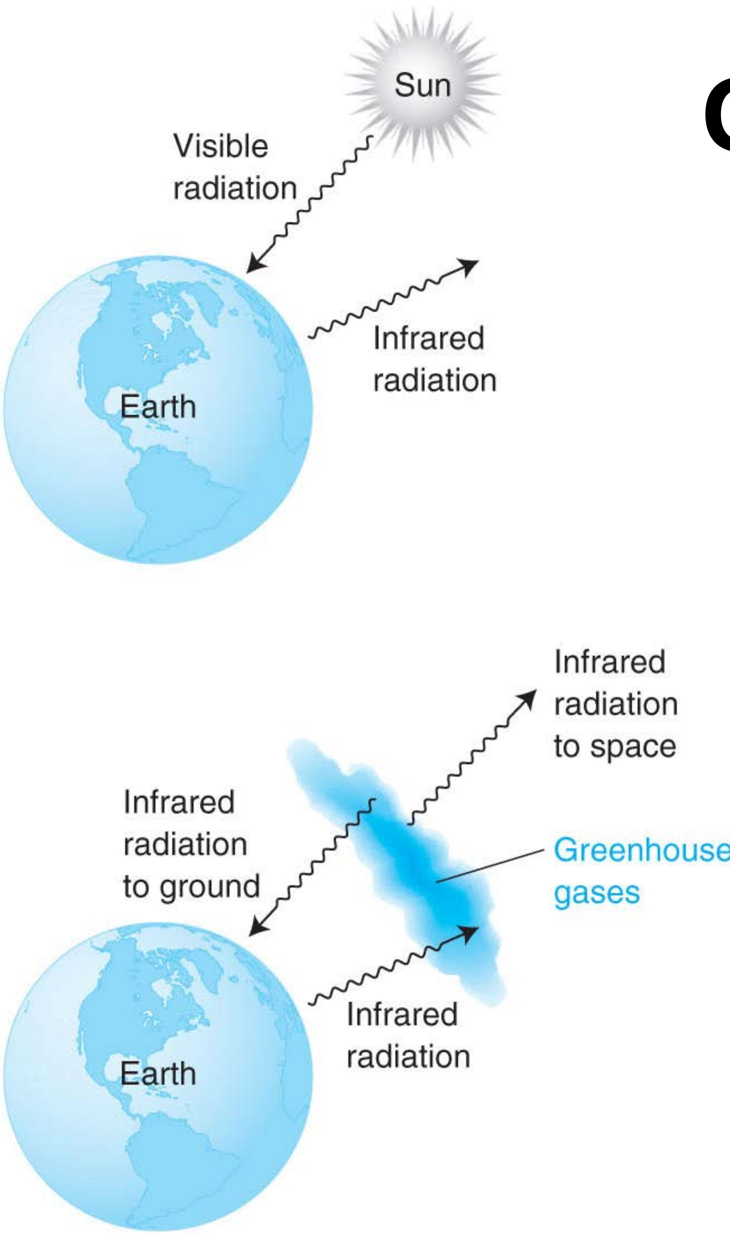
Blackbody Radiation and the Greenhouse Effect



Balance between energy reaching Earth from the sun and energy reradiated to space.

Greenhouse Effect

Average temperature of earth's surface is about **59ºF**. Without any greenhouse gases it would be near **-2ºF**.



greenhouse gases:

carbon dioxide, **CO_2**

methane, CH_4

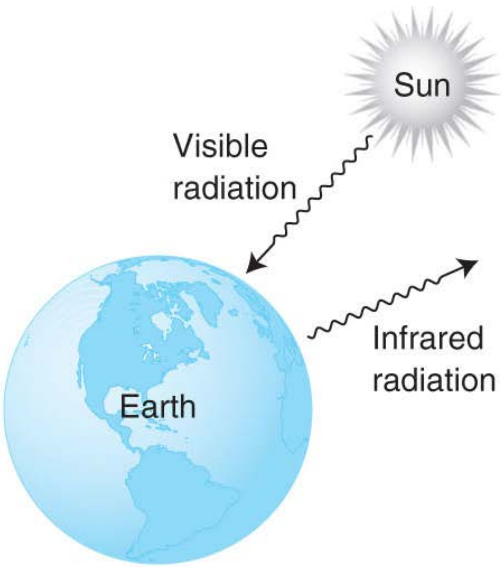
(30 times more potent than CO_2)

Nitrous oxide, N_2O

FIGURE 0-5 *Greenhouse effect.* The sun warms the Earth mainly with visible radiation. Earth emits infrared radiation, which would all go into space in the absence of the atmosphere. Greenhouse gases in the atmosphere absorb some of the infrared radiation and emit some of that radiation back to the Earth. Radiation directed back to Earth by greenhouse gases keeps the Earth warmer than it would be in the absence of greenhouse gases.

Harris, *Quantitative Chemical Analysis,* 8e

Greenhouse Effect



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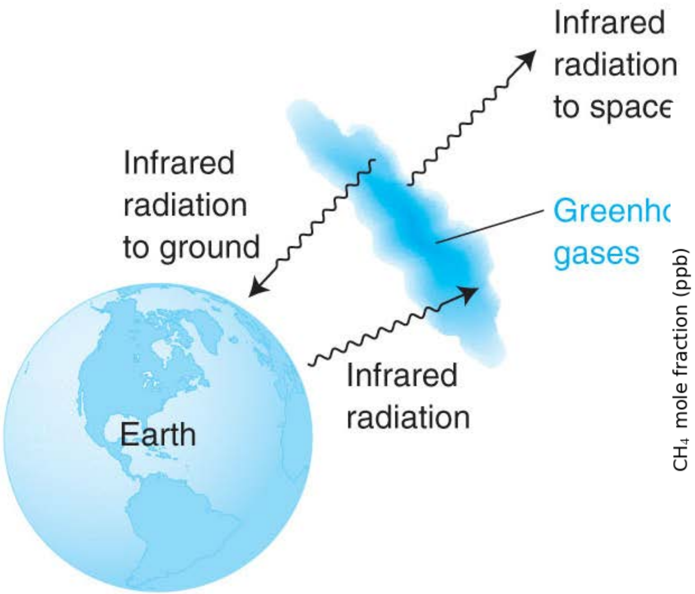
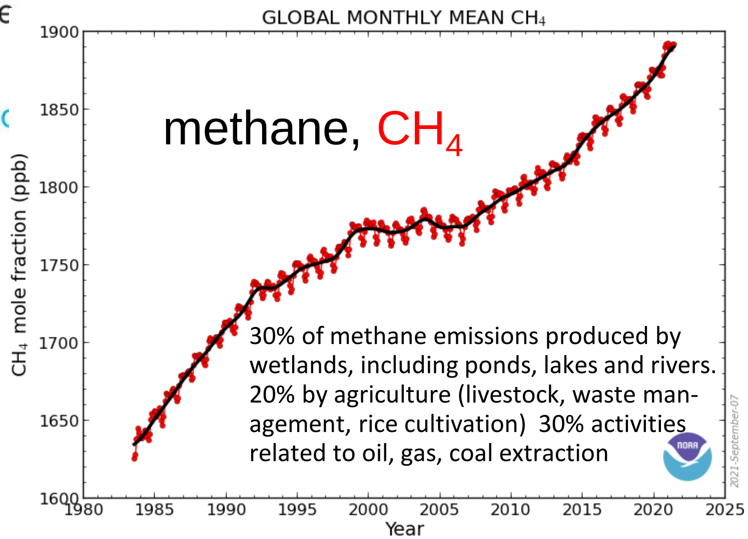


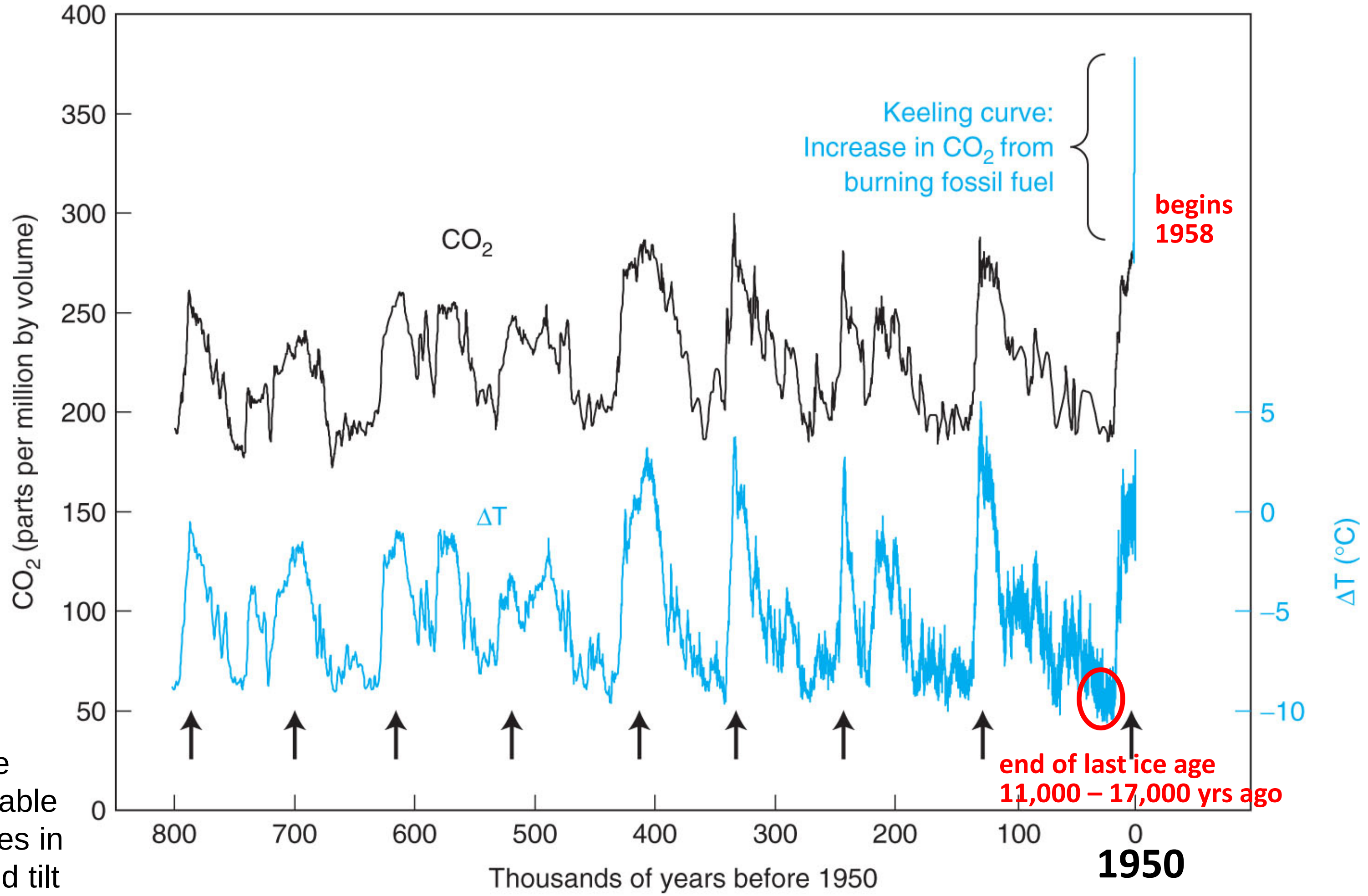
greenhouse gases:

- carbon dioxide, **CO_2**
- methane, CH_4
  (30 times more potent than CO_2)
- Nitrous oxide, N_2O



temperature from $^{16}O/^{18}O$

age from annual layers of snowfall



↑ Temperature change attributable to cyclic changes in Earth's orbit and tilt

1998 - Russia, US, France in Antartica – 3623 meters!

FIGURE 0-6 Significance of the Keeling curve (upper right, color) is shown by plotting it on the same graph with atmospheric CO_2 measured in air bubbles trapped in ice cores drilled from Antarctica. Atmospheric temperature at the level where precipitation forms is deduced from hydrogen and oxygen isotopic composition of the ice. [Vostok ice core data from J. M. Barnola, D. Raynaud, C. Lorius, and N. I. Barkov, http://cdiac.esd.ornl.gov/ftp/trends/co2/vostok.icecore.co2.]

temperature from $^{16}O/^{18}O$

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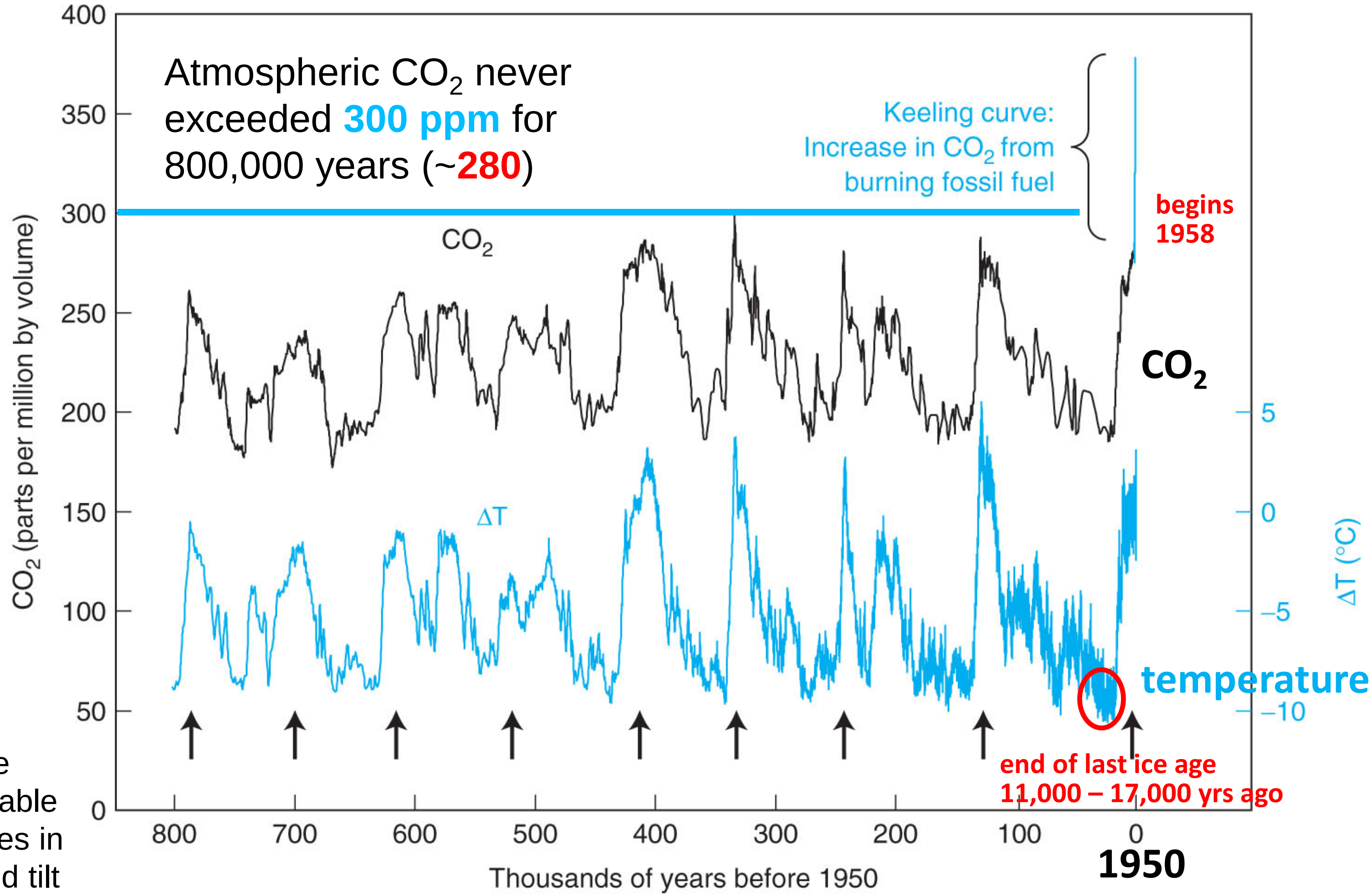


↑ Temperature change attributable to cyclic changes in Earth's orbit and tilt

1998 - Russia, US, France in Antartica – 3623 meters!

last time the atmospheric CO_2 amounts were this high was more than 3 million years ago, when temperature was 2°–3°C (**3.6°–5.4°F**) **higher** than during the pre-industrial era, and sea level was 15–25 meters (**50–80 feet**) **higher** than today

Increase in CO_2 Over Past 60 Years

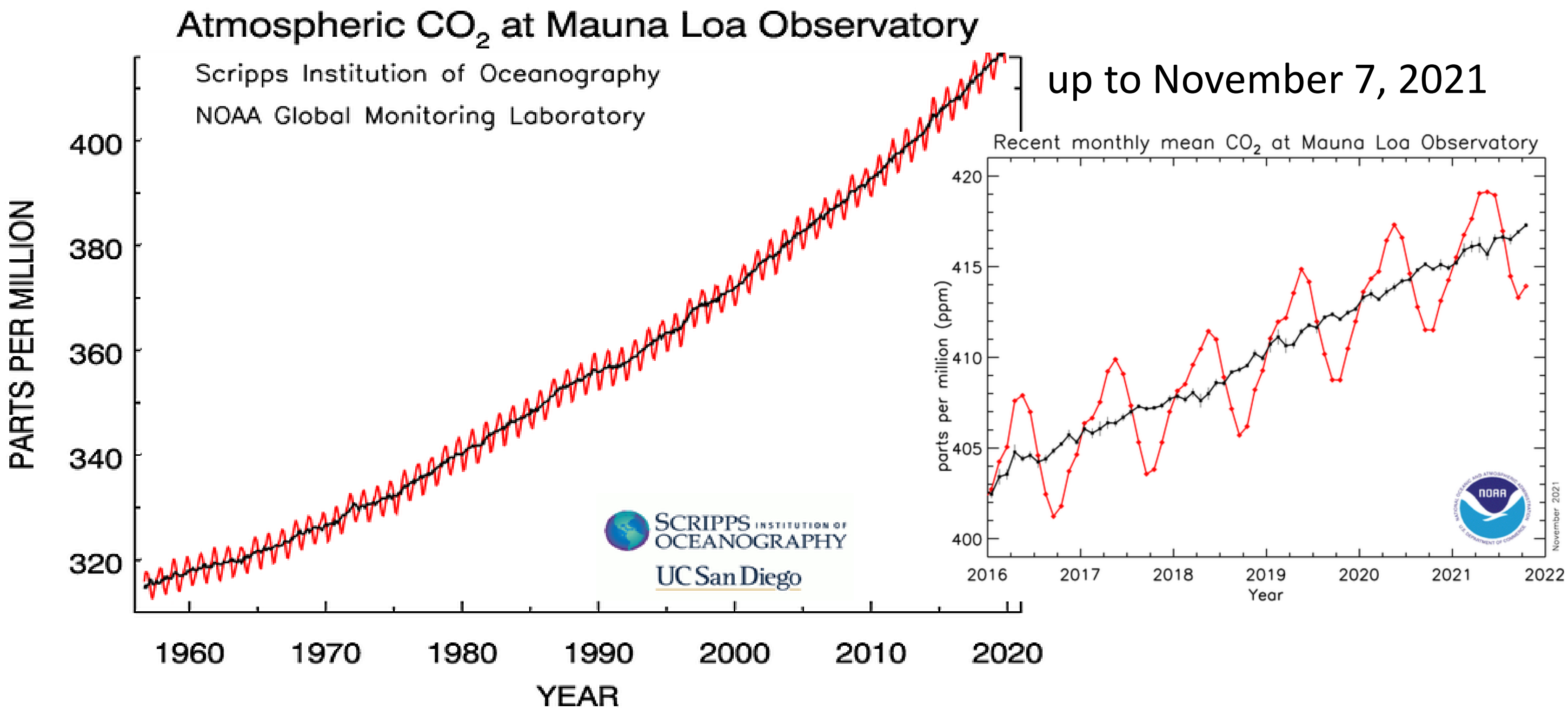
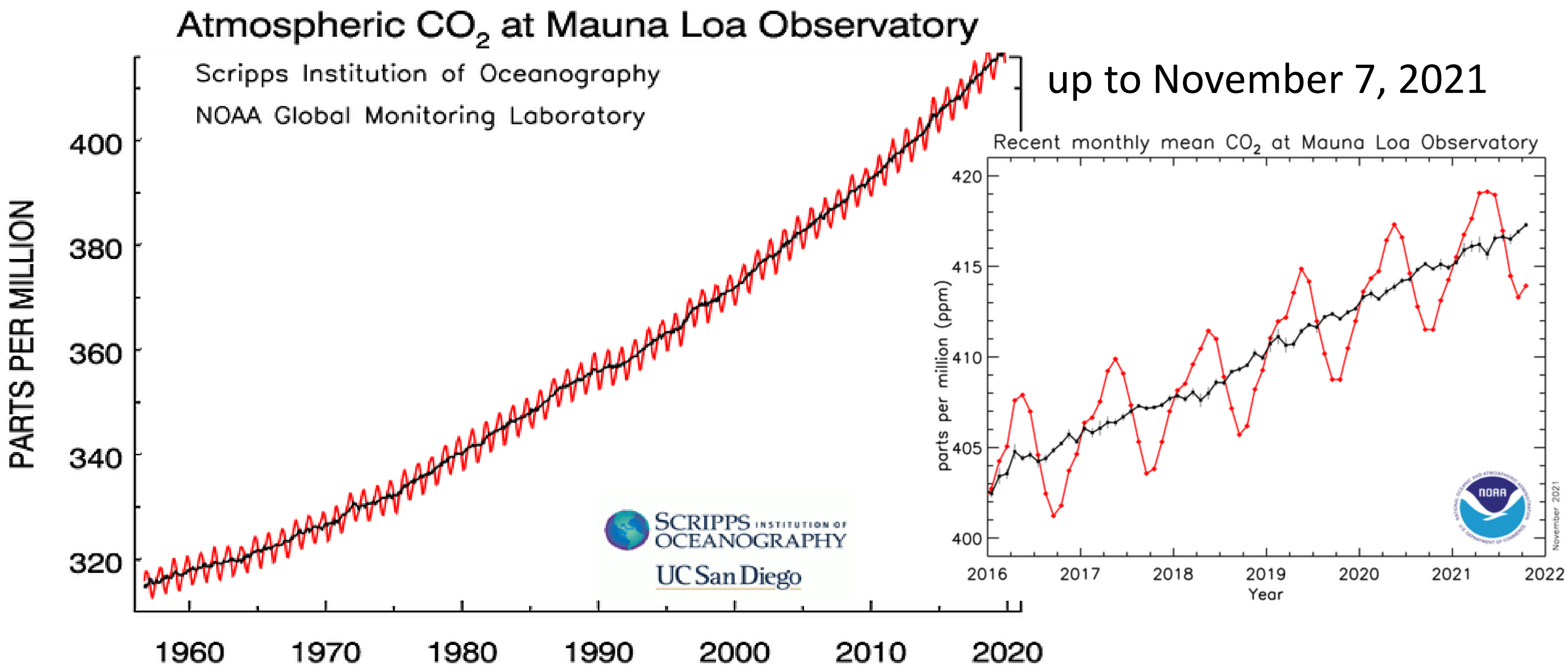


FIGURE 0-4 Monthly average atmospheric CO_2 measured on Mauna Loa. This graph, known as the *Keeling curve*, shows seasonal oscillations superimposed on rising CO_2. [Data from http://scrippsco2.ucsd.edu/data/in_situ_co2/monthly_mlo.csv.]

Historic CO_2 high of 280 ppm over 800,000 years increased to current 416 ppm in past 200 years due to burning fossil fuel (oil, coal, wood, natural gas) and destruction - “clearing” - of earth’s forests.

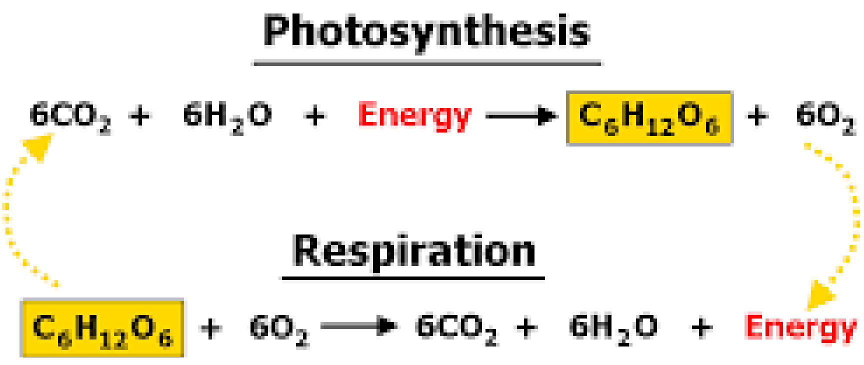
Increase in CO_2 Over Past 60 Years



The atmospheric burden of CO_2 is now comparable to where it was during the Pliocene Climatic Optimum, between 4.1 and 4.5 million years ago, when CO_2 was close to, or above 400 ppm. During that time, sea level was about 78 feet higher than today, the average temperature was 7 degrees Fahrenheit higher than in pre-industrial times.

In February, the United States officially rejoined the Paris Agreement on climate change. Yet, as the measurements from Mauna Loa show, despite decades of negotiation, the global community has been unable to meaningfully slow, let alone reverse, annual increases in atmospheric CO_2 levels.

Nature withdrawing CO_2 from air for plant growth during summer and returning it each succeeding winter



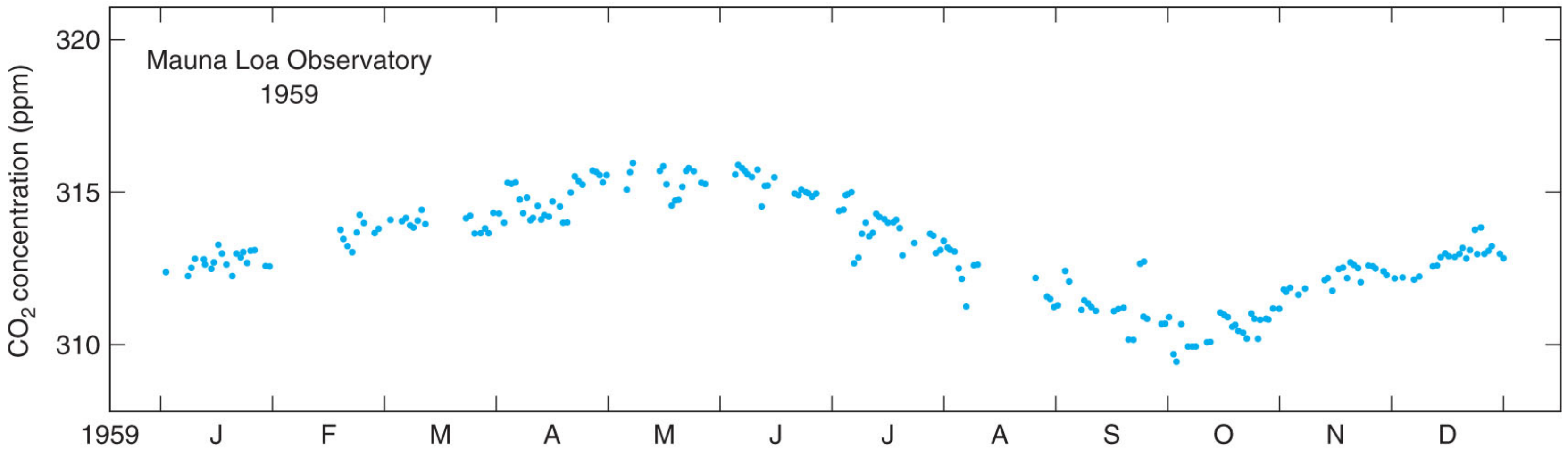
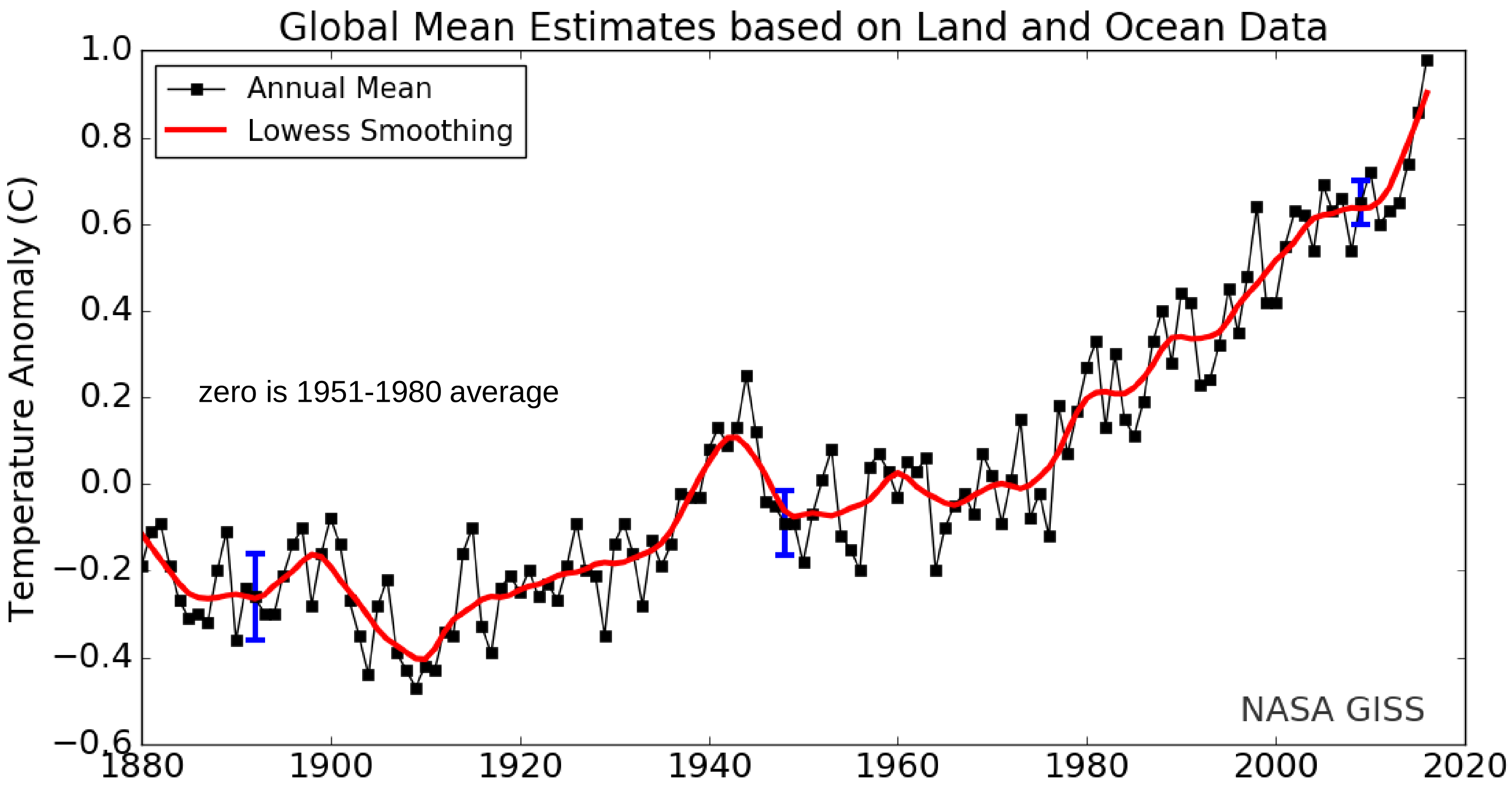


FIGURE 0-3 Atmospheric CO_2 measurements from Mauna Loa in 1958–1959. [J. D. Pales and C. D. Keeling, "The Concentration of Atmospheric Carbon Dioxide in Hawaii," *J. Geophys. Res.* **1965**, *70*, 6053.]

Global Warming



One effect of increasing levels of CO_2 in our atmosphere

sea
butterflies

base of marine
food chain

Pteropod

Low carbonate concentration promotes dissolution of $CaCO_3$ shells and skeletons

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Increasing atmospheric CO_2 increases concentration of CO_2 dissolved in oceans, which consumes carbonate and lowers the pH

$$\underset{(H_2CO_3)}{CO_2(aq) + H_2O(l)} + CO_3^{2-}(aq) \rightleftharpoons 2\,HCO_3^{-}(aq)$$

$$H_2CO_3: K_{a1} = 4.5 \times 10^{-7}, K_{a2} = 4.7 \times 10^{-11}$$

pre-industrial pH of oceans = 8.16
currently ocean pH = 8.04
without change, pH by 2100 = 7.7-7.8

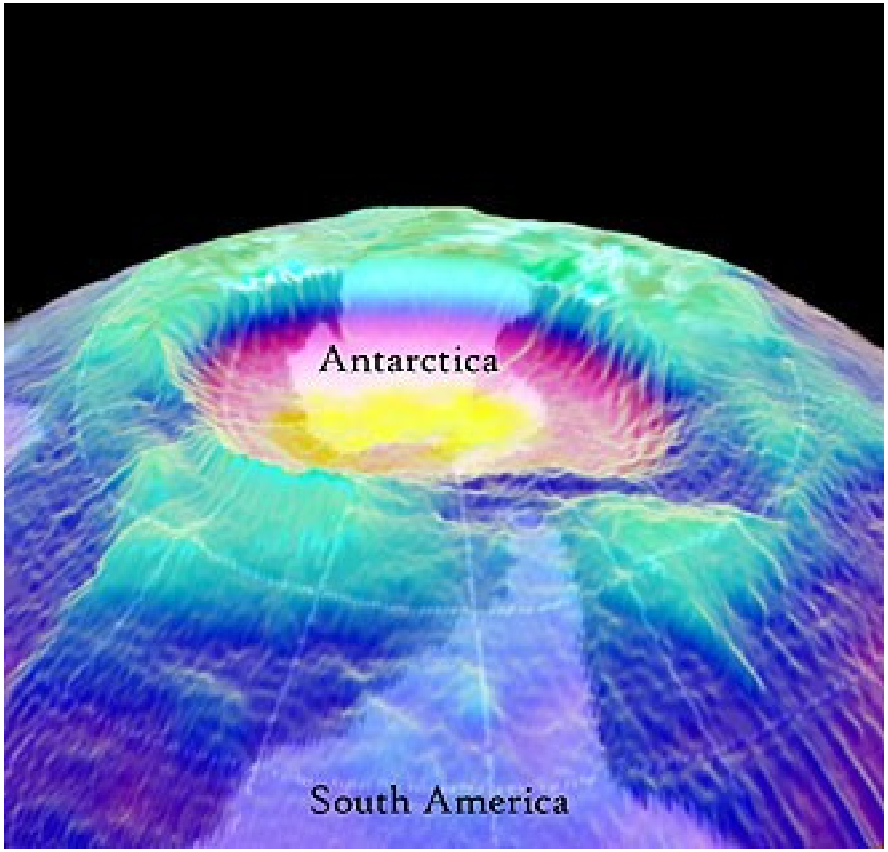
(earth not experienced such low pH in > 20 million years)

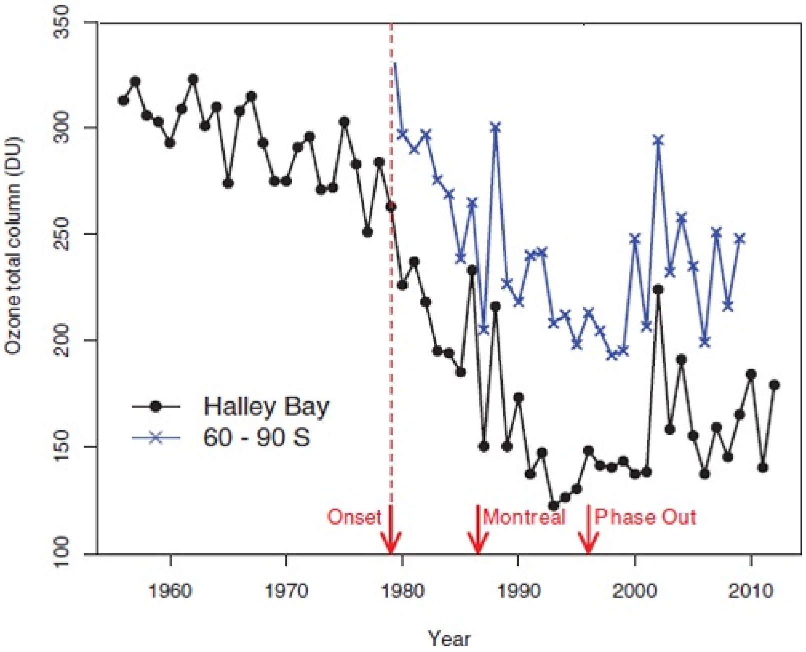
shell beginning to dissolve

The Ozone Hole

A success story – use of Freons stopped (Montreal Protocol) and hole is healing

bans emissions of ozone depleting chemicals





Big hole (size of North America) still there but ozone concentration does not appear to be decreasing further.

(estimates than hole will "heal" – attain pre-1980 levels – by 2060)

FINAL Review

Final Exam:
Tuesday, December 7, 8:00 – 10:00 am, 312 Lincoln Hall

On OWL
- ChemWorks Review Topics
- Mastery Review Topics

On Website:
- Harris Review Topics
- Zumdahl Review Topics
- Equation Sheet for Final

FINAL Review

KNOWN TOPICS

- Isotopes
- Lewis Structures
- Balancing Redox Reaction by Half-Reaction Method
- Titrations
- Nomenclature
- Stoichiometry Calculations
- Colligative Properties