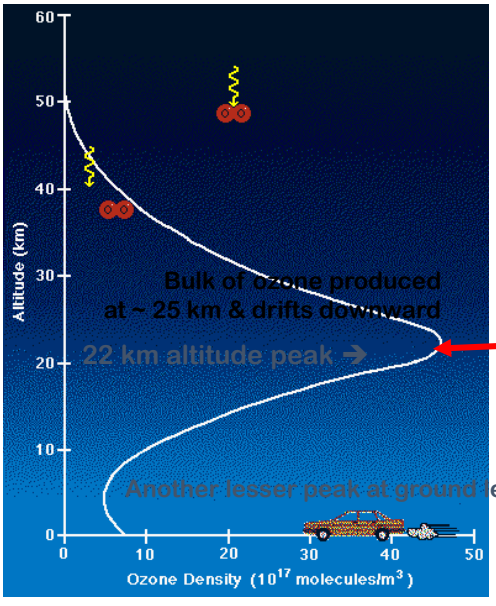
OZONE DEPLETION IN THE STRATOSPHERE

1



First we'll focus on the "GOOD" ozone located in the STRATOSPHERE (the ozone that is being depleted leading to an ozone "hole")

2

WHY IT'S THERE

to: the natural
"Chapman Mechanism

(a series of photochemical reactions)

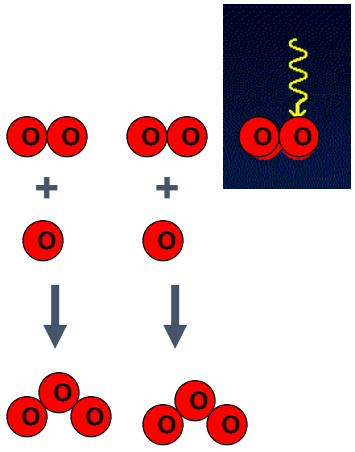
3

THE CHAPMAN MECHANISM

(first proposed in 1930s)

- ozone is continuously produced and destroyed
- through PHOTOCHEMICAL REACTIONS in the stratosphere
- involves oxygen (O_2), molecular oxygen (O), photons of UV radiation, and OZONE (O_3).

4

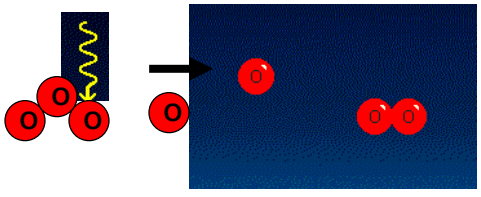


The Chapman Mechanism

Ozone exists in the upper atmosphere as a consequence of photochemical reactions between molecular oxygen and sunlight:

$$O_2 + O_2 + O_2 + \text{sunlight}$$
$$\rightarrow O_2 + O + O + O_2$$
$$\rightarrow O_3 + O_3$$

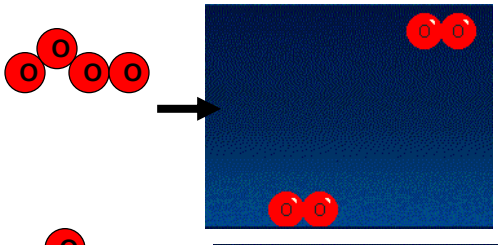
5



Ozone is destroyed naturally by reaction with ultraviolet radiation:

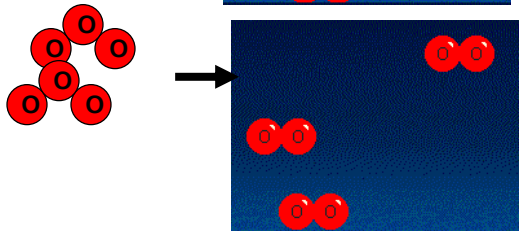
$$O_3 + UV \rightarrow O_2 + O$$

This is part of how the ozone layer protects the earth's surface from ultraviolet radiation.



Ozone is also destroyed naturally by reactions promoted by collisions with atomic oxygen:

$$O_3 + O \rightarrow 2\,O_2$$



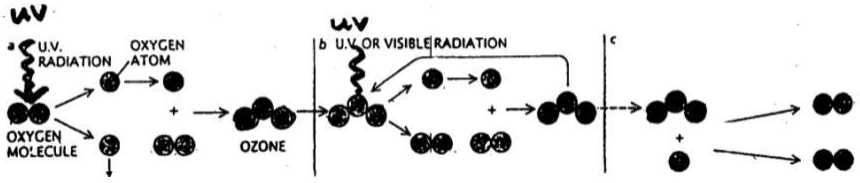
As well as being destroyed by collisions with itself:

$$O_3 + O_3 \rightarrow 3\,O_2$$

6

The Chapman Mechanism

(another view)



Ozone being formed naturally

Ozone being destroyed naturally

Ozone being formed naturally

Ozone being destroyed naturally

7

In theory:

- **a balance of ozone is established over time**

> prevents much of the harmful UV radiation from reaching the earth's surface.

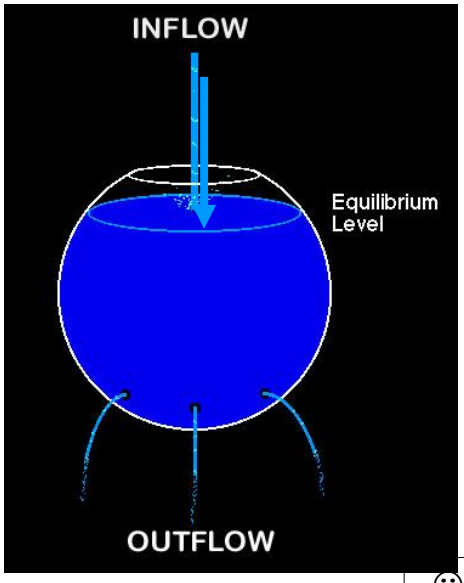
Leads to an "Equilibrium" or "Steady State"

8

STEADY STATE =

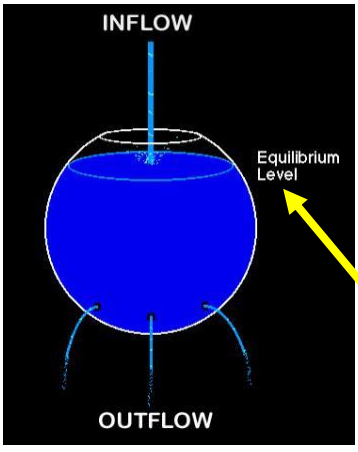
a condition in which the STATE of a system component (e.g. reservoir)

is CONSTANT over time.



☺

9



Steady state can be achieved in a reservoir:

a) **if there are no inflows or outflows, *or***

b) **if the rate of inflow = the rate of outflow.**

Any imbalance in these rates leads to a change in the level of the reservoir.

10

FLOW DIAGRAM OF A STEADY STATE

Inflow

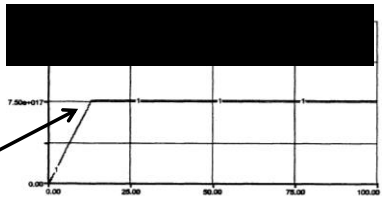
Ozone being formed via natural Chapman mechanism

Reservoir of STRATOSPHERIC OZONE

Outflow

Ozone being destroyed via natural Chapman mechanism

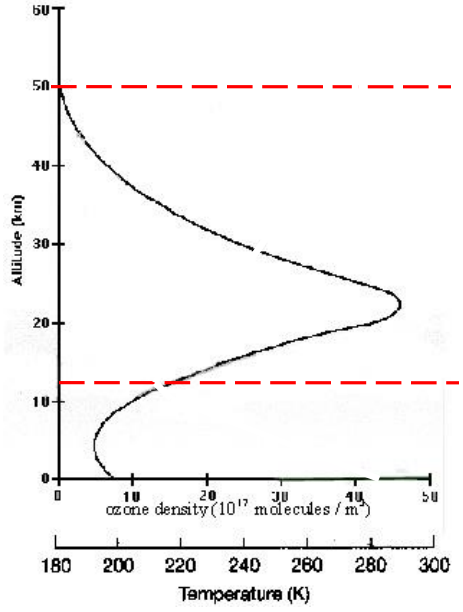
After an initial period of adjustment a steady state is reached ➔ as a horizontal line



Ozone reservoir

☺

11



TEMPERATURE

[increases / decreases]

with increasing altitude in the stratosphere

WHY???

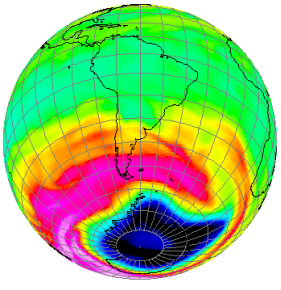
12

Why is there an increase in temperature with altitude in the STRATOSPHERE?

1. It is the closest layer to the sun, hence it is closest to the solar "heat source."
2. It receives large amounts of UV radiation from the sun PLUS it has a high concentration of ozone to absorb this UV.
3. It is the layer which contains most of the GH gases that absorb IR radiation emitted by the Earth's surface.

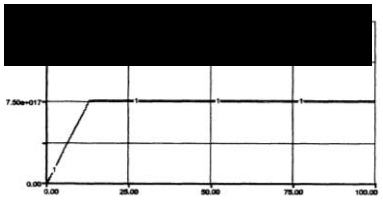
13

THE DESTRUCTION OF STRATOSPHERIC OZONE

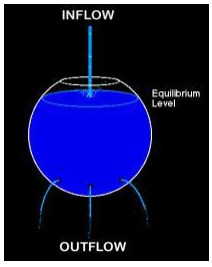


14

The Chapman Mechansim "balance" is being disrupted by the introduction of CFC's and other similar gases into the stratosphere:



Ozone reservoir



CFCs are photo-dissociated into FREE CHLORINE ATOMS (Cl) and other molecular fragments by UV rays

> Chlorine (and other gases such as Nitric oxide, NO) act as catalysts in ozone loss reactions

15

CATALYST =

A compound that increases the rate of a chemical reaction and is itself unchanged by the reaction

Through chemical reactions:

- **the chlorine removes ozone from the stratosphere**
- **and also frees more chlorine atoms to begin the process all over again**

16

Missing Element –
Catalytic Destruction of Ozone

- Four main "families" of chemicals responsible for catalyzing ozone destruction:

1. Nitrogen oxides: NO_x
   - NO + NO_2
2. Hydrogen oxides: HO_x
   - OH + HO_2
3. Chlorine: ClO_x
   - Cl + ClO
4. Bromine: BrO_x
   - Br + BrO

A common type of catalytic destruction cycle (there are others)

$$Y + O_3 \rightarrow YO + O_2$$

$$YO + O \rightarrow Y + O_2$$

where Y = NO, OH, Cl or Br

17

Sources of Catalysts

- Stratospheric NO_x
  - Source: tropospheric N_2O
  - Natural sources (mostly)
  - 10% increase since 1850 (ie, due to anthropogenic activities...mostly fertilizer application)
- Stratospheric HO_x
  - Source: tropospheric CH_4, H_2, H_2O
  - Much is natural, however...
  - 150% increase in tropospheric CH_4 since 1850 (agricultural activities; landfills; other sources)
- Stratospheric Cl and Br
  - Almost entirely due to human activity
  - Sources: tropospheric CFCs, HCFCs, halons

18

CFCs

- *Lecture Question*
  - What are CFCs? What are they used for?

  - CFCs are ***chlorofluorocarbons***; they are small molecules that contain chlorine, fluorine and carbon atoms. Usually there are only 1-2 carbon atoms.
  - CFCs are sometimes called ***Freons*** (that was their trade name for DuPont)
  - CFCs are referred to by a number. The most common CFCs are: CFC-11, CFC-12, CFC-113 (formulas on the next page)
  - HCFCs are CFCs that contain hydrogen. This makes them more reactive to the OH radical, decreasing their tropospheric lifetime. That means that, on a pound-per-pound basis, HCFCs ("soft CFCs") destroy less stratospheric ozone than CFCs ("hard CFCs") because a smaller fraction of HCFCs "survive" to reach the stratosphere

19

STRATOSPHERIC OZONE PRODUCTION AND LOSS

Chapman reactions

$O_2 + h\nu(\lambda<243nm) \rightarrow O + O$ *oxygen photolysis*

$O + O_2 + M \rightarrow O_3 + M$ *ozone formation*

$O + O_3 \rightarrow O_2 + O_2$ *ozone destruction*

$O_3 + h\nu(\lambda<310nm) \rightarrow O(^1D) + O_2$

$O_3 + h\nu(\lambda<1180nm) \rightarrow O + O_2$ *oxygen photolysis*

NO2 photolysis (lower stratosphere) + TROPOSPHERE

$NO_2 + h\nu(\lambda<243nm) \rightarrow NO + O$ *NO_2 photolysis*

$O + O_2 + M \rightarrow O_3 + M$ *ozone formation*

Catalytic destruction

$X + O_3 \rightarrow XO + O_2$

$XO + O \rightarrow X + O_2$

Net $O + O_3 \rightarrow O_2 + O_2$ *ozone destruction*

[X = H, OH, NO, Cl, Br, etc]

20

CHAPMAN MECHANISM FOR STRATOSPHERIC O_3

1) $O_2 + h\nu \rightarrow O + O$ $\quad J_1 \simeq 5\times10^{-12}\ s^{-1}$
2) $O + O_2 + M \rightarrow O_3 + M$ $\quad k_2 = 6\times10^{-34}(T/300)^{-2}$
3) $O_3 + h\nu \rightarrow O + O_2$ $\quad J_3 = 2\times10^{-3}\ s^{-1}$
4) $O + O_3 \rightarrow O_2 + O_2$ $\quad k_4 = 1\times10^{-11}\exp(-2100/T)$

Reactions 2 & 3 very fast → O & O_3 in steady state

$k_2[O_2][M][O] = J_3[O_3]$ defines ratio $[O]/[O_3]$:

$$[O] = [O_3]\cdot\frac{J_3}{k_2[O_2][M]} \qquad (i)$$

Reactions 2 & 3 INTERCONVERT the 'ODD OXYGEN', $[O]+[O_3]$

Time scale for Reactions 1 & 4: hrs at 40 km, years at 20km
Rate of change of odd oxygen

$$\frac{d([O]+[O_3])}{dt} = 2J_1[O_2] - 2k_4[O][O_3]$$

Steady state only in upper stratosphere: = 0; [O] from (i)

$$[O_3]^2 = \frac{2J_1[O_2]}{2k_4}\cdot\frac{k_2[O_2][M]}{J_3}$$

since $[O_2] = 0.21[M]$

$$[O_3] = J_1^{1/2}\left(\frac{k_2}{k_4 J_3}\right)\cdot 0.21\,[M]^{3/2}$$

effect of altitude ↑ CONSTANT ↖

THEREFORE $[O_3]$ MUST GO THROUGH A MAXIMUM

21

RELEASE OF ACTIVE SPECIES IN THE STRATOSPHERE

- BY PHOTOLYSIS :

$$CFCl_3 \xrightarrow{h\nu} CFCl_2 + Cl$$
$$CF_3Br \xrightarrow{h\nu} CF_3 + Br$$
$$N_2O \xrightarrow{h\nu} N_2 + O(^1D)$$

- BY REACTION :

$$O(^1D) + N_2O \rightarrow 2NO$$
$$OH + CHF_2Cl \rightarrow H_2O + CF_2O + Cl$$
$$OH + CH_3Br \rightarrow H_2O + CH_2O + Br$$
$$O(^1D) + H_2O \rightarrow 2OH$$
$$OH + CH_4 \rightarrow H_2O + CH_3$$
$$\hookrightarrow H_2O + CO_2$$

22

If appropriate values of constants and P, T (= M) for 40 km, the value of $[O_3]$ is TOO HIGH BY A FACTOR OF 4. k_4 is much slower than originally thought.

CATALYTIC REACTIONS

X = OH, H Hampson, 1965
X = NO, NO_2 Crutzen, 1969
X = Cl, ClO Cicerone, 1974

NITROGEN OXIDES

5) $NO + O_3 \rightarrow NO_2 + O_2$ $k_5 = 2\times10^{-12}\exp(-1400/T)$
6) $NO_2 + h\nu \rightarrow NO + O$ $J_6 \simeq 10^{-2}\ s^{-1}$
2) $O + O_2 + M \rightarrow O_3 + M$

no net reaction: NULL CYCLE for odd oxygen.

$$[NO] = \frac{[NO_2]}{[O_3]} \cdot \frac{J_6}{k_5}$$

In the stratosphere [O] increases with height, then

7) $NO_2 + O \rightarrow NO + O_2$ $k_7 = 9\times10^{-12}$

Reaction (7) removes odd oxygen and so reacting (5)+(7) give CATALYTIC OZONE LOSS

$$[NO] = \frac{[NO_2]}{[O_3]} \frac{J_6 + k_7[O]}{k_5}$$

$$-\frac{d([O]+[O_3])}{dt} = k_5[NO][O_3] + k_7[NO_2][O] + J_6[NO_2]$$

substitute $= 2k_7[NO_2][O]$

ACCOUNTS FOR ~ 50% OF OZONE LOSS

RATE DETERMINING STEP

23

CHLORINE OXIDES

$CF_2Cl_2 + h\nu \rightarrow Cl + CF_2Cl$

$+CH_4 \rightarrow$ HCl – main stratospheric form of INORGANIC CHLORINE at 40 km

8) $OH + HCl \rightarrow H_2O + Cl$
9) $Cl + O_3 \rightarrow ClO + O_2$ } RAPID INTERCONVERSION & OZONE LOSS
• 10) $ClO + O \rightarrow Cl + O_2$ }
11) $Cl + CH_4 \rightarrow HCl + CH_3$ • = Rate det° step

$$-\frac{d([Cl]+[ClO])}{dt} = k_8[OH][HCl] - k_{11}[Cl][CH_4] = 0$$

$$([Cl]+[ClO]) = [OH]\ \frac{k_7[HCl]}{k_8[CH_4]}$$

↓ INCREASES WITH Z — CONSTANT WITH Z

At 40 km major loss route for ozone

COUPLING WITH CHLORINE & NITROGEN OXIDES

AT 25–35 km CHLORINE NITRATE is a major ClO_x RESERVOIR

12) $ClO + NO_2 + M \rightarrow ClONO_2 + M$
13) $ClONO_2 + h\nu \rightarrow Cl + NO_3$

'TIES UP' active chlorine in a form that doesn't deplete ozone.

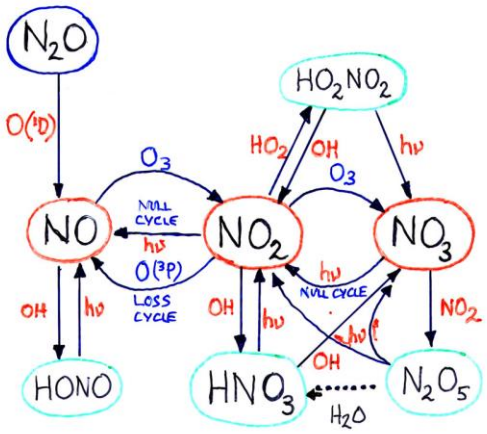
ALSO HAVE NO PRESENT

14) $ClO + NO \rightarrow Cl + NO_2$ NULL CYCLE
6) $NO_2 + h\nu \rightarrow NO + O$ ODD OXYGEN RETURNED:

NITROGEN OXIDES REDUCE EFFICIENCY OF O_3 LOSS BY ClO_x

24

NITROGEN OXIDES IN THE STRATOSPHERE

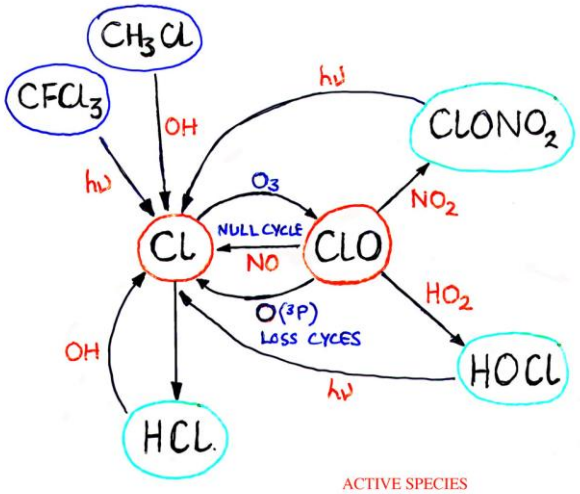


REACTIVE SPECIES
RESERVOIRS
SOURCE GASES & O_3
····· heterogeneous reation

•••• heterogeneous reactions on sulphate aerosol

25

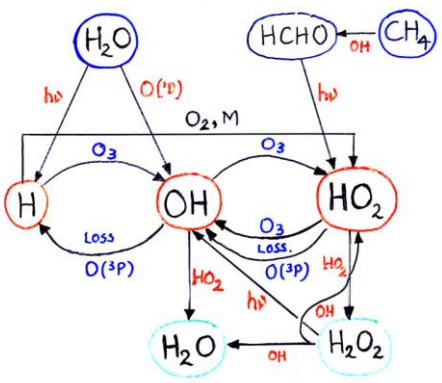
CHLORINE CHEMISTRY IN STRATOSPHERE



ACTIVE SPECIES
RESERVOIRS
SOURCE GASES O_3

26

HYDROGEN CHEMISTRY IN THE STRATOSPHERE



OZONE LOSS via HO_x:

mesosphere
$H + O_3 \rightarrow OH + O_2$
$OH + O \rightarrow H + O_2$
$\Rightarrow O + O_3 \rightarrow 2O_2$

upper stratosphere
$OH + O_3 \rightarrow HO_2 + O_2$
$HO_2 + O \rightarrow OH + O_2$
$\Rightarrow O + O_3 \rightarrow 2O_2$

lower stratosphere
$HO_2 + O_3 \rightarrow OH + 2O_2$
$\Rightarrow O_3 + O_3 \rightarrow 3O_2$

27

OZONE DEPLETION CYCLES INVOLVING HALOGENS THE LOWER STRATOSPHERE

Involving ClOx/NOx coupling

$$ClO + NO_2 = ClONO_2$$
$$ClONO_2 + h\nu = Cl + NO_3$$
$$NO_3 + h\nu = NO + O_2$$
$$NO + O_3 = NO_2 + O_2$$
$$Cl + O_3 = ClO + O_2$$

net $O_3 + O_3 = 3O_2$

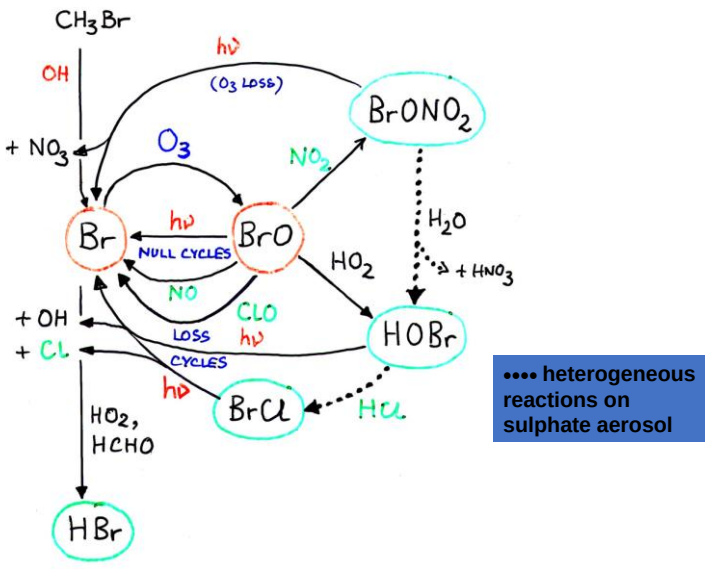
Involving NOx/Halogen (X = Br or I) coupling

$$XO + HO_2 = HOX + O_2$$
$$HOX + h\nu = X + HO$$
$$OH + O_3 = HO_2 + O_2$$
$$X + O_3 = XO + O_2$$

net $O_3 + O_3 = 3O_2$

28

BROMINE CHEMISTRY IN THE STRATOSPHERE



29

WHY ANTARCTICA?

ozone "hole(s)"

REGIONALITY **SEASONALITY**

> it is most severe over Antarctica in S.H. spring (Sep, Oct);

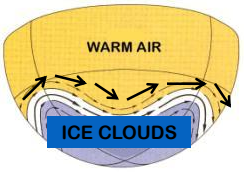
> a less severe depletion (not a true hole) occurs over the Arctic in N.H. spring (Feb, Mar)

30

special conditions that make ozone depletion most severe over polar regions (esp. Antarctica) are:

CIRCUMPOLAR CIRCULATION PATTERN

winter which isolates the stratosphere inside a vortex and acts like a "containment vessel" in which chemical reactions may occur in near isolation



presence of POLAR STRATOSPHERIC ICE CLOUDS -- on the surfaces of these extremely cold cloud particles certain chemical reactions are more efficient and faster

Key Concept

31

[Go to movie clip]

32