Fundamentals of Earth's Atmosphere

AOSC / CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett

Class Web Site: <u>http://www.atmos.umd.edu/~rjs/class/spr2019</u> Email: Ross: <u>rsalawit@umd.edu</u> or <u>rjs@atmos.umd.edu</u> Walt: wtribett@umd.edu

Goals:

- 1) Tie up loose ends from last lecture
- 2) Barometric law (pressure vs height)
- 3) Thermal structure (temperature vs height)
- 4) Geostrophy (balance of pressure force & Coriolis Force ⇔ storms)
- 5) Ferrel Cell (mean circulation Earth's atmosphere ⇔ climate regimes)

Lecture 3 7 February 2019

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In class, I had shown a version of the figure from a National Academies of Sciences report entitled *Surface Temperature Reconstructions for the Last 2000 Years*, published in 2006.

The original source of this figure is Chapter 2 of the 2001 IPCC report:



Figure 2.20: Millennial Northern Hemisphere (NH) temperature reconstruction (blue) and instrumental data (red) from AD 1000 to 1999, adapted from Mann *et al.* (1999). Smoother version of NH series (black), linear trend from AD 1000 to 1850 (purple-dashed) and two standard error limits (grey shaded) are shown.

https://archive.ipcc.ch/ipccreports/tar/wg1/pdf/TAR-02.PDF Mann *et al.*, *GRL*, 1999: https://agupubs.onlinelibrary.wiley.com/doi/10.1029/1999GL900070

Lots more info in:



https://www.amazon.com/Hockey-Stick-Climate-Wars-Dispatches/dp/0231152558

This is a great book to get an understanding of the political war being waged over the climate change issue today, as well as a bit about how science works. It is not intended to explain climate science, although it does cover some of the techniques used in putting together an estimate of earth's surface temperature over the past 1000 years (the so-called "hockey stick"). But that is not the major part of either the book or climate science. The hockey stick is important not for scientific reasons but because it has become an icon, conveying visually that the stable climate that fostered the creation of human civilization supporting 7 billion people has undergone a radical change in the last 100 years. And there is no end in sight. First paragraph of top Amazon review by **Wendy Fehlauer**

Book published in 2012 so lacks salacious details of the recent political war being waged over climate change.

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Tropospheric Pollutants (The Air We Breathe)

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Table 1.2 U.S. National Ambient Air Quality Standards					
Pollutant	Standard (ppm)	Approximate Equivalent Concentration (µg/m ³)			
Carbon monoxide					
8-hr average	9 10,000				
1-hr average	35	40,000			
Nitrogen dioxide					
Annual average	0.053	100			
Ozone					
8-hr average	0.075	147			
1-hr average	0.12	235			
Particulates*					
PM ₁₀ , annual average	-	50			
PM ₁₀ , 24-hr average	-	150			
PM _{2.5} , annual average	-	15			
PM _{2.5} , 24-hr average [†]		35			
Sulfur dioxide					
Annual average	0.03	80			
24-hr average	0.14	365			
3-hr average	0.50	1,300			

*PM₁₀ refers to all airborne particles 10 μ m in diameter or less. PM_{2.5} refers to particles 2.5 μ m in diameter

or less.

—The unit of ppm is not applicable to particulates.

 $^{\dagger}\text{PM}_{2.5}$ standards are likely to be revised after 2011.

Source: U.S. Environmental Protection Agency. Standards also exist for lead, but are not included here. Chapter 1, Chemistry in Context

AT3, Q1:

What was the U.S. NAAQS for exposure to ozone over an 8 hr period of time in 2012, the time the 7th edition of *Chemistry in Context* was published, in units of parts per million? 0.075 ppm

AT3, Q2:

Express the answer to Qu 1 in units of parts per billion. (0.075 parts / 1×10^6) × (1×10^9) = 75 ppb

AT3, Q3:

Based on your own internet research, what is the current U.S. NAAQS standard for ozone?

2015 EPA NAAQS Standard for O_3 is 0.070 ppm or 70 ppb

Air Quality Standards and Why We Care

Year	Averaging Period	EPA Surface Ozone Standard
1979	1 hr	125 ppb
1997	8 hr	85 ppb
2008	8 hr	75 ppb
2015 [#]	8 hr *	70 ppb

 * The 8 hr standard is met when the 3-yr average of the annual 4th highest daily maximum 8 hr O_3 is less than 70 ppb



[#] On October 1, 2015 the EPA lowered the NAAQS for ground-level ozone 70 ppb, based on extensive scientific evidence about the harmful effects of tropospheric ozone

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Significant Improvements in *Local* Air Quality since early 1980s



http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

Tropospheric Ozone Production

Shown in Lecture 2

 $\begin{array}{l} \mathrm{CO} + \mathrm{OH} \rightarrow \mathrm{CO}_2 + \mathrm{H} \\ \mathrm{H} + \mathrm{O}_2 + \mathrm{M} \rightarrow \mathrm{HO}_2 + \mathrm{M} \\ \mathrm{HO}_2 + \mathrm{NO} \rightarrow \mathrm{OH} + \mathrm{NO}_2 \\ \mathrm{NO}_2 + \mathrm{hv} \rightarrow \mathrm{OH} + \mathrm{OO}_2 \\ \mathrm{O+O}_2 + \mathrm{M} \rightarrow \mathrm{O}_3 + \mathrm{M} \end{array}$

Net: $CO + 2 O_2 \rightarrow CO_2 + O_3$

More complicated tropospheric O_3 production pathway $RH + OH \rightarrow R + H_2O$ $R + O_2 + M \rightarrow RO_2 + M$ $RO_2 + NO \rightarrow RO + NO_2$ $RO + O_2 \rightarrow HO_2 + R'CHO$ $HO_2 + NO \rightarrow OH + NO_2$ $2 \times NO_2 + hv \rightarrow NO + O$ $2 \times O + O_2 + M \rightarrow O_3 + M$

Net:
$$RH + 4O_2 \rightarrow R'CHO + H_2O + 2O_3$$

Note: Chemists use the symbol R to represent molecules based upon CH_3 Examples of RH and R'CHO : CH_4 (methane) $\rightarrow CH_2O$ (formaldehyde) : C_2H_6 (ethane) $\rightarrow CH_3CHO$ (acetaledhyde) : C_3H_8 (propane) $\rightarrow CH_3COCH_3$ (acetone)

Section 1.8 of CC provides a description of the vocabulary of chemistry relevant for this class

AT1, Q2: Nitrogen oxides, carbon monoxide, and hydrocarbons emitted by <u>combustion of fossil fuels</u> (mainly coal and gasoline) lead to production of tropospheric O₃

Sunlight is required for production of O₃ because [OH] & [HO₂] are very small at night

Trees and plants emit hydrocarbons such as isoprene (C_5H_8) or pinene ($C_{10}H_{16}$) that can also lead to production of tropospheric O_3 in the presence of elevated [NO_x]

Methane (CH₄), the primary component of natural gas, burns <u>much more cleanly</u> than either coal or gasoline and as such is touted as the "cleanest" fossil fuel.

What is one potential problem of switching from coal to natural gas?

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Speaking of Chemical Nomenclature

Nitrogen Dioxide: NO₂

Radical involved with numerous aspects of tropospheric and stratospheric chemistry



https://www.youtube.com/watch?v=0XTkO8KypUY

Nitrous Oxide aka Dinitrogen monoxide: N₂O

Very long-lived, <u>nearly inert</u>, well mixed greenhouse gas. Rising abundance linked mainly to human use of fertilizer. Causes global warming. Decomposes in the stratosphere, leading to production of NO₂



https://www.youtube.com/watch?v=ZIHIQhJIWNs

Nitrous: "Relating to or containing nitrogen" https://www.yourdictionary.com/nitrous

Pressure versus Altitude



- Pressure = Force per unit area
- · Graph shows how "force" of atmosphere varies as a function of altitude
- Pressure shown in units of mbar : 1 mbar = 10³ dynes/cm²
- 1 dyne = gm cm / sec²; therefore 1 mbar = 10³ gm / cm sec²
- · Also:
 - European community prefers to write hPa; 1 hPa is exactly equal to 1 mbar
 - 1 atmosphere = p/p_{STANDARD}, where p_{STANDARD} = 1013.25 mbar (or 1013.25 hPa)

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Pressure versus Altitude



Derivation of the Barometric Law involves use of the Ideal Gas Law: $p \ Vol = n \ R \ T$ where p is pressure, Vol is volume, n is the number of moles of a gas, R is the gas constant (8.3143×10⁷ $\frac{\text{ergs}}{\text{K mole}}$), and T is temperature as shown on Extra Slide 1 at end of Class Notes (you will not be tested on this!)

· Barometric law describes the variation of Earth's pressure with respect to altitude:

Pressure (z) = Pressure (surface) × $e^{-z/H}$ where H is called the "scale height" Can show H = R_{EARTH} T (z) / grav , Since R_{EARTH} = 2.88 × 10⁶ ergs / K gm grav = 981 cm sec⁻² and T(lower trop) ≈ 272 K then H (z=0) = 8.0 × 10⁵ cm = 8 km

Pressure versus Altitude





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Pressure (z) = Pressure (surface) × $e^{-z/H}$ where H is called the "scale height" Can show H = R_{EARTH} T (z) / grav , Since R_{EARTH} = 2.88 × 10⁶ ergs / K gm grav = 981 cm sec⁻² and T(lower trop) ≈ 272 K then H (z=0) = 8.0 × 10⁵ cm = 8 km

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Pressure versus Altitude



• Barometric law describes the variation of Earth's pressure with respect to altitude:

Pressure (z) = Pressure (surface) $\times e^{-z/H}$ Two plots convey the same information !

Pressure versus Altitude



• Barometric law describes the variation of Earth's pressure with respect to altitude:

Pressure (z) = Pressure (surface) $\times e^{-z/H}$

Let's take a closer look at log pressure versus altitude, in the troposphere

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· Barometric law describes the variation of Earth's pressure with respect to altitude:

Pressure (z) = Pressure (surface) $\times e^{-z/H}$

How does pressure vary as a function of depth, in the ocean ?

Temperature versus Altitude



• T falls wrt increasing altit until the tropopause, then rises wrt altit until the stratopause, then falls wrt to rising altitude

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Atmospheric Radiation

- Solar irradiance (<u>downwelling</u>) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K "black body" temperature)
- Thermal irradiance (<u>upwelling</u>) at top of the atmosphere occurs at wavelengths between ~5 and 50 μm (~245 K "black body" temperature)



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Effective Temperature

Earth absorbs solar energy "as a disk" \Rightarrow (1 – Albedo) × S π R_e² Earth emits thermal energy "as a sphere" $\Rightarrow \sigma 4\pi$ R_e²T_{EFF}⁴

$$(1-Albedo) \times S = 4 \sigma T_{EFF}^4$$

or

$$T_{EFF} = \{ (1 - Albedo) \times S / 4 \sigma \}^{1/4}$$

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Effective Temperature

Let's take a closer look at S = (1370 W m^{-2})



FAQ 1.1, Figure 1. Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming solar radiation is absorbed by the Earth's surface. This energy is transferred to the atmosphere by warming the air in contact with the surface (thermals), by evapotranspiration and by longwave radiation that is absorbed by douds and greenhouse gases. The atmosphere in turn radiates longwave energy back to Earth as well as out to space. Source: Kieli and Tenberth (1997).

Effective Temperature



distance of Earth from the Sun. So by definition, <u>Earth's orbit is 1 Au from the Sun</u>

2) The diagram above represents orbits as perfect spheres, which is suitable for our study of effective temperatures. In reality, of course, planets orbit the Sun in an elliptical manner.

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$$T_{EFF} = \{ (1 - Albedo) \times S / 4 \sigma \}^{1/4}$$

633 students: find T_{EFF} for Earth, using: $\sigma ~=~ 5.67 \times 10^{-8} ~W ~m^{-2} ~K^{-4}$ S $~=~ 1370 ~W ~m^{-2}$

Albedo = 0.3

433 student whose last name begins with letters A-M: Find T_{EFF} for **Mars** using: $\sigma = 5.67 \times 10^{-8}$ W m⁻² K⁻⁴ S = 1370 W m⁻² Albedo = 0.17 **Distance from Sun = 1.5 AU**

433 student whose last name begins with letters N-Z: Find T_{EFF} for **Venus** using:

 $σ = 5.67 \times 10^{-8}$ W m⁻² K⁻⁴ S = 1370 W m⁻² Albedo = 0.75 **Distance from Sun = 0.72 AU**

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Effective Temperature

My Favorite Planets



Venus: $T_{\text{SURFACE}}\approx753\text{ K}$

 $T_{\text{EFFECTIVE}} \approx ???$

Earth: T_{SURFACE} ≈ 288 K

 $T_{EFFECTIVE} \approx ???$

 $\begin{array}{l} Mars \\ T_{SURFACE} \approx 217 \ K \end{array}$

 $T_{EFFECTIVE} \approx ???$

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Geological Evolution of Earth's Atmosphere: *Earth, Mars, and Venus*

	Earth	Venus	Mars
Radius (km)	6400	6100	3400
Mass (10 ²⁴ kg)	6.0	4.9	0.6
Albedo	0.3	0.8	0.22
Distance from Sun (A.U.)	1	0.72	1.52
Surface Pressure (atm)	1	91	0.007
Surface Temperature (K)	~15 °C	~ 460 °C	-140 °C to 20 °C
N ₂ (mol/mol)	0.78	3.4×10 ⁻²	2.7 ×10 ⁻²
O ₂ (mol/mol)	0.21	6.9 ×10 ⁻⁵	1.3 ×10 ⁻³
CO ₂ (mol/mol)	3.7 ×10 ⁻⁴	0.96	0.95
H ₂ O (mol/mol)	1 ×10 ⁻²	3 ×10 ⁻³	3 ×10 ⁻⁴
SO ₂ (mol/mol)	1 ×10 ⁻⁹	1.5 ×10 ⁻⁴	Nil
Cloud Composition	H ₂ O	H_2SO_4	Mineral Dust

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Geological Evolution of Earth's Atmosphere: *Earth. Mars. and Venus*



Billions of years ago Venus had water. Most of this would have been in the form of vapor, since Venus is closer to the Sun. Water vapor is a greenhouse gas so heat from the Sun would have been trapped, temperature would have risen, and CO_2 would have been "baked" out of carbonate rocks. These circumstances likely led to increasing temperature in an strongly positive, upward spiraling fashion, leading to a "hot house" planet that persists today. https://www.sciencefocus.com/space/why-are-venus-and-mars-so-different-to-earth

Scientists debate whether a runaway greenhouse effect could occur on Earth https://en.wikipedia.org/wiki/Runaway_greenhouse_effect

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Temperature versus Altitude

Let's take a closer look at T_{FFF} = 255 K



Temperature versus Altitude

Let's take a closer look at T_{EFF} = 255 K



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Temperature versus Altitude



• T falls wrt increasing altit until the tropopause, then rises wrt altit until the stratopause, then falls wrt to rising altitude

If the troposphere is dry, dT/dz = – grav / c_p where c_p is specific heat of air at constant pressure = 1 × 10⁷ erg gm⁻¹ K⁻¹ Note: 1 erg = 1 dyne cm = gm cm² sec⁻² ⇔ dT/dz^{DRY} = – 981 cm sec⁻²/ (10⁷ cm² sec⁻² K⁻¹) × 10⁵ cm/km = 9.8 K / km

Dry adiabatic lapse rate

Temperature versus Altitude



• T falls wrt increasing altit until the tropopause, then rises wrt altit until the stratopause, then falls wrt to rising altitude

If the troposphere is dry, dT/dz = - grav / c_p where c_p is specific heat of air at constant pressure = 1 × 10⁷ erg gm⁻¹ K⁻¹ Note: 1 erg = 1 dyne cm = gm cm² sec⁻² ⇔ dT/dz^{DRY} = - 981 cm sec⁻²/ (10⁷ cm² sec⁻² K⁻¹) × 10⁵ cm/km = 9.8 K / km Dry adiabatic lapse rate

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Temperature versus Altitude



• T falls wrt increasing altit until the tropopause, then rises wrt altit until the stratopause, then falls wrt to rising altitude

Fourth chart expresses abundance of ozone concentration, or ozone density, or $[O_3]$, in units of molecules / cm³

Back to the ATs

AT3, Q4:

According to *Chemistry in Context*, if all of the ozone in Earth's atmosphere could be isolated and brought to the surface at a pressure of 1 atmosphere and a temperature of 15°C), the resulting gas would have a thickness of how many centimeters?



1 Dobson Unit is defined to be a 0.01 millimeter thickness of air, at "standard temperature and pressure" Today we have about 300 Dobson Units (CC) = 300 × 0.01 millimeter = 3 millimeter or 0.3 cm of ozone, isolated and compressed to STP, between us and outer space.

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AT3, Q4:

According to *Chemistry in Context*, if all of the ozone in Earth's atmosphere could be isolated and brought to the surface at a pressure of 1 atmosphere and a temperature of 15°C), the resulting gas would have a thickness of how many centimeters?

Back to the ATs



Back to the ATs

AT3, Q4:

According to Chemistry in Context, if all of the ozone in Earth's atmosphere could be isolated and brought to the surface at a pressure of 1 atmosphere and a temperature of 15°C), the resulting gas would have a thickness of how many centimeters? 0.5 cm

AT3. Q5:

if all of the molecules in the entirety of Earth's atmosphere could be isolated and brought to the surface (at a pressure of 1 atmosphere and a temperature of 15°C), the resulting gas would have a thickness of about 7.4 x 10⁵ cm

Compute the mean mixing ratio of ozone throughout Earth's atmosphere (this is a simple ratio of two numbers), express the answer in parts per million.

Mean mixing ratio of ozone: 0.5 cm / 7.4×10^5 cm = 6.8×10^{-7} (no units!)

Note: mixing ratio has used throughout this class means number mixing ratio or:

moles of a particular gas moles of all gases in the air sample

1 moles of a particular gas To convert 6.8×10^{-7} to ppm, need to realize 1 ppm corresponds to: 10⁶ moles of all gases in the air sample

Hence, $6.8 \times 10^{-7} \times 1$ ppm / 10^6 = 0.68 ppm *OR* ppb

Compare your answer to the NAAQS for O₃ given in your answer to either Q1 or Q3.

Specifically:

Is the mean mixing ratio of O₃ throughout Earth's atmosphere larger or smaller than the current U.S. NAAQS for O₃? and

What figure in the assigned material from CC provides the "explanation" to the comparison of these two values?

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Back to the ATs

AT3, Q4:

According to Chemistry in Context, if all of the ozone in Earth's atmosphere could be isolated and brought to the surface at a pressure of 1 atmosphere and a temperature of 15°C), the resulting gas would have a thickness of how many centimeters?

AT3, Q5:

if all of the molecules in the entirety of Earth's atmosphere could be isolated and brought to the surface (at a pressure of 1 atmosphere and a temperature of 15°C), the resulting gas would have a thickness of about 7.4 x 10⁵ cm

Compute the mean mixing ratio of ozone throughout Earth's atmosphere (this is a simple ratio of two numbers), express the answer in parts per million.

(no units!) Mean mixing ratio of ozone: 0.5 cm / 7.4×10^5 cm =

moles of a particular gas

Note: mixing ratio has used throughout this class means number mixing ratio or: moles of all gases in the air sample

1 moles of a particular gas To convert 6.8×10^{-7} to ppm, need to realize 1 ppm corresponds to:

10⁶ moles of all gases in the air sample

Hence, $6.8 \times 10^{-7} \times 1 \text{ ppm} / 10^6 =$ ____ **ppm *OR***____ **ppb**

Compare your answer to the NAAQS for O₃ given in your answer to either Q1 or Q3.

Specifically:

Is the mean mixing ratio of O₃ throughout Earth's atmosphere larger or smaller than the current U.S. NAAQS for O₃? and

What figure in the assigned material from CC provides the "explanation" to the comparison of these two values?

Mean mixing ratio of O₃ in Earth's Atmosphere >> than U.S. NAAQS Much higher mixing ratios of O_3 in the stratosphere than ever exists near the surface

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Temperature versus Altitude



• T falls wrt increasing altit until the tropopause, then rises wrt altit until the stratopause, then falls wrt to rising altitude

Chart on far right expresses ozone mixing ratio, O_3 mr in dimensionless units, where O_3 mr = $[O_3] / [M]$, where [M] is the concentration (or density) of air

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Coriolis Force

So far, we've reviewed temperature, pressure, and the balance between solar energy input to the atmosphere and terrestrial radiation leaving the atmosphere.

There's one more piece of the puzzle that we need to be familiar with.



Coriolis Force



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http://lasp.colorado.edu/~bagenal/3720/CLASS15/15EVM-Dyn1.html

Earth's rotation provides an apparent force that deflects air to the right in the Northern Hemisphere, to the left in the Southern Hemisphere.

Force is proportional to sin(latitude), so vanishes at the equator

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Geostrophy



Figure 8.16 Track of an air parcel in the vicinity of a low pressure region in the Northern Hemisphere. The parcel is initially at rest but then adjusts to the pressure gradient force and the Coriolis force to achieve geostrophic balance.



Figure 8.17 Same situation as in 8.16, except that the parcel is in the vicinity of a high pressure region in the Northern Hemisphere.

From "The Atmospheric Environment", M. B. McElroy

Geostrophic balance: balance between Coriolis Force and pressure gradient

Geostrophy

NH Weather System:



Cyclonic Flow: when the wind swirls counter-clockwise in the NH

Hurricane: Cyclonic flow occurring in the N Atlantic or NE Pacific Ocean east of the dateline. **Typhoon:** Cyclonic flow occurring over the NW Pacific Ocean, west of the dateline.

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Next Lecture: Climates of the Past

Next Reading:

Chemistry in Context, Secs 2.2, 3.0, 3.1, 3.2 (~14 pgs)

as well as 8 pages from *Global Warming: The Complete Briefing* by Houghton 7 pages from *Paris Beacon of Hope*

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