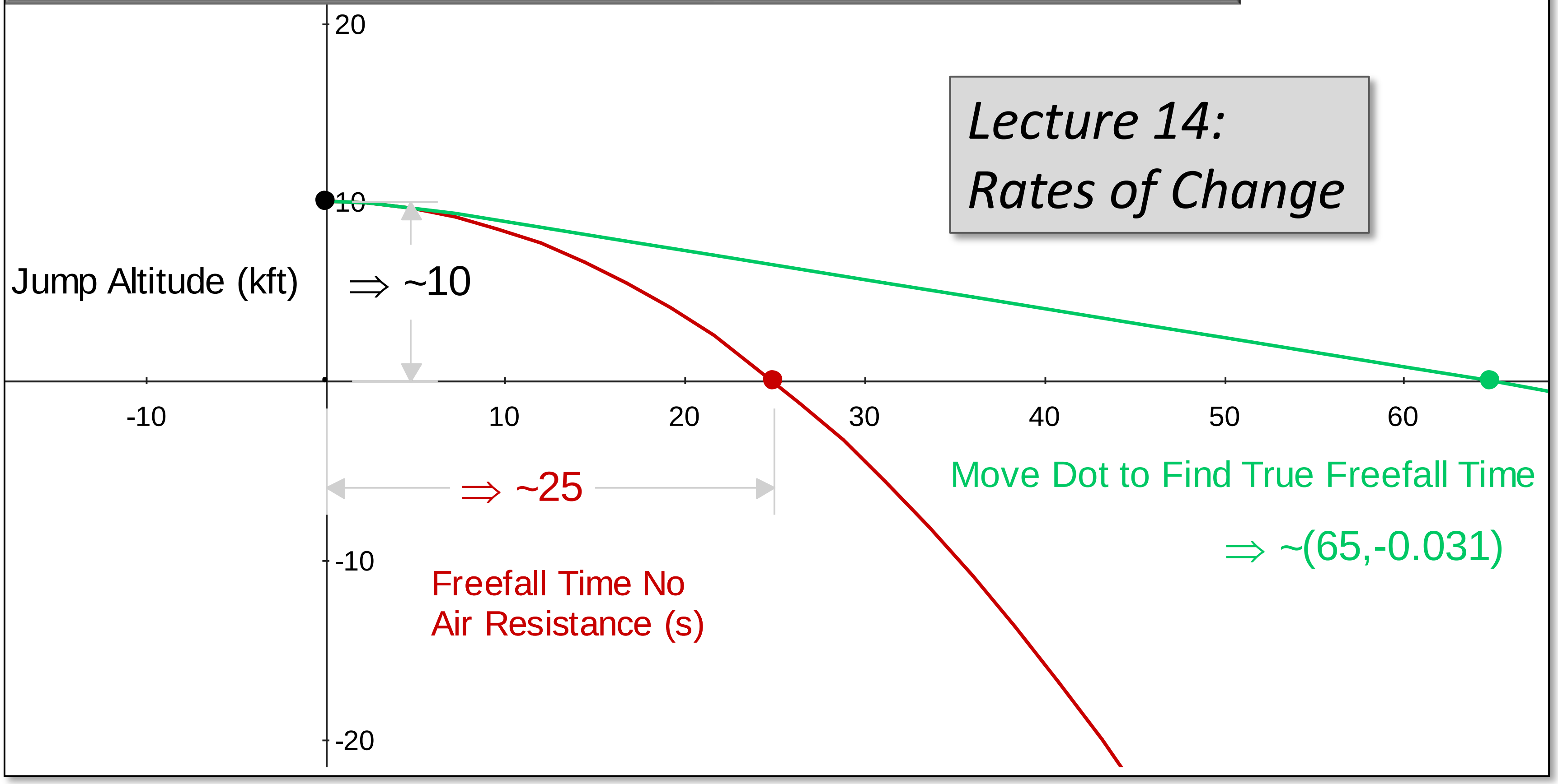
# Learning Calculus With Geometry Expressions™

by L. Van Warren



## Lecture 14: Rates of Change

# *Chapter 4: Rates and Extremes*

| LECTURE | TOPIC |
|---|---|
| **14** | **RATES OF CHANGE** |
| 15 | RELATED RATES |
| 16 | EXTREMA – MAXIMA AND MINIMA |
| 17 | DERIVATIVE TESTS AND MEAN VALUE THEOREM |
| 18 | OPTIMIZATION |

# Inspiration

*- Renate Schmid / MFO*

**Cédric Villani, Ph.D.** - Rising Star – Born 1973

Known for work in Boltzmann Equations of Statistical Mechanics

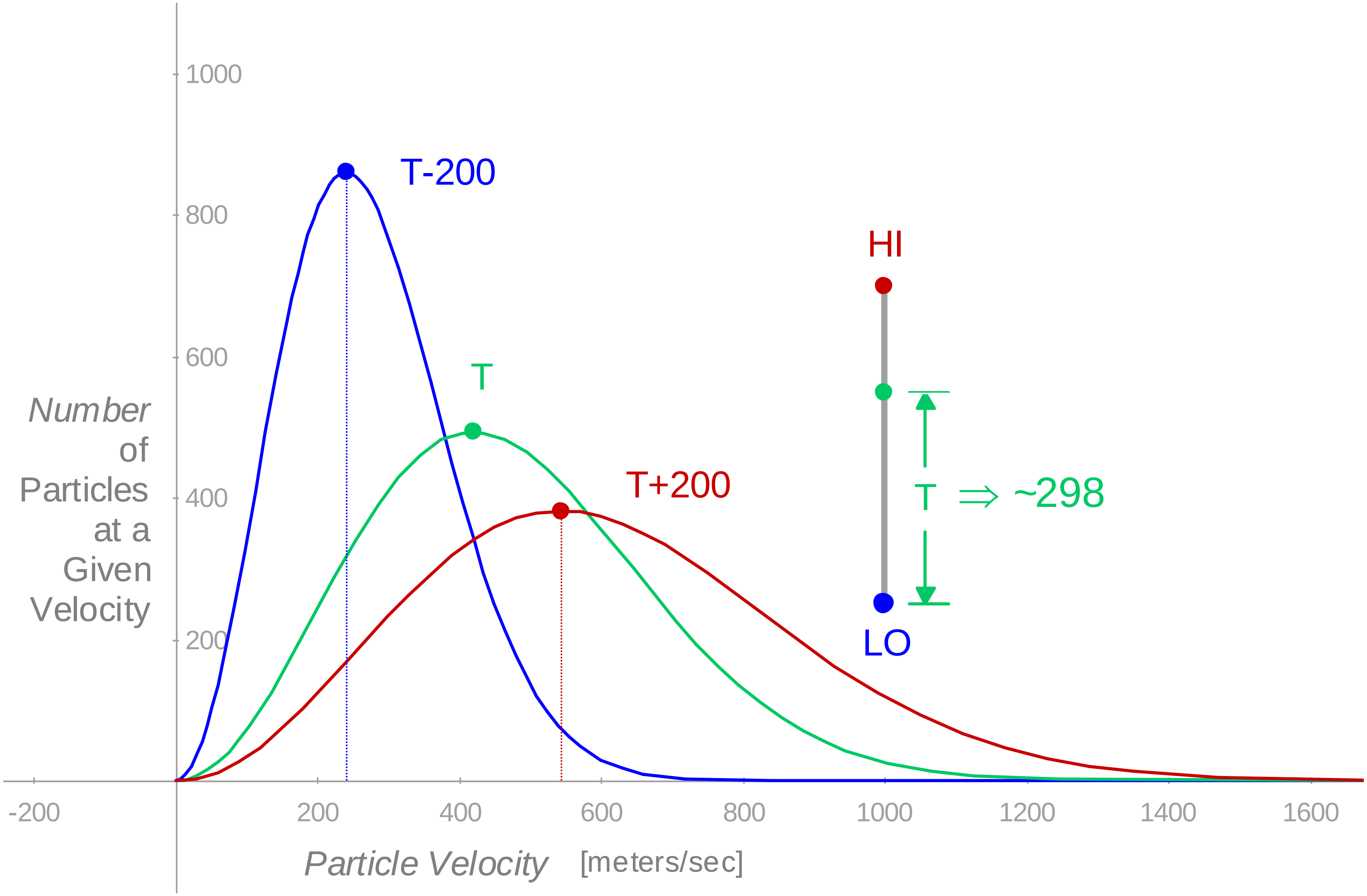
Fluent in English, French, Italian
Plays Piano

| | |
|---|---|
| Residence | Paris, France |
| Doctoral advisor | Pierre-Louis Lions |

Notable awards:

| | |
|---|---|
| Herbrand Prize | 2007 |
| EMS Prize | 2008 |
| Fermat Prize | 2009 |
| Fields Medal | 2010 |

# MAXWELL-BOLTZMANN DISTRIBUTION OF GAS PARTICLE VELOCITIES



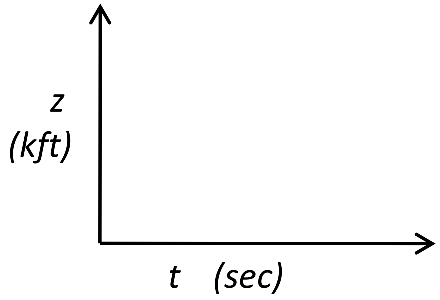
# THIS FALLING BUSINESS

One of the best positions for freefall is the hard arch, arms flung back, head back, and legs relaxed. Like a badminton birdie, the hard arch stabilizes your fall and prevents tumbling and spinning.

Parachutes come in handy for freefall, especially when multiple jumps are planned. An altimeter is worn to track downward progress. For the math of this falling business, we define a few terms…

*Cal Lesser by Barry Maple, learnskydiving.co.uk*

# TERMS OF FALLING:



Time on t axis (formerly x)
Altitude on z axis (formerly y)

Position is Altitude = z = z = $f'(t)$;
Velocity is Fall rate = v = dz/dt = $f''(t)$;
Acceleration is Gravity (g) = a = dv/dt = $f'''(t)$;
Jerk is Opening Shock = j = da/dt = $f'''(t)$;

# POSITION, VELOCITY, ACCELERATION

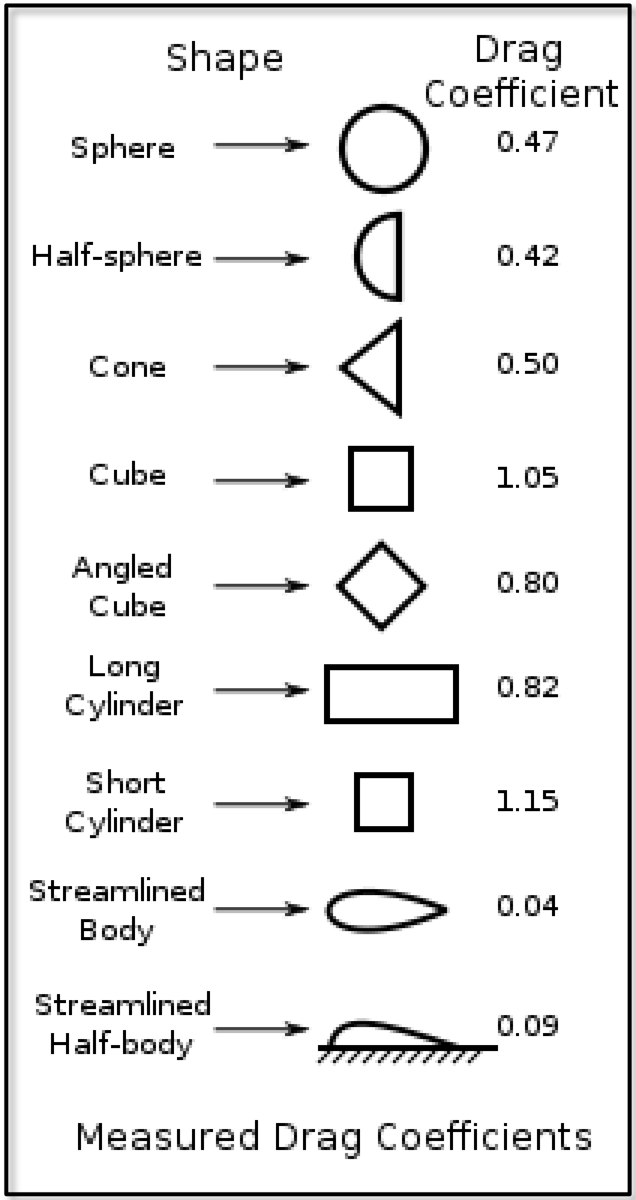
$z = \frac{1}{2} g t^2$ = Feet fallen in t sec.

$v = g t$ = Speed after t sec.

$a = g$ = Gravity

$= 32.2$ ft/s$^2$

$= 9.8$ m/s$^2$



| Shape | Drag Coefficient |
|---|---|
| Sphere | 0.47 |
| Half-sphere | 0.42 |
| Cone | 0.50 |
| Cube | 1.05 |
| Angled Cube | 0.80 |
| Long Cylinder | 0.82 |
| Short Cylinder | 1.15 |
| Streamlined Body | 0.04 |
| Streamlined Half-body | 0.09 |

Measured Drag Coefficients

## THIS FALLING BUSINESS

One of the great accomplishments of calculus has been as a predictive tool to explain the behavior of falling objects. We know that the acceleration due to gravity, g, it is 32.2 feet per second squared at sea level, or 9.81 meters per second in metric units. If we take downward acceleration as positive we have:

$$a = v' = \frac{dv}{dt} = -g$$

We can ask the question, “What function, when differentiated gives the constant g”? Asking this is equivalent to asking . “What is the inverse operation of taking the derivative?” or “What is the antiderivative?”. We will answer in copius detail later. For now we assume a search is required. In the end, it will turn out we have to do a search anyway and a good starting strategy becomes a good end game too. If we differentiate:

$$v = \frac{dz}{dt} = -g \cdot t$$

we obtain an expression for the velocity as a function of time, which happens to be linear.

# THIS FALLING BUSINESS - CONTINUED

As in other sports, we use the principle that, "If a play works, call it again."

$$v = \frac{dz}{dt} = -g \cdot t$$

This time we ask, "What function, when differentiated gives us the equation above?" After some trial and error searching we discover:

$$z = z_0 - \frac{1}{2} g \cdot t^2$$

We now have an expression for the position of an object as a function of time – in the absense of air resistance or drag. This is quite useful. It sets a upper bound on the distance an object can fall after *t* seconds. No object in freefall can fall further on Earth, in a given time, than this. The constant $z_0$ specifies the release altitude of the falling object.

Exercises: (1) Differentiate the equations starting with z = f(t).

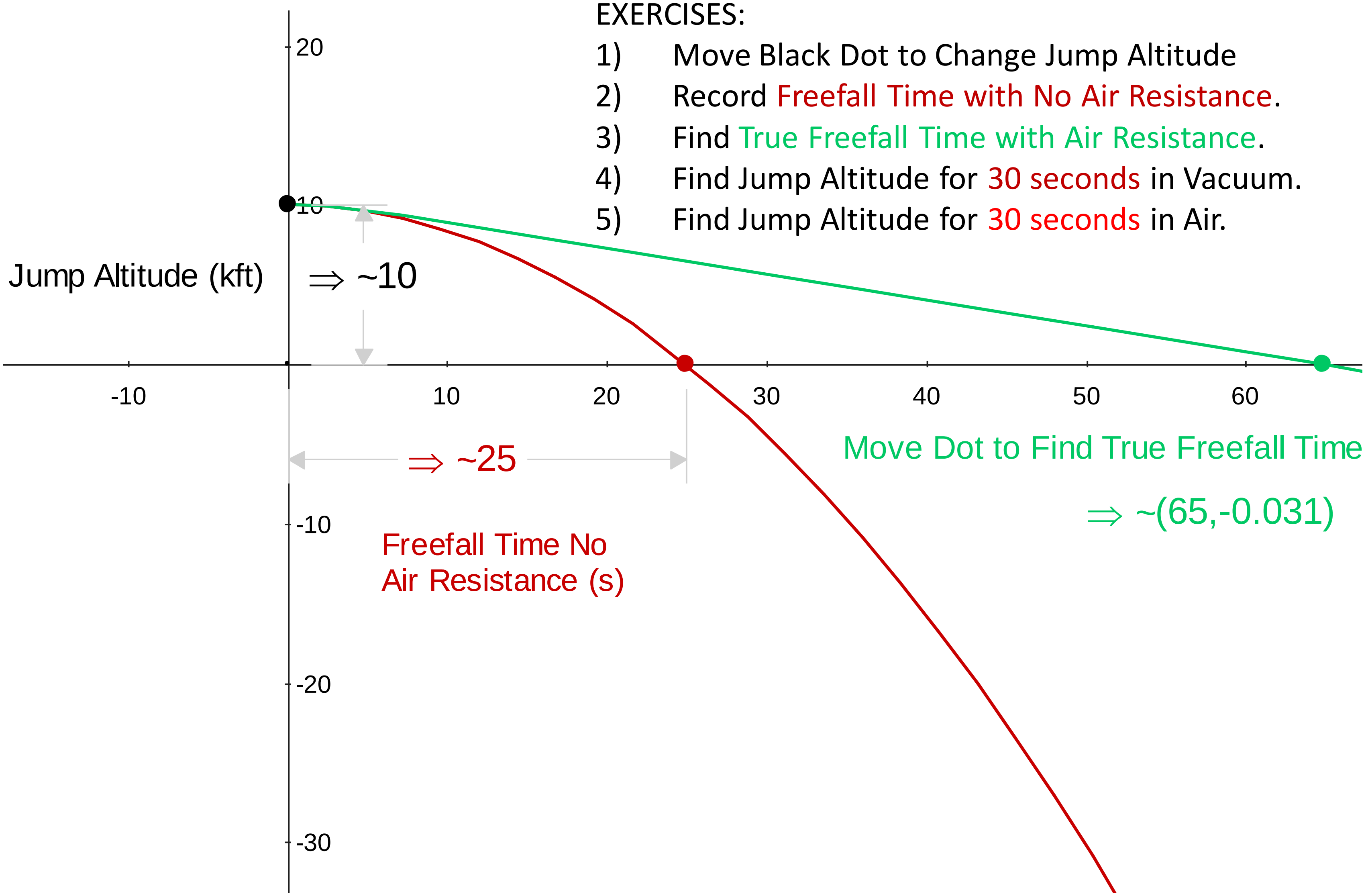
(2) Verify they produce the velocity and acceleration respectively.

Lecture14-ThisFallingBusiness.gx

# THIS FALLING BUSINESS:

EXERCISES:

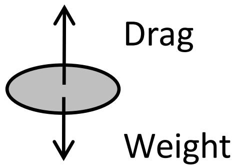
1) Move Black Dot to Change Jump Altitude
2) Record Freefall Time with No Air Resistance.
3) Find True Freefall Time with Air Resistance.
4) Find Jump Altitude for 30 seconds in Vacuum.
5) Find Jump Altitude for 30 seconds in Air.



# THIS FALLING BUSINESS – A REAL DRAG

Unfortunately air resistance plays havoc with the simplicity of our first approach. The following development is included for those who want to see the next step. It starts with Newton's second law which requires us to sum forces on the body:

$$\sum F_z = m \cdot a$$



The subscript of z says that we are summing falling forces vertically.

Rather than just finding the antiderivative twice, we sum the forces acting on the falling object to find that mass times acceleration equals the aerodynamic drag minus the weight.

$$m \cdot a = [Drag] - [Weight] = \left[\frac{1}{2}\rho \cdot v^2 \cdot C_d \cdot A\right] - [m \cdot g]$$

$\rho$ = air density
$C_d$ = drag coefficient
$A$ = frontal area

We work in a consistent system of units to insure correctness.

## THIS FALLING BUSINESS – ORDINARY DIFFERENTIAL EQUATIONS

The equation we just wrote can be simplified by lumping all the constants together to yield:

$$\frac{d}{dt}\left(\frac{dz}{dt}\right)=\frac{dv}{dt}=k\cdot v^2-g$$

An equation that expresses the derivative of a quantity in terms of that same quantity is called a differential equation. We won't solve this here, but using wxMaxima™ we discover that:

$$z=z_0-\frac{ln(e^{2\sqrt{gk}\cdot t}+1)}{k}+\sqrt{\frac{g}{k}}\cdot t+\frac{ln(2)}{k}$$

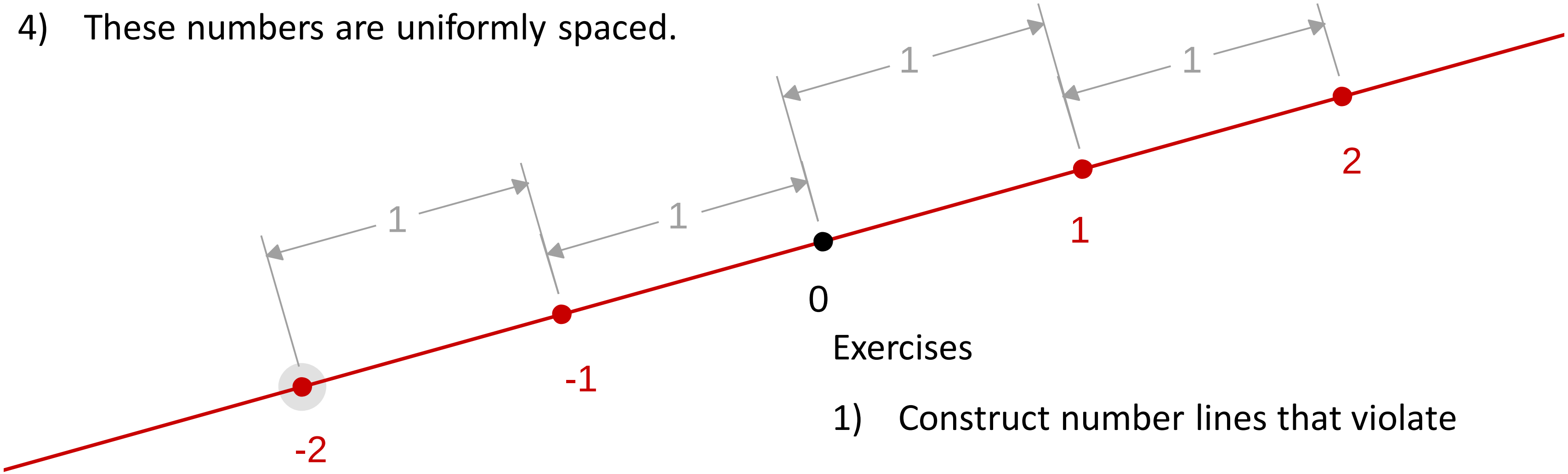
and like Archimedes we run down the street in our jumpsuit declaring, "Voila! What was difficult before has now become possible!" You can run this file for yourself. Its name is: *Lecture14-ThisFallingBusiness.wxm*. Scale factors and constants are are in a spreadsheet called *Lecture14-ThisFalling Business.xls*. This ends the "extra credit" development.

# A DIGRESSION

Lecture14-ADigression0.gx

Consider a number line and the seemingly innocent assumptions therein:

1) Values increase from left to right.
2) A zero point exists.
3) There are positive and negative numbers.
4) These numbers are uniformly spaced.



Exercises

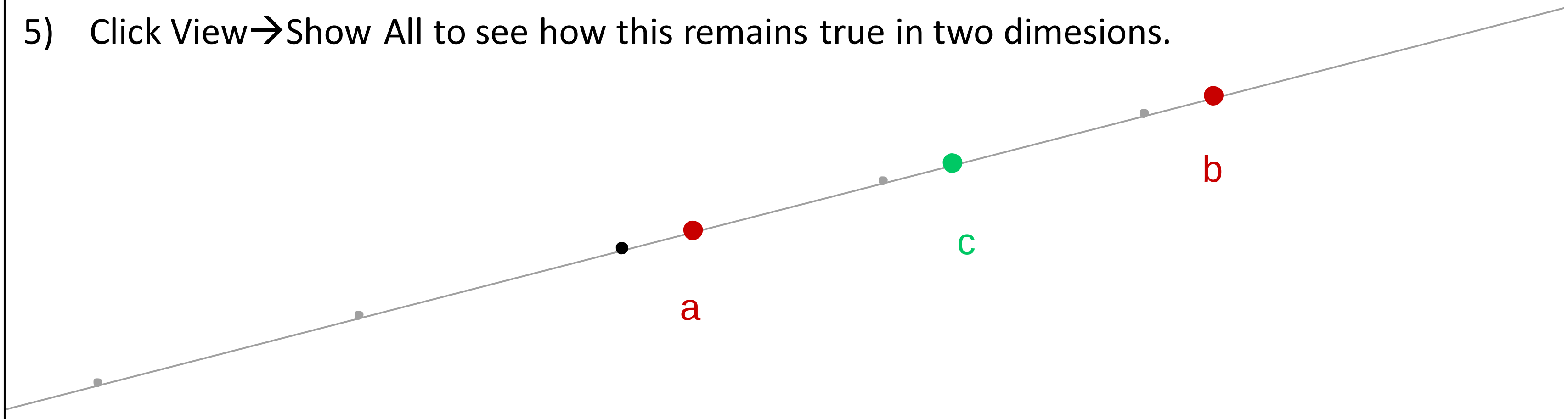
1) Construct number lines that violate each assumption above.
2) Discuss the implications of doing this.

# SOME EMERGENT TRUTHS

Lecture14-ADigression1.gx

Now consider two numbers a and b on this line, and a third related one, c:

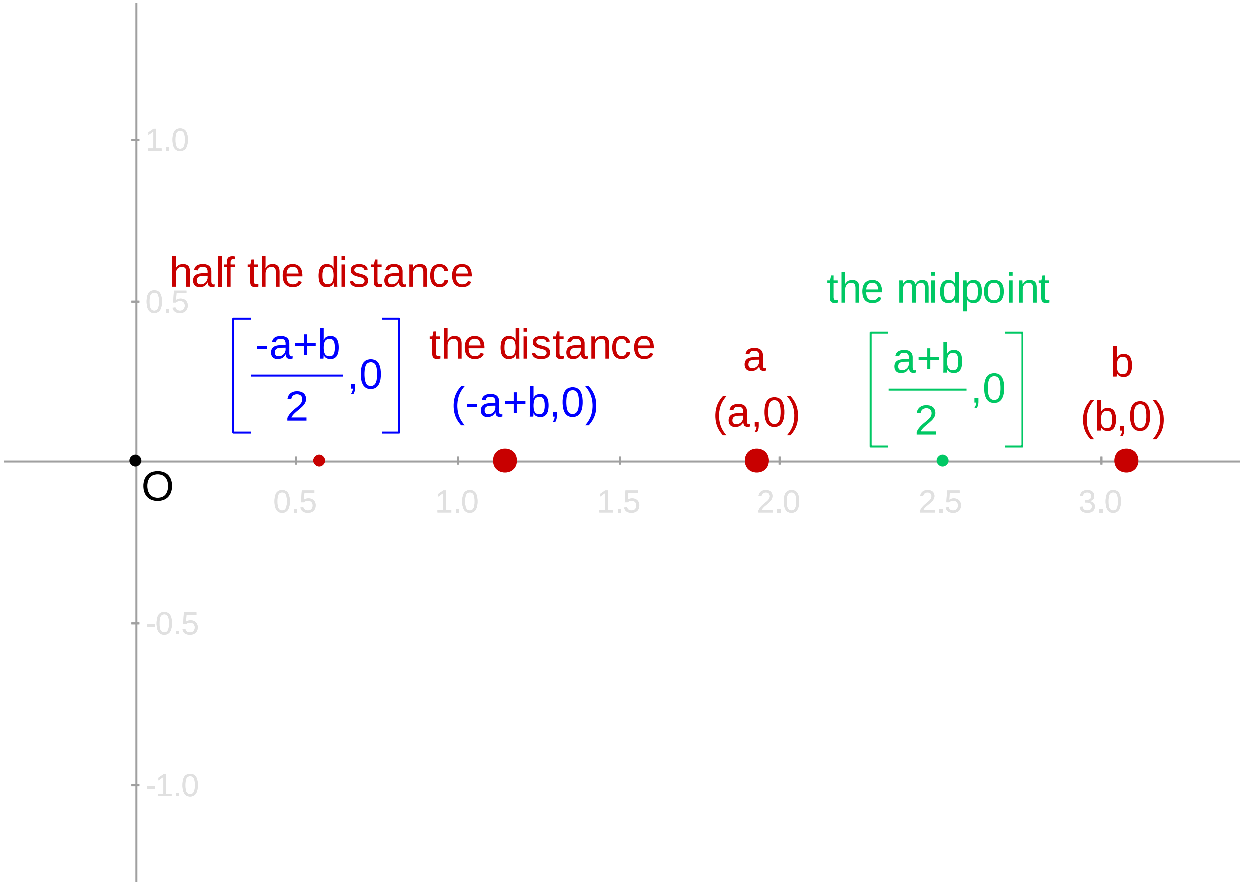
1) The distance between a and b is always b – a.
2) When c = (a+b)/2, it always exactly halfway between a and b.
3) This remains true whether a and b are positive, negative or both.
4) Drag each of the three points and convince yourself of this.
5) Click View→Show All to see how this remains true in two dimesions.



# MORE EMERGENT TRUTHS

Lecture14-ADigression2.gx

The half-sums and half-differences of a and b are significant:



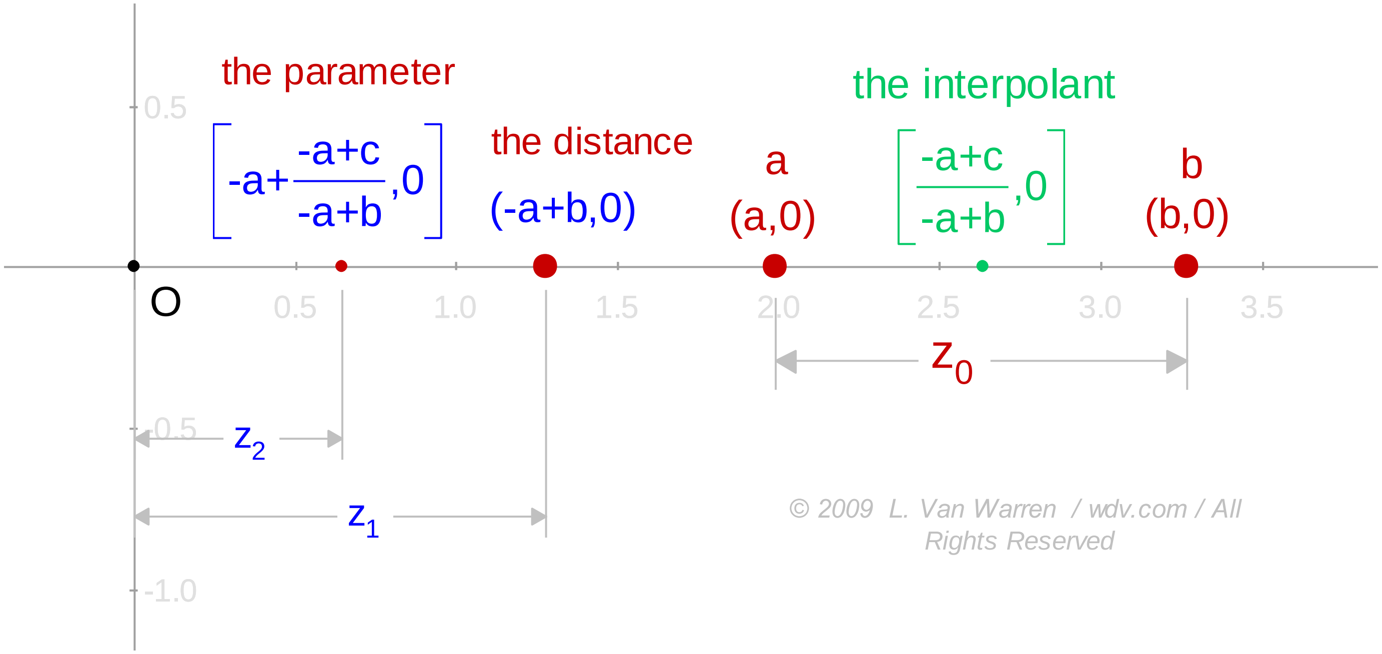
# PARAMETERIZATION AND INTERPOLATION

Lecture14-ADigression3.gx

A number anywhere between a and b can be interpolated using a parameter.

If the parameter is based on the distance between a and b we call it:

An Arc Length Parameterization

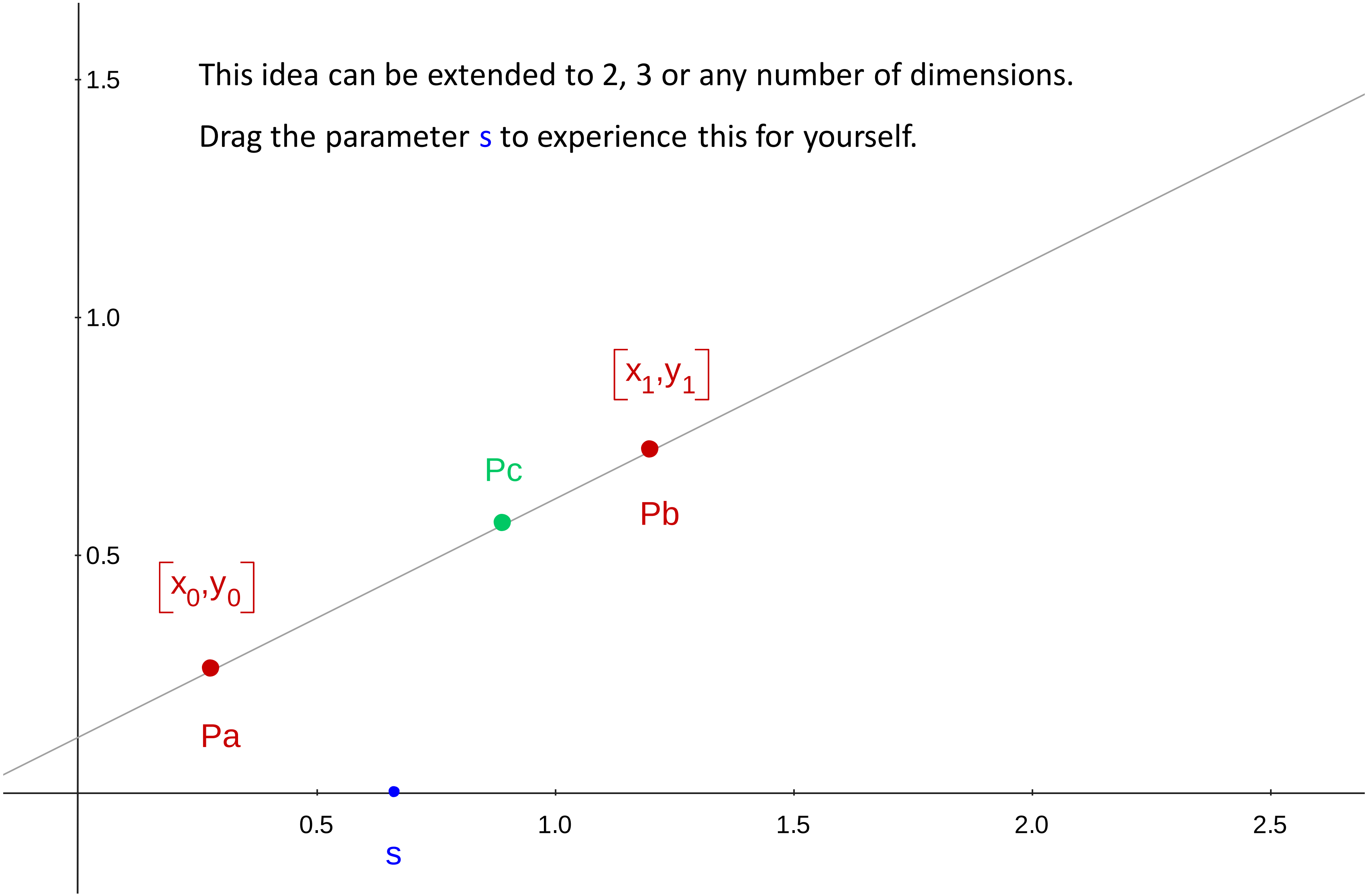


# PARAMETERIZATION AND INTERPOLATION

Lecture14-ADigression4.gx

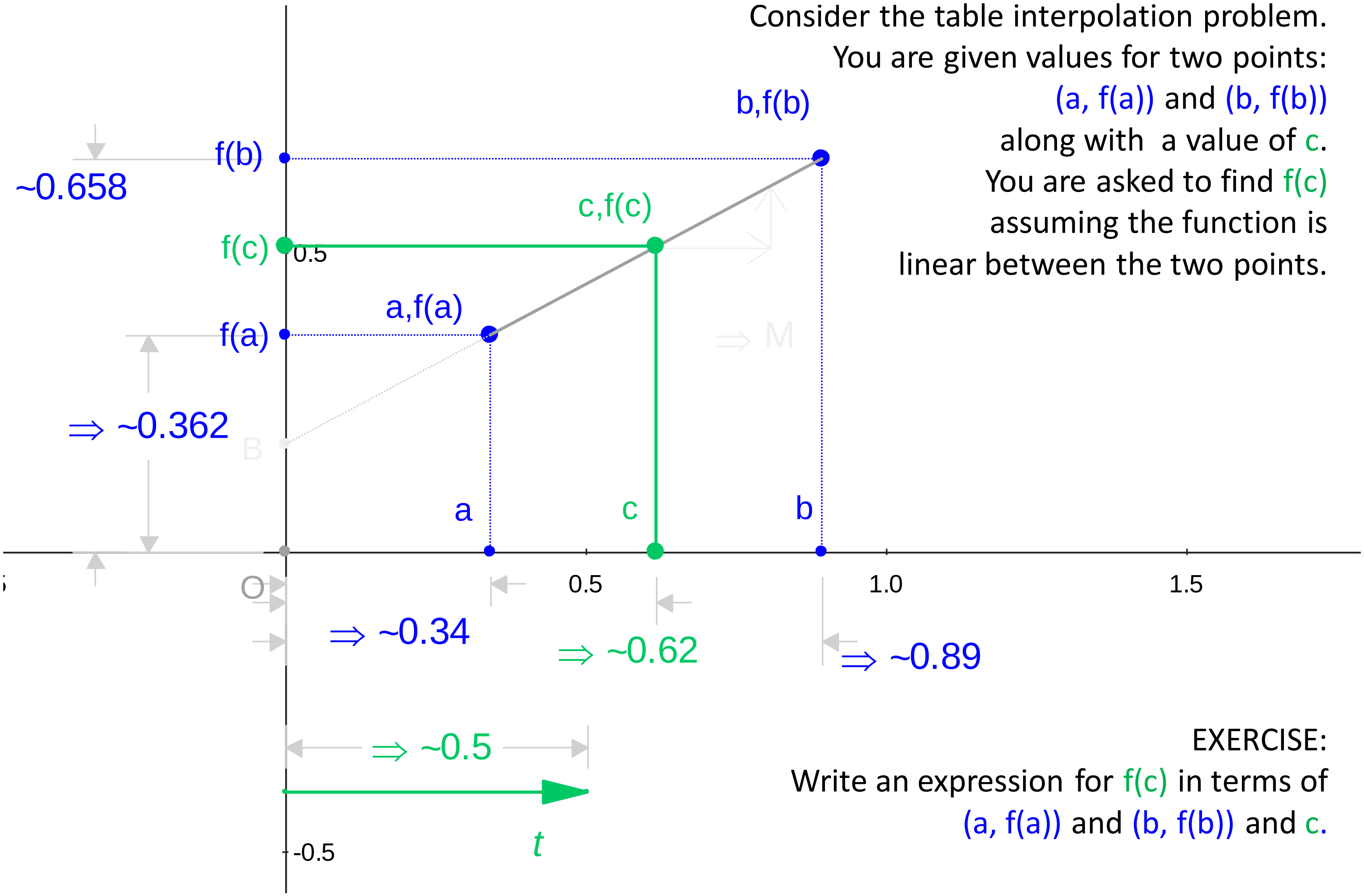
This idea can be extended to 2, 3 or any number of dimensions.

Drag the parameter s to experience this for yourself.



Lecture14-ADigression5.gx

# LINEAR INTERPOLATION

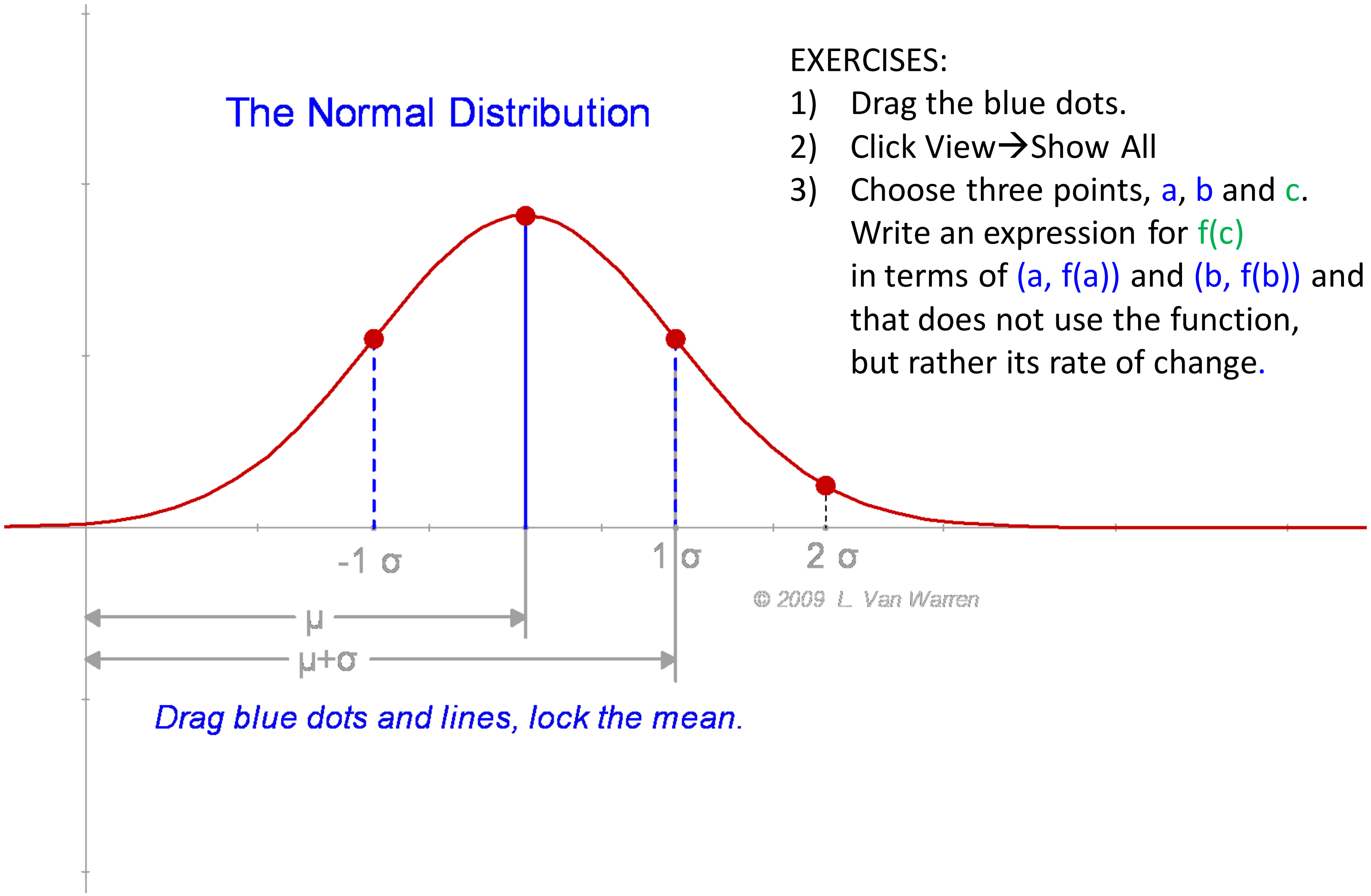


Consider the table interpolation problem.
You are given values for two points:
(a, f(a)) and (b, f(b))
along with a value of c.
You are asked to find f(c)
assuming the function is
linear between the two points.

EXERCISE:
Write an expression for f(c) in terms of
(a, f(a)) and (b, f(b)) and c.

# NONLINEAR INTERPOLATION

Lecture14-ADigression6.gx



*Drag blue dots and lines, lock the mean.*

EXERCISES:

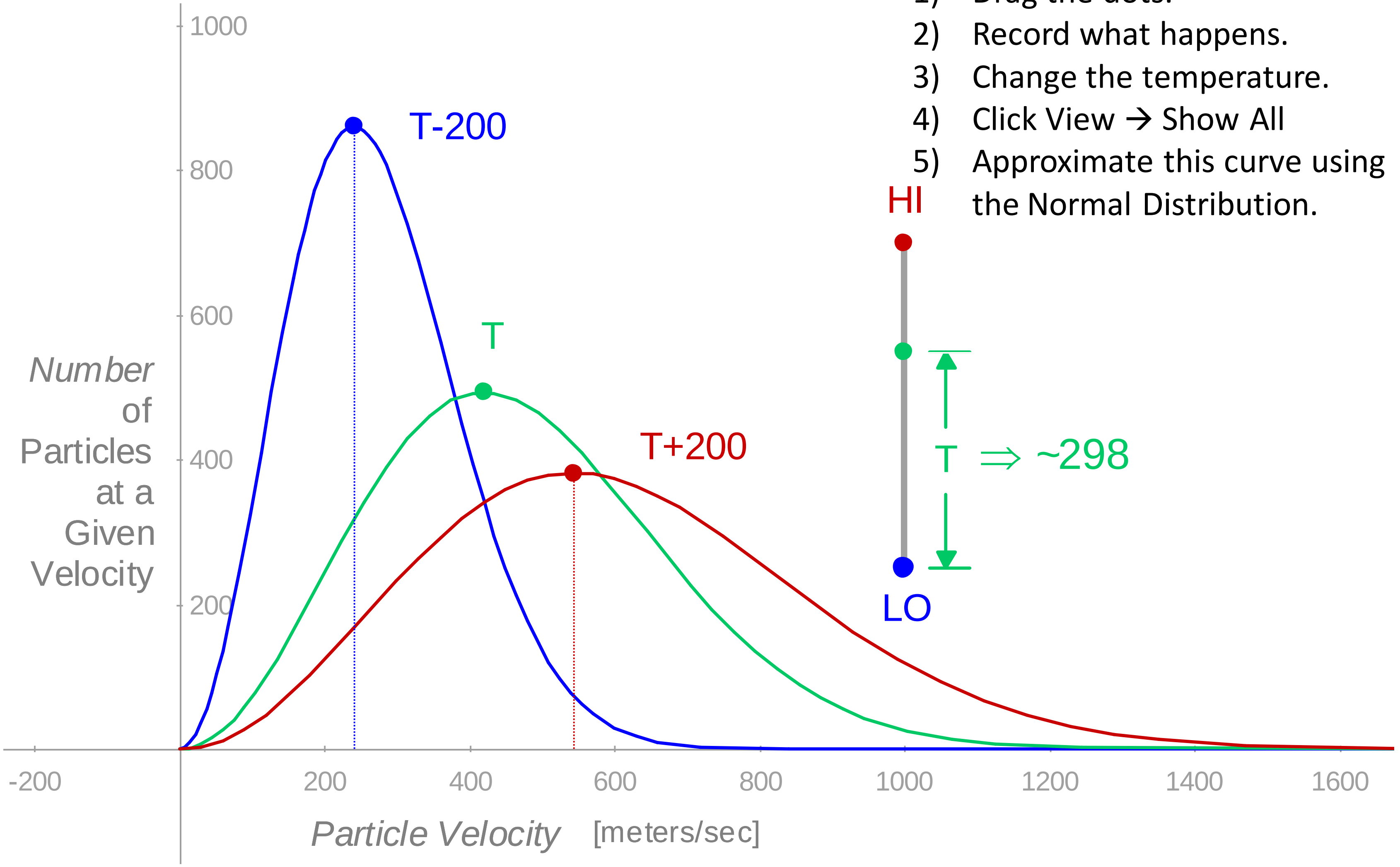
1) Drag the blue dots.
2) Click View→Show All
3) Choose three points, a, b and c.
   Write an expression for f(c)
   in terms of (a, f(a)) and (b, f(b)) and c
   that does not use the function,
   but rather its rate of change.

# MAXWELL-BOLTZMANN DISTRIBUTION OF GAS PARTICLE VELOCITIES

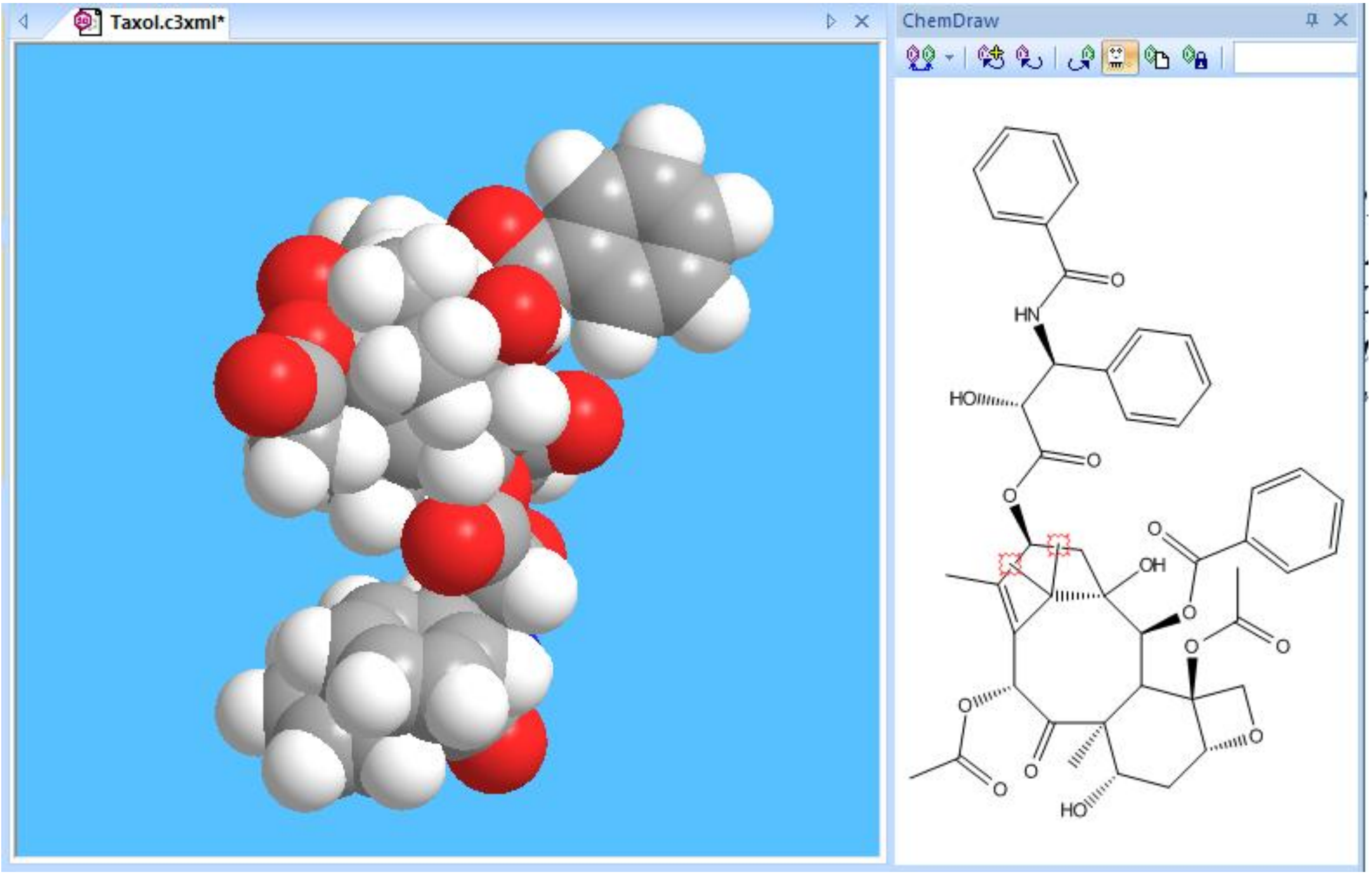
Lecture14-TheMaxwellBoltzmannDist.gx

EXERCISES:

1) Drag the dots.
2) Record what happens.
3) Change the temperature.
4) Click View → Show All
5) Approximate this curve using the Normal Distribution.



# REACTION RATES IN CHEMISTRY



# ZERO, FIRST AND SECOND ORDER REACTIONS

A chemical reaction can be written in a polynomial-like form as:

$$aA + bB \rightarrow cC$$

For example:

$$2H_2 + O_2 = 2H_2O$$

Chemical reactions fall into three categories, classified by the rate at which they occur.

**1)** ***Zero-Order Reactions***: reaction rate does not depend on reactant concentration.

**2)** ***First-Order Reactions***, reaction rate depends on one reactant's concentration.

**3)** ***Second-Order Reactions***, rate depends on product of reactants concentrations.

For an excellent discussion of the measurement of reaction rates visit David N. Blauch's Chemical Kinetics Site at Davidson.

# OPERATOR OVERLOADING

Square braces [ ] are used for two different ideas:

1) **Interval Arithmetic**: x = [0, 4] means 0 <= x <= 4,

2) **Chemical Concentration:** [A] = How many particles of chemical A in a volume. The units are expressed as: moles/liter of total volume.

- When the same operator has two different meanings, we say the operator “overloaded”. We distinguish the meaning by the context.

# Precious Metals, Ammonia and the Inverse Process

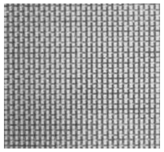
Some metals that are very scarce have a unique place in chemistry. Metals such as platinum enable reactions to occur that would not occur by themselves. Such materials are called catalysts. One important reaction is the creation of ammonia gas from nitrogen and methane. This reaction feeds the world by enabling the creation of fertilizers. Ammonia is made by the Haber process at high temperature (400° C) and pressure (200 atmospheres):

$$N_2 + 3\,H_2 \longrightarrow \quad \longrightarrow 2\,NH_3$$

*Magnetite Catalyst - $Fe_3O_4$*

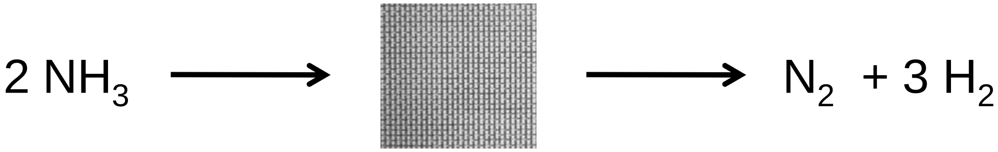
The reaction can be undone by passing ammonia gas through a heated platinum gauze.

$$2\,NH_3 \longrightarrow \quad \longrightarrow N_2 + 3\,H_2$$



*Platinum Gauze Catalyst*

# ZERO-ORDER CHEMICAL REACTIONS



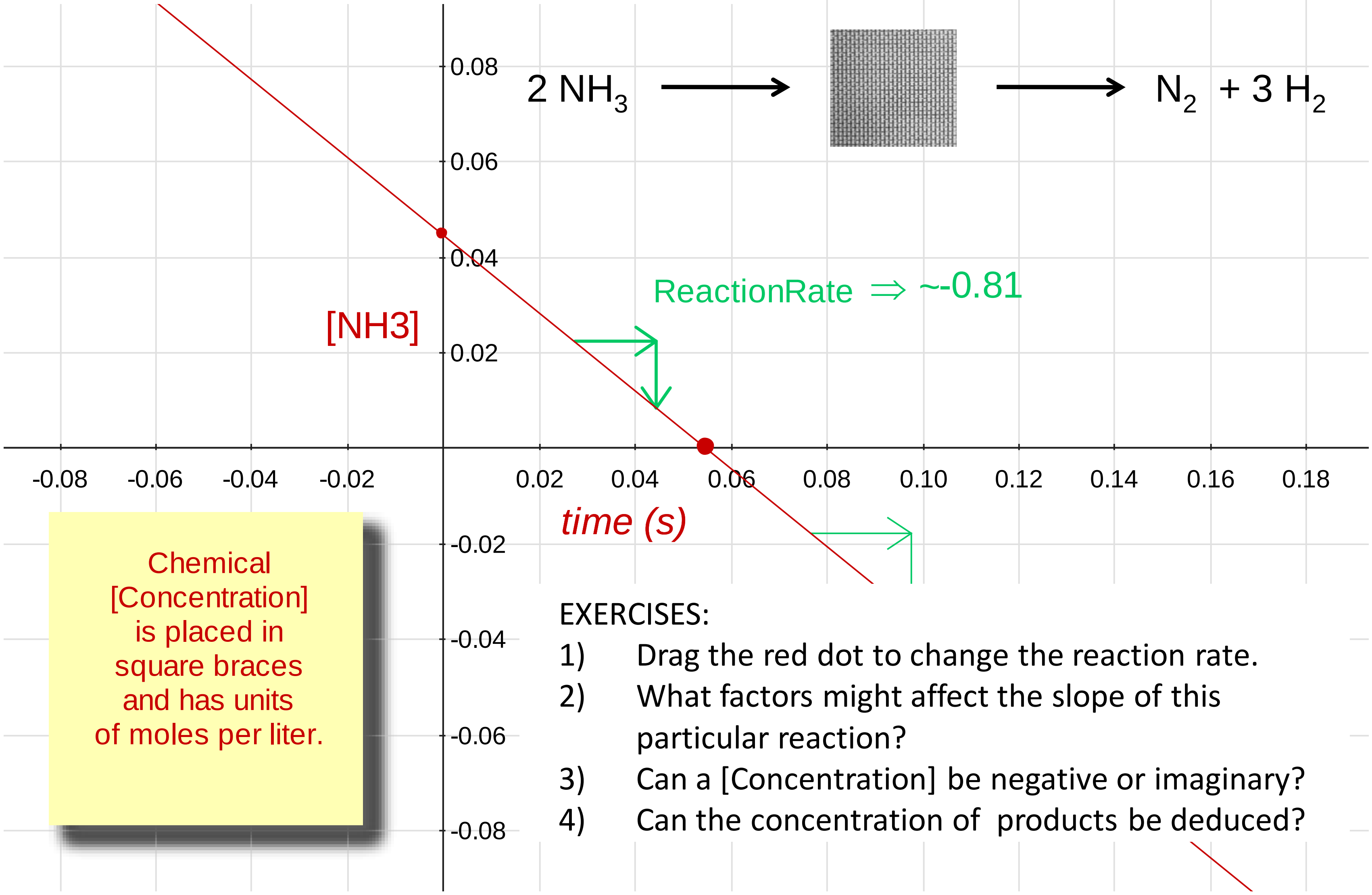
$$2\,NH_3 \longrightarrow \qquad \longrightarrow N_2 + 3\,H_2$$

The breakdown of ammonia is a zero-order reaction, so named, because the breakdown does not depend on the amount of ammonia, but rather on the amount of catalyst. Since the catalyst is not consumed during the reaction, it does not appear in the equation. In this reaction, both the accumulation of products and loss of reactant is linear. The change in the concentration of products and reactants is measured in units of moles per liter. Because the surface area of the platinum is fixed, the number of reaction sites is constant, and this fixes the rate of breakdown. Another term for reaction rate, is rate of reaction (ROR), synonyms that say how fast the concentration of reactants and products is changing.

The zero order case is modeled next.

# Zero-Order Chemical Reactions

Lecture14-ZeroOrderKinetics.gx



$2\ NH_3 \longrightarrow \quad \longrightarrow N_2 + 3\ H_2$

Chemical
[Concentration]
is placed in
square braces
and has units
of moles per liter.

EXERCISES:

1) Drag the red dot to change the reaction rate.
2) What factors might affect the slope of this particular reaction?
3) Can a [Concentration] be negative or imaginary?
4) Can the concentration of products be deduced?

# FIRST-ORDER REACTIONS

When the rate of a reaction is governed by the concentration of a single rate-limiting reactant we say the reaction is first order. It is modeled by the rate equation:

$$rate\ of\ reaction = r = \frac{d[A]}{dt} = k \cdot [A]$$

where the concentration of [A] is in moles per liter of volume and is understood to be a function of time. The rate constant k has units of inverse seconds: sec$^{-1}$, or *frequency*.

Said again: For a first-order reaction, the reaction rate is directly proportional to the concentration of one of the reactants.

## FIRST-ORDER REACTIONS

$$ {}^{3}_{1}T \rightarrow {}^{3}_{2}He + e^{-} + \overline{\nu}_{e} $$

First order reactions include not only chemical reactions, but nuclear reactions such as the decay of Tritium shown above. The above equation says that Tritium (2 neutrons + 1 proton) decays to Helium$_3$ (1 neutron + 2 protons) via spontaneous release of a fast electron and an electron antineutrino. This gives rise to “radioactive decay” and the concept of half life.

As a first order reaction proceeds, there is less of the reactant left to participate in the reaction. Therefore, by nature, a first order reaction is not linear but rather exponential!

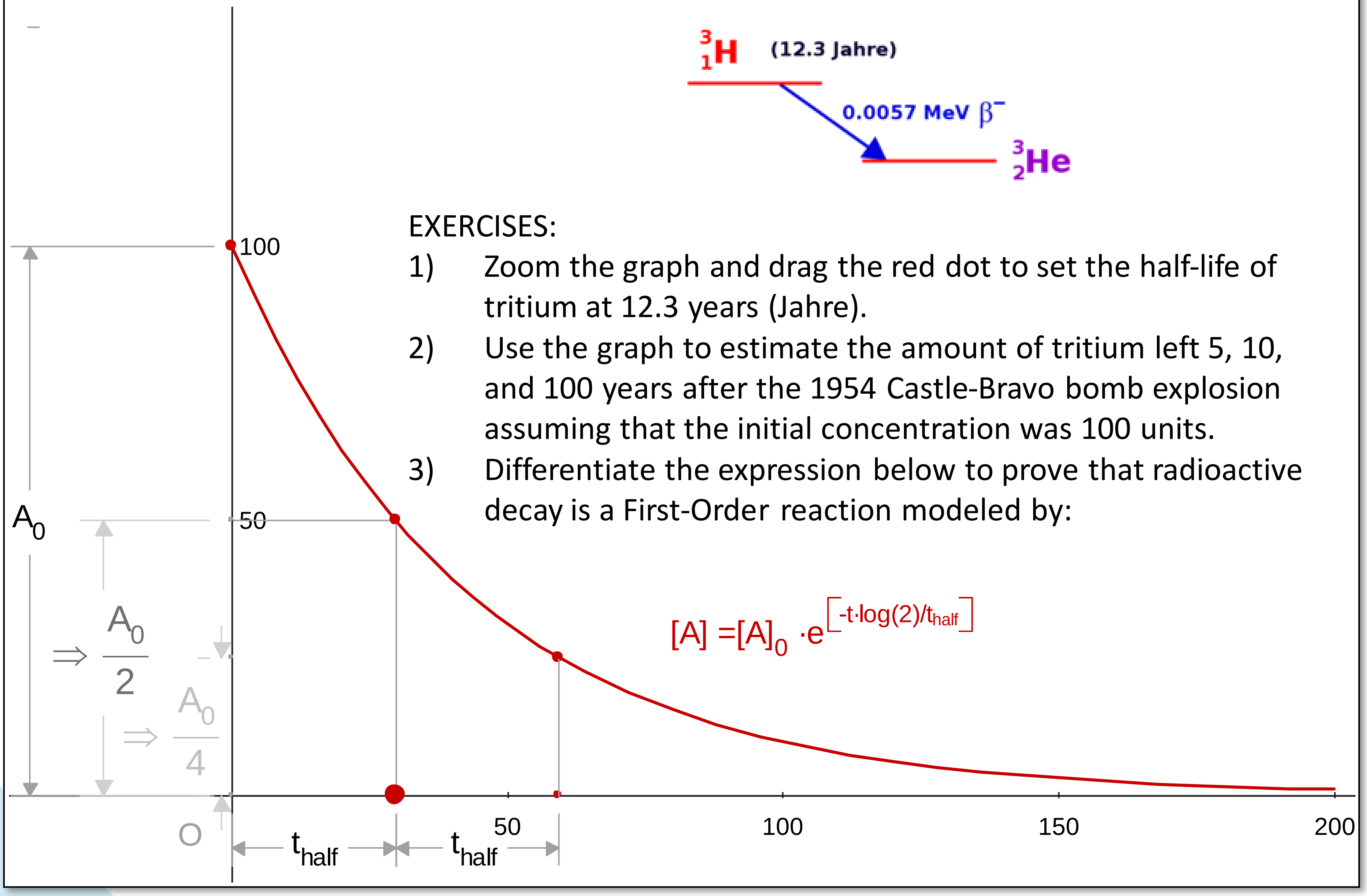
One product that will glow for a decade is made by placing Tritium gas inside a phosphor coated tube →

*- photo courtesy firebox.com*

This first-order reaction case is modeled next:

# First-Order Reactions

Lecture14-FirstOrderReaction.gx



EXERCISES:

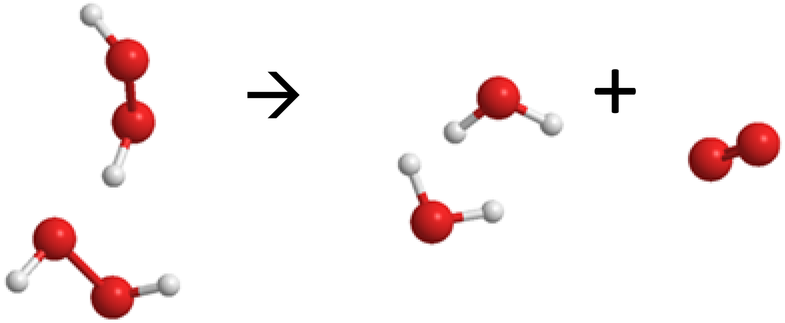
1) Zoom the graph and drag the red dot to set the half-life of tritium at 12.3 years (Jahre).
2) Use the graph to estimate the amount of tritium left 5, 10, and 100 years after the 1954 Castle-Bravo bomb explosion assuming that the initial concentration was 100 units.
3) Differentiate the expression below to prove that radioactive decay is a First-Order reaction modeled by:

$$[A] = [A]_0 \cdot e^{\left[-t\cdot\log(2)/t_{half}\right]}$$

# OTHER COMMON FIRST-ORDER REACTIONS

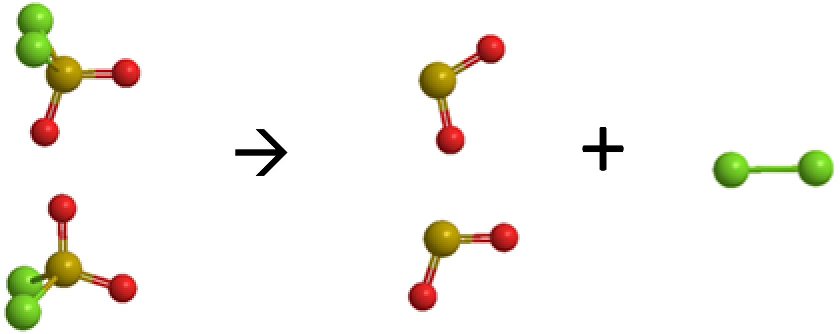
**Hydrogen Peroxide**, a household bleaching agent, decomposes to water and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$



**Sulfuryl Chloride**, a fumigant, decomposes completely to sulfur dioxide and chlorine gas:

$$2SO_2Cl_2 \rightarrow 2SO_2 + Cl_2$$



# DIFFERENT SITUATION – SIMILAR EQUATIONS

Before we discuss more complex reactions, lets take a moment to notice that The Business of Falling shares a similarity to the Zero-Order Chemical Reaction. Many times the equations that describe one situation can be used to describe another, seemingly unrelated one.

Where we had z for altitude in the falling case, we have the concentration of ammonia $[NH_3]$ in the zero-order reaction case.

Where we had $v = dz/dt$ fall rate, we have $r=d\,[NH_3]/dt = k$ in the zero-order reaction case.

In the falling case, the jumper subjected to air resistance reaches a terminal velocity, after which they fall at a constant rate. In the zero-order reaction the same situation occurs once the platinum catalyst saturates with reactant.

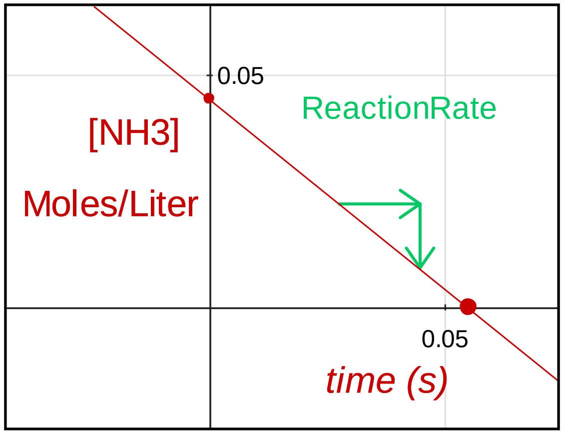
# CHEMICAL REACTION RATES

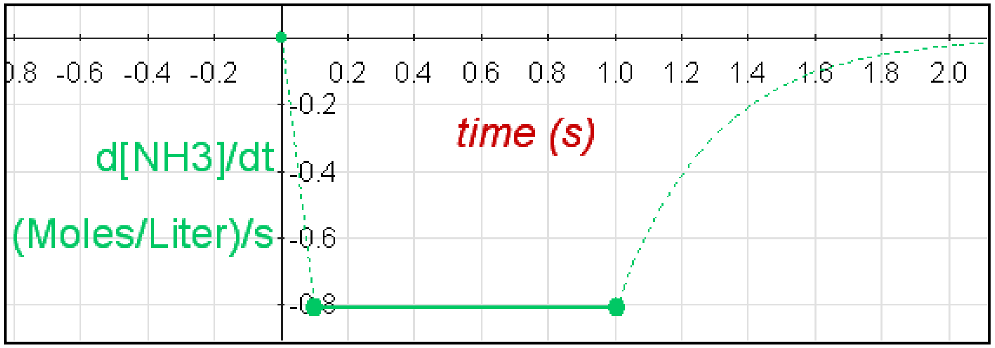
Lecture14-ZeroOrderConstant.gx

Just as with the falling case, it is useful to look at the original variable and the derivatives at the same time. This allows one to see the relationships between position, velocity and higher-order rates of change.

The derivatives may be placed on the same graph as the original function, but it is important to remember that the units are always different. The original variable carries its original units, the derivative carries those same units divided by time when rates are involved. When modeling reactions, we make assumptions such as:

1) the reaction rate reaches a constant value instantly.
2) the reaction stops abruptly.





# SECOND-ORDER CHEMICAL REACTIONS

There are six types of chemical reactions. Reactions which take the form:

$$aA + bB \rightarrow cC$$

are called ***direct-combination*** or ***synthesis reactions***, where $A$, $B$ and $C$ are the chemical species and $a$, $b$ and $c$ are the coefficients that balance the equation - stoichiometrically.

When a reaction proceeds to conclusion without the formation of intermediate states the reaction rate is given by:

$$reaction\ rate = k[A]^a[B]^b$$

Where the order of the reaction is given by a + b. For the second-order reaction we have:

$$reaction\ rate = k[A][B]$$

The burning of high sulfur coal creates sulfur trioxide which leads to sulfuric acid rain by the reaction:

# ACID RAIN: A SECOND-ORDER CHEMICAL REACTION

We want to model the concentration of sulfuric-acid ($H_2SO_4$) rain, resulting from the combination of sulfur trioxide ($SO_3$), from burning coal, and atmospheric moisture ($H_2O$). The chemical equation for this reaction is :

$$1\ \mathrm{SO_3} + 1\ \mathrm{H_2O} \rightarrow 1\ \mathrm{H_2SO_4}$$

This is a second-order reaction which proceeds rapidly. For brevity let:

$$A = [\mathrm{SO_3}] \quad B = [\mathrm{H_2O}] \quad C = [\mathrm{H_2SO_4}]$$

Our rate equation is:

$$\frac{dA}{dt} = k\ A\ B$$

Our stoichiometry is:

$$1A + 1B \xrightarrow{yields} 1C$$

# ACID RAIN: CONT'D

Let's solve for the concentration of the product, sulfuric acid, *C*. At the beginning of the reaction, we assume the following initial conditions apply:

$$C_{t=0} = C_0 = 0 \qquad A_{t=0} = A_0 \neq 0 \qquad B_{t=0} = B_0 \neq 0$$

Now we express A and B in terms of C using stoichiometry:

$$A = A_0 - C \qquad B = B_0 - C$$

Every time we make one mole of *C* we use up one mole of *A* and one of *B*, thus the rate equation becomes:

$$\frac{dC}{dt} = -\frac{dA}{dt} = -\frac{dB}{dt}$$

Which when combined with the original equation: $\frac{dA}{dt} = k\,A\,B$

Can thus be transformed into: $\frac{dC}{dt} = -\frac{dA}{dt} = -\frac{dB}{dt} = -k\,AB = -k(A_0 - C)(B_0 - C)$

Using the initial conditions above.

# ACID RAIN: CONT'D

Thus we have exploited stoichiometry to go from one equation in three unknowns (A, B, C) to one equation in one unknown (C) to obtain an equation for the rate of change of the concentration of C.

Trimming our grand equation, we obtain:

$$\frac{dC}{dt} = -k\,(A_0 - C)(B_0 - C)$$

Which we note contains C multiplied by itself.

Discovering the function *C* that satisfies this first order differential equation requires integration techniques we will soon investigate. Using wxMaxima™ (see Lecture14-SecondOrderSolution.wxm) yields:

$$C = -\frac{A_0 B_0\left(e^{(B_0 - A_0)kt} - 1\right)}{B_0 - A_0 e^{(B_0 - A_0)kt}}$$

# ACID RAIN: CONT'D

Note that math is a like chemistry, where equations "react" with each other to form new ones. This is deeply mysterious. We make the rules for math and they lead to unanticipated places. Who makes them for chemistry?

Before we model this result, we need to repeat the argument, this time solving for the concentration of the reactants instead of the products. Since one part of A reacts with one part of B, the equations for A and B will be similar. But before we solve the whole system, we just observe:

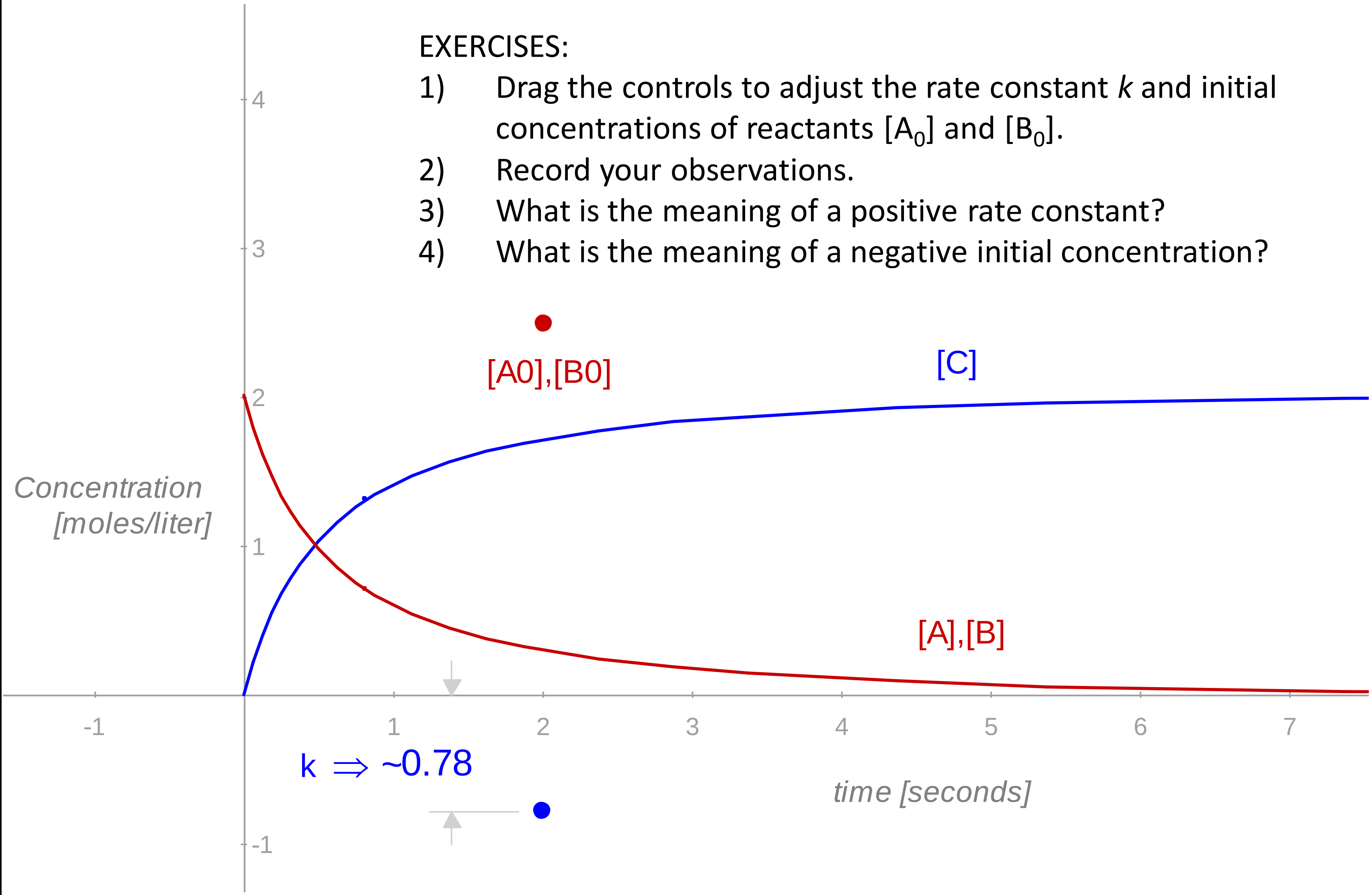
$$A = A_0 - C \;\; and \;\; B = B_0 - C$$

Since C is known as well as $A_0$ and $B_0$, we are done.

We plot the three equations for [A], [B] and [C] using Geometry Expressions™ to obtain the rate of change of concentration versus time.

# Second-Order Reactions

Lecture14-SecondOrderKinetics.gx



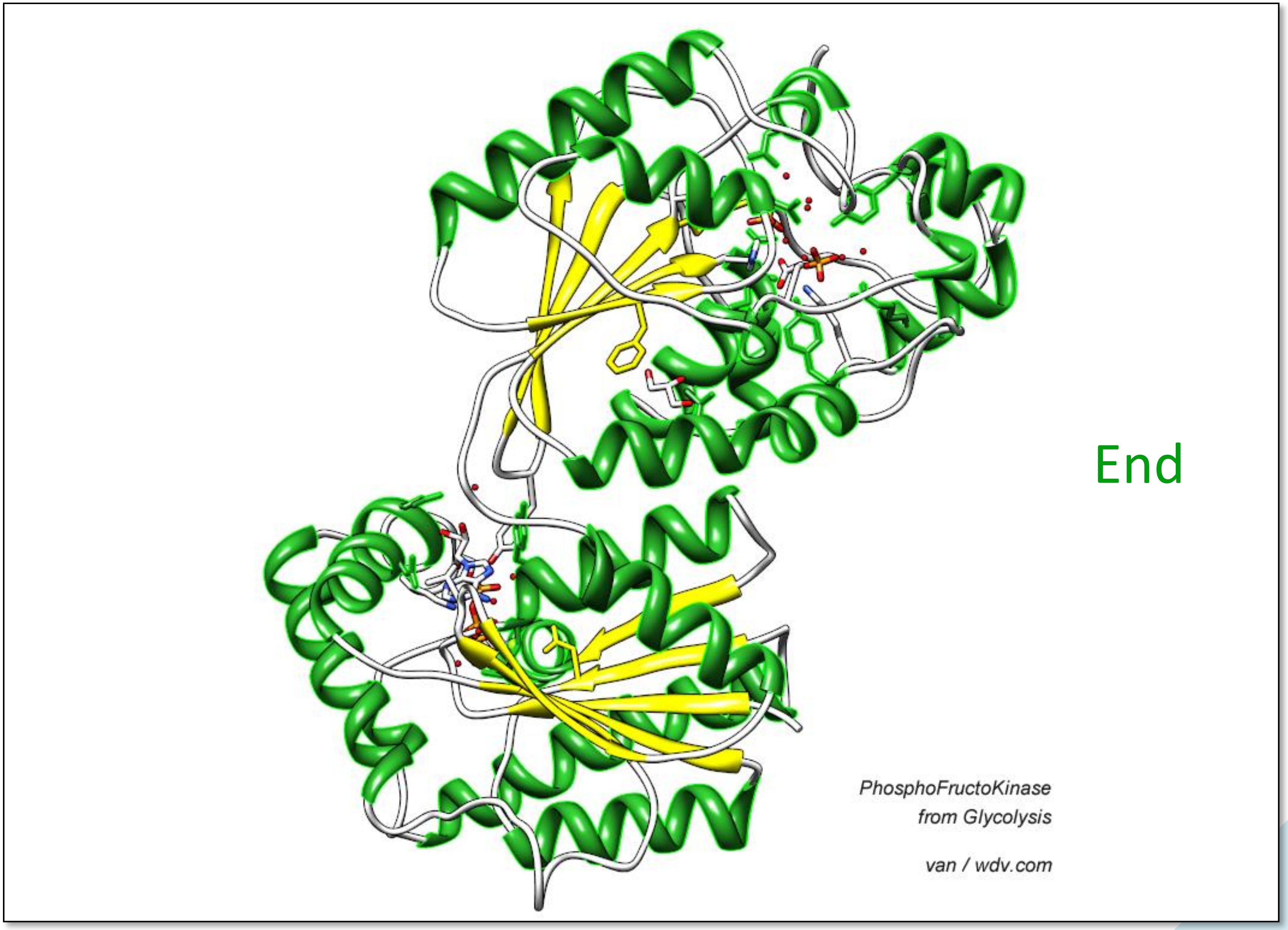
EXERCISES:

1) Drag the controls to adjust the rate constant *k* and initial concentrations of reactants $[A_0]$ and $[B_0]$.
2) Record your observations.
3) What is the meaning of a positive rate constant?
4) What is the meaning of a negative initial concentration?

# CHEMISTRY RATE-OF-REACTION REFERENCES

1. Six Types of Chemical Reactions
2. Differential Rate Laws
3. Rate Equations
4. Algebra of Products and Reactants
5. Chemical Synthesis Reactions
6. Acid Rain
7. Direct Combination Reactions: Sodium Oxide

$Na_2O + H_2O \rightarrow 2\ NaOH$



PhosphoFructoKinase
from Glycolysis

van / wdv.com

End