Computer-based Exercises in Physical Chemistry

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Why do we need

It’s easy to plot and appreciate chem

Why should I learn about computers?

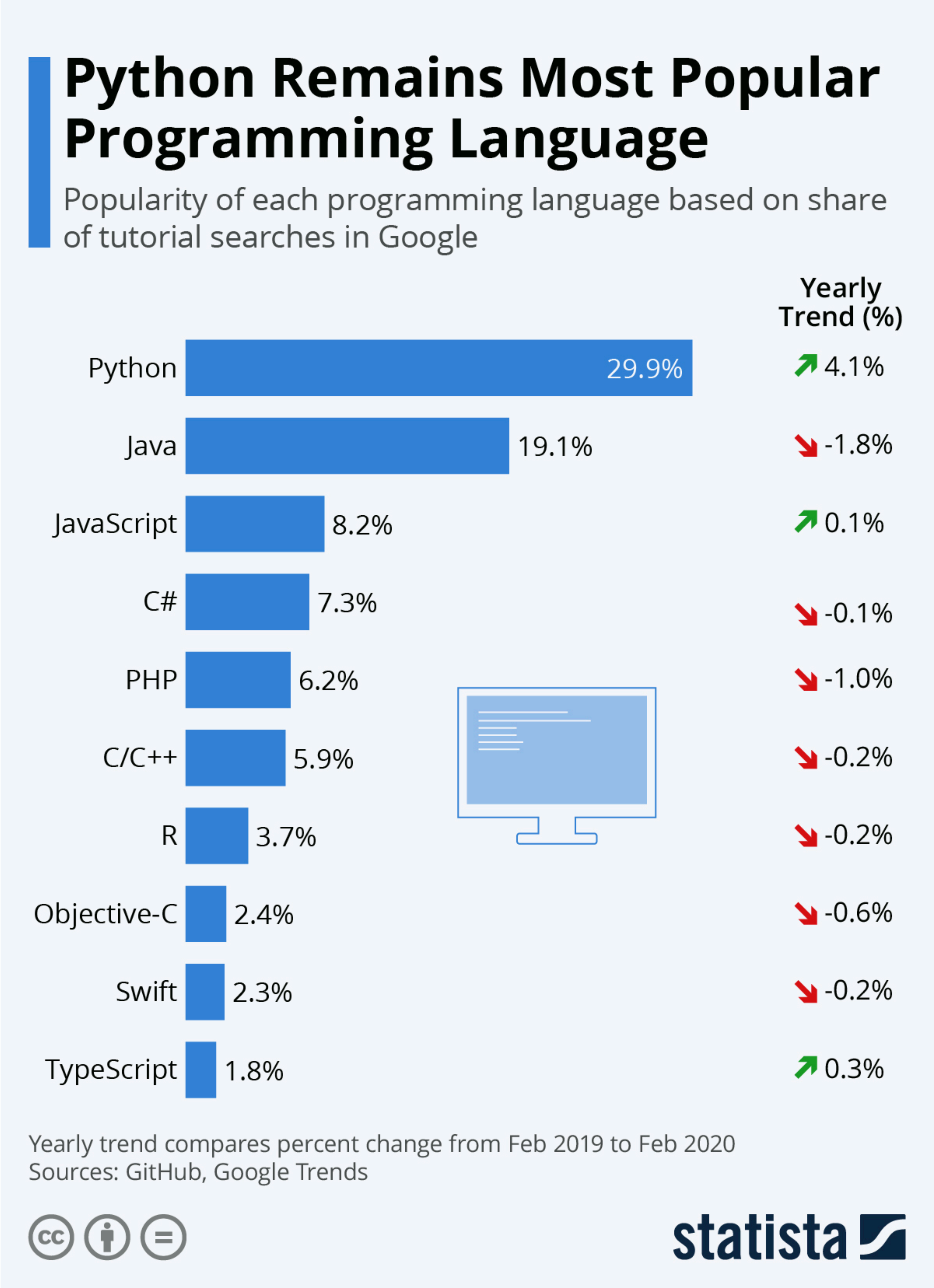
Often equations are difficult to solve manually.
Computer is a versatile equipment where one can perform several virtual experiments relevant for chemistry.

I want to have Python in my computer but I don’t know how to install it. What to do?

<u>Don’t be shy to ask around.</u>

Take help from friends, teachers, or research scholars in your institute.

Choosing a programming language



Q: What's the best programming language to learn for science student with no previous programming experience

A: Python

Python is

- free
- easy to reference in the internet
- has a lot of libraries for visualisation, numerical methods, and data-analysis
- more libraries means less coding effort *so that one can focus on the research problem at hand*

SciPy

NumPy

matplotlib

IP[y]: IPython Interactive Computing

pandas $y_{it} = \beta' x_{it} + \mu_i + \epsilon_{it}$

scikit learn

Why should I learn about computers?

Plotting function
Simple Statistics
Solving simple problems
Solving Advanced problems

Mathematics and Numerical Methods

Plotting function
Simple Statistics
Solving simple problems
Solving Advanced problems

A warm up problem

1.0 atm of nitrosyl chloride is introduced into a reaction vessel. The compound dissociates into nitric oxide and chlorine according to the reaction

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

If the equilibrium constant of the reaction is known to be 2.18, find the partial pressure of the gases at equilibrium

Answer

At equilibrium, $P_{\text{NOCl}} = 1 - 2x$, $P_{\text{NO}} = 2x$, and $P_{\text{Cl}_2} = x$.

Equilibrium-constant implies $\dfrac{P_{\text{NO}}^2 P_{\text{Cl}_2}}{P_{\text{NOCl}}^2} = \dfrac{(2x)^2 x}{(1-2x)^2} = K_{\text{eq.}} = 2.18$

The expression can be rearranged as a cubic equation $4x^3 - 8.72x^2 + 8.72x - 2.18 = 0$ which needs to be solved to determine the value of x (from which the partial pressures can be calculated)

Since $1 \geq P_{\text{NOCl}} \geq 0$ we know that $1 \geq 1 - 2x \geq 0$ or $x \geq 1/2$.

Cubic equation

We know how to solve a quadratic equation and find two solutions.

We are taught to rearrange the cubic equation into simple forms like (for example)

$(x - d)(ax^2 + bx + c) = 0$, in order to find the third solution.

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Now, let's see if a computer and Python can help us!

Graphical solution of the cubic equation

In [1]:

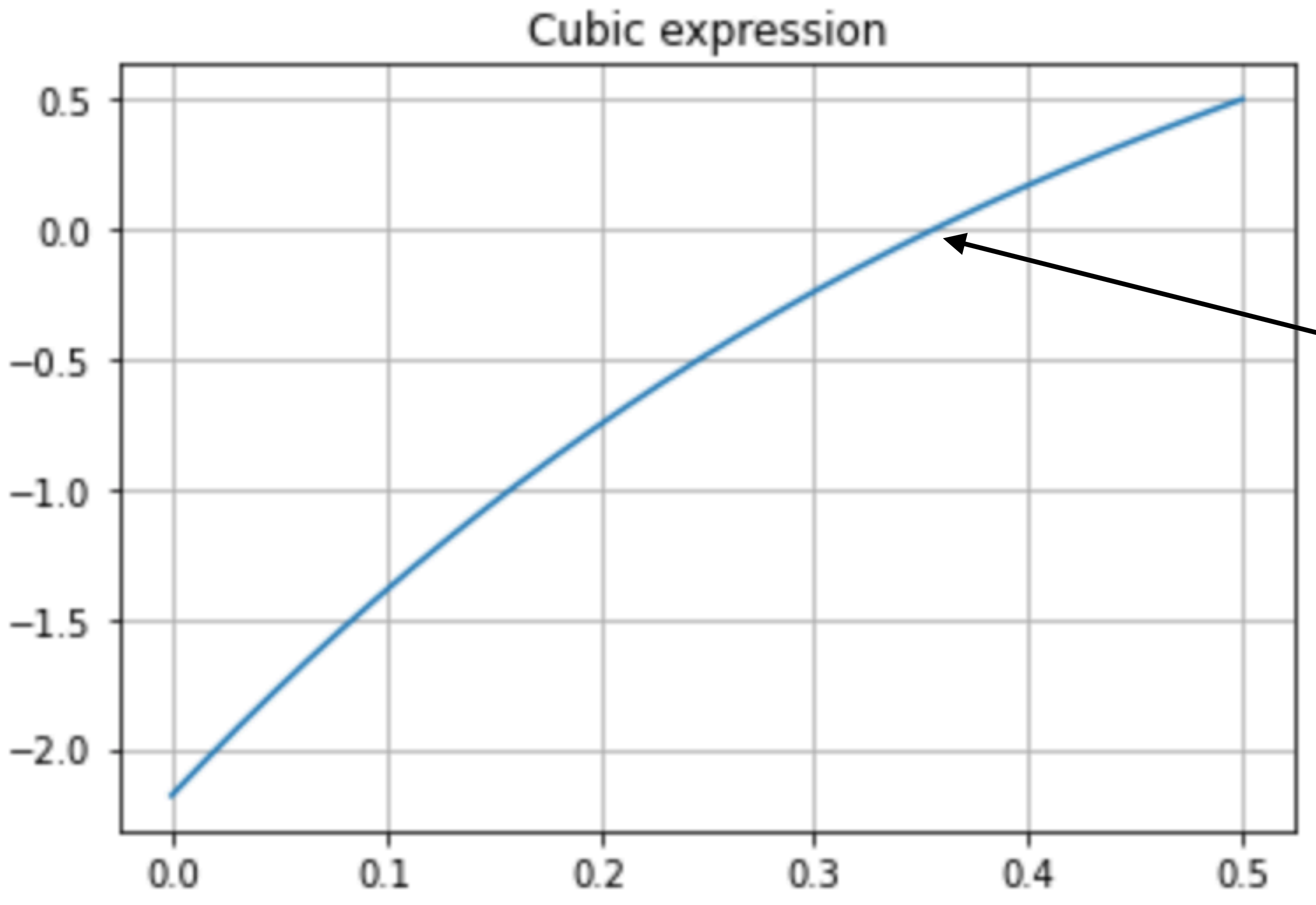
```
import numpy as np
import matplotlib.pyplot as plt

#=== x-values
x_min=0.0
x_max=0.5
x_grids=501
x=np.linspace(x_min, x_max, x_grids)

#=== f(x) values
f=4*x**3 - 8.72*x**2 + 8.72*x - 2.18

#=== plot
plt.plot(x,f)
plt.title('Cubic expression')
plt.grid()
plt.show()
```

x-range is fixed between 0 and 1/2 (using our previous knowledge of the problem)



The solution seems to be around x= 0.35

Numerical solution using secant method

In [2]:
```
from scipy import optimize

def f(x):
    f=4*x**3 - 8.72*x**2 + 8.72*x - 2.18
    return f

xguess=0.1
solution=optimize.root_scalar(f, fprime=None, x1=xguess+0.01, method='secant', bracket=None, x0=xguess, \
                              options={'tol':1e-6, 'maxiter':100})
solution
```

Out[2]:
```
      converged: True
           flag: 'converged'
 function_calls: 7
     iterations: 6
           root: 0.3560857818097863
```

- Secant method is a modified version of the Newton-Raphson method.
- Newton-Raphson requires that the derivative of the function is also known.
- In secant method, the derivative is approximated numerically using a finite-step (hence, finite-derivative)
- So, along with x0 (the initial guess for the root), another point x1 must also be specified.
- The derivative for the first iteration is estimated as $f'(x_0) \approx (f(x_1) - f(x_0))/(x_1 - x_0)$

The answer

At equilibrium, $P_{\mathrm{NOCl}} = 1 - 2x$, $P_{\mathrm{NO}} = 2x$, and $P_{\mathrm{Cl_2}} = x$.

```
In [3]: x=solution.root
        print("The partial pressure of NOCl is ",1-2*x)
        print("The partial pressure of NO is ",2*x)
        print("The partial pressure of Cl2 is ",x)

The partial pressure of NOCl is  0.28782843638042743
The partial pressure of NO is  0.7121715636195726
The partial pressure of Cl2 is  0.3560857818097863
```

The IPython notebook can be downloaded from https://github.com/raghurama123/Comp_PhysChem_Basic

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Are you surprised that the sum of all partial pressures exceed the initial pressure of 1 atm?

A problem in integration

Debye's theory of molar heat capacity (Debye-T^3 law) of a monoatomic crystal states

$$\overline{C}_V(T) = 9R\left(\frac{T}{\Theta_\mathrm{D}}\right)^3 \int_0^{\Theta_\mathrm{D}/T} \frac{x^4 e^x}{(e^x-1)^2} dx$$

where R is the gas constant and $\Theta_\mathrm{D} = 309$ K is the Debye temperature. Given that for copper, , find the molar heat capacity at $T = 90$ K.

Experimentally measured value is $14.49\,\mathrm{J}\cdot K^{-1}\cdot\mathrm{mol}^{-1}$

Numerical integration using quadrature

In [1]:
```
import numpy as np
from scipy import integrate

R=8.314     # gas constant in J K^-1 mol^-1

Theta_D=309 # Debye Temperature of copper in K

T = 90     # given K at which we want molar heat capacity

def fn_I(x):
    fn_I= x**4 * np.exp(x) / (np.exp(x)-1)**2
    return fn_I

# For fine-tuning the integration settings see the scipy documenation
# https://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.quadrature.html

Integral=integrate.quadrature(fn_I, 0.0, Theta_D/T)

print("The value of the integral is: ",Integral[0], " with a numerical error of ", Integral[1])

CV=9*R*(T/Theta_D)**3*Integral[0]

print("Heat capacity of Cu at T = 103 K is: ",CV, " J mol^-1 K^-1")
```

lower limit

upper limit

```
The value of the integral is:  7.9788851408858035  with a numerical error of  6.324787538147802e-08
Heat capacity of Cu at T = 103 K is:  14.751861725666032  J mol^-1 K^-1
```

Agrees well with the experimentally measured value: $14.49\,\mathrm{J}\cdot K^{-1}\cdot\mathrm{mol}^{-1}$