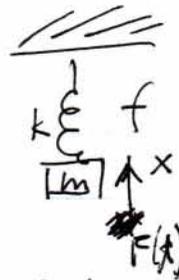


RC circuit



m	\rightarrow	L	— — —
f	\rightarrow	R	— — —
k	\rightarrow	$\frac{1}{C}$	— — —
x	\rightarrow	q	$\frac{dq}{dt} = I$
F	\rightarrow	Voltage	— — —

accel'n \downarrow

Total Force = $m \frac{d^2x}{dt^2} = -kx - f \frac{dx}{dt} + F(t)$

\uparrow DRIVING FORCE

$L \frac{d^2q}{dt^2} = -\frac{q}{C} - R \frac{dq}{dt} + V(t)$

~~ANALYSIS~~ ZERO-MASS LIMIT: ($L=0$) \Rightarrow "RC" CIRCUIT

$f \frac{dx}{dt} + kx \stackrel{F(t)=0}{=} 0$ (TRANSIENT RESPONSE: DISPLACE MASS, LET GO)

$\left(\frac{dx}{x} = -\frac{k}{f} dt \right)$

Sol'n $x = x_0 e^{-t/\tau}$

Verify: $f \left(-\frac{1}{\tau}\right) x_0 e^{-t/\tau} + k x_0 e^{-t/\tau} = 0$

$\frac{f}{\tau} = k$

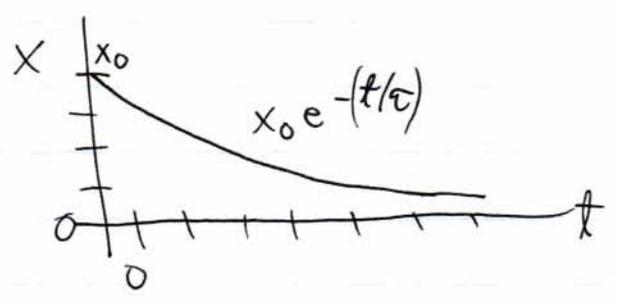
$\tau = \frac{f}{k}$

OR, $f \rightarrow R$
 $k \rightarrow \frac{1}{C}$

$\tau = RC$

TIME CONSTANT FOR CHANGE IN CURRENT

\uparrow i.e., charge dissipates to zero with time

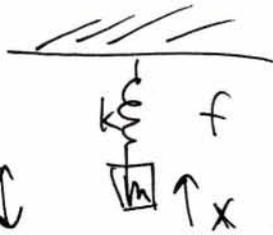


C4130



Massless Wt-on-Spring

RC Filter: Suppose we try to drive spring UP + DOWN w-osc's force:

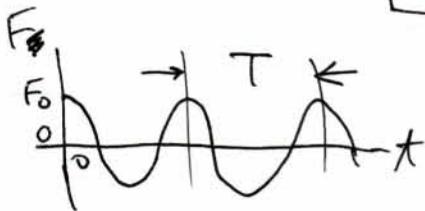


$$\text{Force} = m \frac{d^2 x}{dt^2} = -kx - f \frac{dx}{dt} + F_0 \cos wt \stackrel{m=0}{=} 0$$

Claim: Steady-State sol'n is of form:

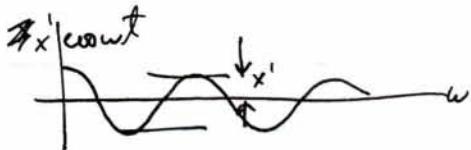
$$x = \frac{F_0}{k} \left(\frac{1}{1 + \omega^2 \tau^2} \right) \cos wt + \frac{F_0 f}{k^2} \left(\frac{\omega}{1 + \omega^2 \tau^2} \right) \sin wt$$

same ω !
Response at
freq of
driver

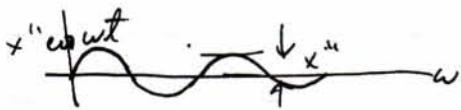


$$T = \frac{1 \text{ sec}}{\nu \text{ cycles/sec}} = \frac{2\pi \text{ rad/cycle}}{\omega \text{ rad/sec}}$$

Steady-State
In-phase
Response



90°-out of
phase response



VERIFY:
$$-k \frac{F_0}{k} \left(\frac{1}{1 + \omega^2 \tau^2} \right) \cos wt - \frac{k f F_0}{k^2} \left(\frac{\omega}{1 + \omega^2 \tau^2} \right) \sin wt$$

$$-f \left(\frac{F_0}{k} \right) \left(\frac{1}{1 + \omega^2 \tau^2} \right) (-\omega) \sin wt - \frac{f^2 F_0}{k^2} \left(\frac{\omega}{1 + \omega^2 \tau^2} \right) (\omega) \cos wt + F_0 \cos wt \stackrel{?}{=} 0$$

$$A \cos wt + B \sin wt = 0 \text{ iff } A = B = 0$$

A {

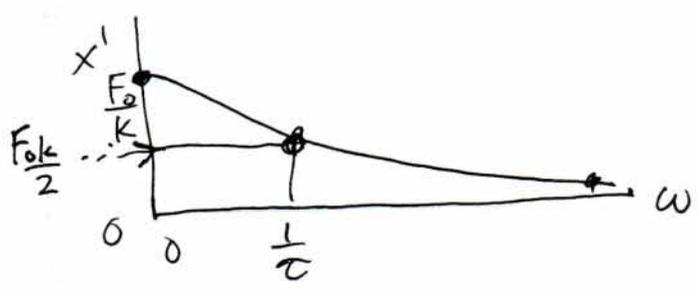
$$-\left(\frac{1}{1 + \omega^2 \tau^2} \right) - \frac{f^2 \omega^2}{k^2} \left(\frac{1}{1 + \omega^2 \tau^2} \right) + 1 = 0 \text{ Mult by } 1 + \omega^2 \tau^2$$

$$-1 - \frac{f^2 \omega^2}{k^2} + 1 + \omega^2 \tau^2 = 0$$

$$\tau^2 = \frac{f^2}{k^2}$$

$$\tau = \frac{f}{k} \leftrightarrow RC$$

Now look at ^{AMPLITUDE OF} RESPONSE AS A FUNC OF DRIVING FREQ: (x') ^{constant}



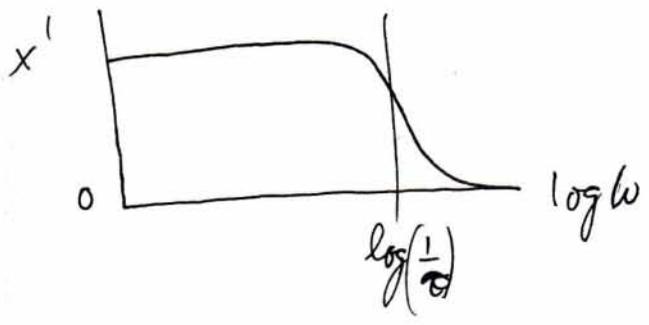
$$x' = \frac{F_0}{k} \left(\frac{1}{1 + \omega^2 \tau^2} \right)$$

$$\lim_{\omega \rightarrow 0} x' = \frac{F_0}{k}$$

$$\lim_{\omega \rightarrow \infty} x' = 0$$

$$\lim_{\omega \rightarrow \frac{1}{c}} x' = \frac{1}{2} \left(\frac{F_0}{k} \right)$$

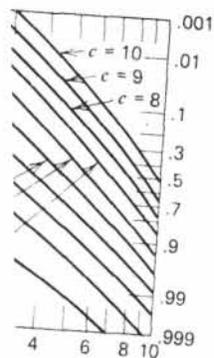
OR



LOW-PASS FILTER!!!

~~NON-TOO DOUBBLE, MIXER, PHASE SENSITIVE DETECTION~~

Procedure. Poisson probability
 particularly when the number of
 identical examples.
 event will occur *at least* C



probability, P , that an event will
 occur m times if the number of occurrences is \bar{m} . (From
 Baltimore, Md., 1956, p. 105.)

8.D. CHROMATOGRAPHY

BECAUSE THEY SCORE TOO MANY!

The Poisson distribution arises in a natural way in the theory for certain kinds of chromatography (liquid-liquid partition and the more recent and useful gas-liquid, gel, ion-exchange, and affinity chromatography). As usual, the derivation is based on an intuitive, artificial model: it is supposed that the chromatograph column can be taken to consist of a stack of hypothetical disks, or plates, each containing a volume, V , of solvent (see Figure 8-7).

From Fig. 8-7 and its legend, it is clear that after a total of N infinitesimal increments of solvent have been added, with equilibration between each successive addition, the resultant concentration in a given plate (say, the m th plate counting down from the top) will follow a binomial distribution:

$$[C(m)] = [C]_0 \frac{N!}{m!(N-m)!} \left(\frac{dV}{V}\right)^m \left(1 - \frac{dV}{V}\right)^{(N-m)} \quad (8-30)$$

where $[C(m)]$ is the concentration of solute in the m th plate. Inspection of Eq. 8-30 quickly shows that since $(dV/V) \ll 1$, and $N \gg 1$ (in a typical

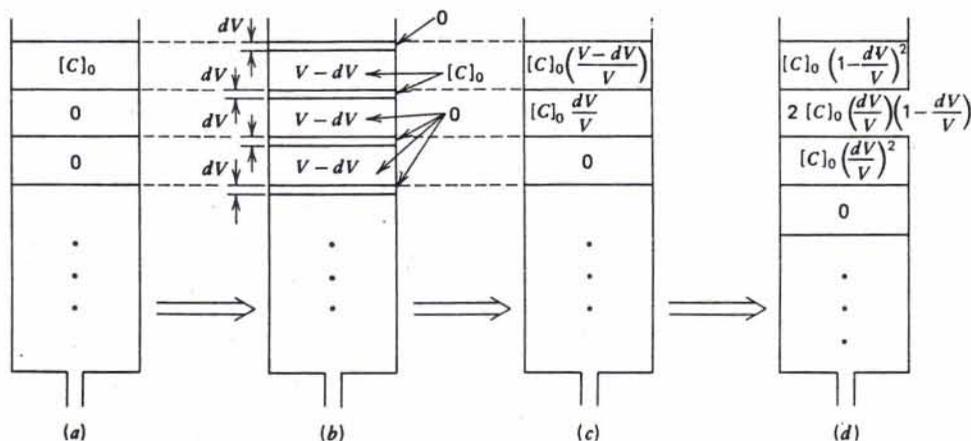


FIGURE 8-7. Schematic chromatography with intermittent flow of solvent. At the beginning of the experiment (a), the column is treated as a stack of many separate hypothetical "plates," with the sample occupying the topmost plate. Then (b) a small volume of solvent, dV is added, with a corresponding dV of solvent allowed to issue from the bottom of the column. The first plate then contains volume dV of solute concentration zero and volume $(V - dV)$ of concentration, $[C]_0$. On equilibration (c), the first plate assumes a homogeneous composition of solute concentration, $[C]_0[(V - dV)/V] = [C]_0[1 - (dV/V)]$, while the second plate contains concentration $[C]_0(dV/V)$ of solute. When the same process is repeated, and equilibration again allowed to proceed, the distribution of solute among the various hypothetical plates of the column is shown in (d). The binomial nature of the distribution can now be demonstrated by induction.

gas chromatograph, there may be several hundred thousand plates), it is possible to apply the Poisson limit to Eq. 8-30 by the same reasoning used to obtain Eq. 8-9, with the identifications,

$$a = (dV/V) \ll 1 \quad (8-31)$$

$$Na = \bar{m} = N(dV/V) = \frac{v}{V} \quad (8-32)$$

where v is the volume of solvent that has passed through the column, to give

Fraction of initial material residing in the m th hypothetical plate	$= P_N(m) = \frac{[C(m)]}{[C]_0} = \frac{(v/V)^m e^{-(v/V)}}{m!}$	(8-33)
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In Eq. 8-33, $\bar{m} = v/V$ represents the number of plate volumes of solvent that has passed through the column. A graphical illustration of Eq. 8-33 is shown in Fig. 8-8, in which each solid curve is a plot of solute concentration

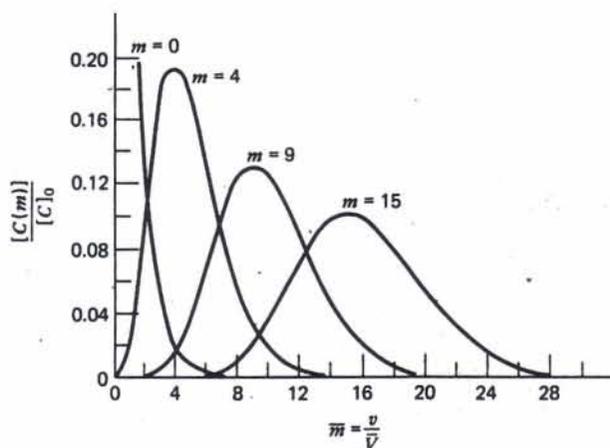


FIGURE 8-8. Relative solute concentration, $[C(m)]/[C]_0$, in the m th hypothetical "plate" of the chromatograph column of Fig. 8-7, as a function of the number of plate volumes of solvent, v/V , that has passed through the column. If m is the last plate of the column, the corresponding curve will give the concentration of solute in successive volume fractions issuing from the column, as in a typical experiment (see Fig. 8-9). (From E. W. Berg, *Physical and Chemical Methods of Separation*, McGraw-Hill, N. Y., 1963, p. 110.)

in the m th plate, as a function of the number of plate volumes of solvent that has passed through the column. It is to be noted that the concentration profile on the column (i.e., concentration as a function of plate number for a fixed amount of eluent passed through the column) begins with a skewed shape (Fig. 8-1b) and gradually becomes more symmetric as the solute spreads out while the concentration "peak" moves down the column. However, in the usual column chromatography experiment, solute concentration is monitored as the solution leaves the column; thus, while the solute profile on the column is at first a narrow "peak" as the first solute fractions issue from the last plate of the column, the concentration profile on the column will have broadened considerably by the time the later fractions from the same "peak" have left the column. In other words, the expected solute concentrations for fractions collected as they leave the column will be skewed, showing a "tail" as the final fractions leave the column, as seen in Fig. 8-8. A practical example is shown in Fig. 8-9, which is a gas-liquid chromatogram of various amino acids, each of which has been derivatized to make it easier to vaporize. The gas-liquid-chromatography ("glc") column itself may consist simply of a glass capillary tube (say, 0.02 cm inner diameter and a few hundred feet long), coated with solvent, while the (vaporized) sample is forced through the column by an inert "carrier" gas such as nitrogen. Alternatively, the column may be packed beforehand with some nonvolatile substance on which the liquid coating can be introduced as described above. Separation of different solutes is based on differences in

(GRADIENT ELUTION)