

Avoid Common Pitfalls When Using Henry's Law

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Here is practical guidance on the use of Henry's law in engineering calculations and how to account for the temperature dependence of the Henry's constant — which is often ignored but which can be crucial for accurate process design.

Henry's law and the Henry's constant are widely used in chemical and environmental engineering. Unfortunately, many people do not appreciate that the Henry's "constant" is not a true constant, but instead has a significant non-linear temperature dependence. Ignoring this temperature dependence can lead to serious inaccuracies.

This article discusses the temperature dependence of the Henry's constant and suggests ways of estimating this dependence when data are limited or not available. It also briefly discusses other common pitfalls to be avoided when using Henry's law. The focus is on dilute aqueous systems, such as those found in environmental applications, but much of the information is also appropriate for other applications.

Thermodynamic basics

CEP published a series of articles by Carroll (1–3) covering many aspects of Henry's law and its uses in chemical engineering. This article will not repeat the material presented there, but will summarize a few key concepts that are relevant to this discussion.

In a given solvent, the Henry's constant for solute i , H_i , is defined as an infinite-dilution limit:

$$H_i = \lim_{x_i \rightarrow 0} \frac{f_i}{x_i} \quad (1)$$

where f_i and x_i are the fugacity and the mole fraction of the solute, respectively. (Variables other than mole fraction are sometimes used to describe the amount of solute; this will be discussed later.)

Equation 1 may be applied at any temperature or pres-

sure, and the solvent may be a liquid, a vapor, a supercritical fluid, or even a solid. Most applications, however, involve a liquid solvent. Furthermore, it is usually convenient to define H_i at a pressure equal to the solvent's vapor pressure. (Reference 1 explains how to use these values at higher pressures.) When restricted to the solvent's vapor-pressure curve, H_i becomes a function of temperature only. For environmental work at pressures near ambient, this "restricted" Henry's constant is adequate. (The pressure dependence is ignored in the remainder of this article.) More-complex methods covering wide ranges of temperatures and pressures, such as those encountered in geochemistry, may be found elsewhere (4–6).

Since real systems never reach the limit of infinite dilution, most applications of Henry's law involve the use of Eq. 1 without the infinite-dilution limit. The assumption that f_i/x_i remains constant for non-zero values of x_i is reasonable for many environmental applications, where the goal is to describe the solubility or volatility of small amounts of contaminants in water.

With the proportionality between f_i and x_i established by Henry's law for one phase (e.g., an aqueous phase being purified), one needs only a model for f_i in the other phase in order to design a separation process based on phase equilibrium. For steam or air stripping, where the coexisting phase is a vapor, an ideal-gas assumption is often sufficient, or corrections for nonideality may be added. If the coexisting phase is a liquid (for example, in liquid-liquid extraction), Raoult's law is the simplest assumption; this may be corrected by a liquid-phase activity model as appropriate.

Nomenclature

C_i	= any of various measures of composition in the liquid phase (various units may be used)
$\Delta C_{p,sol}$	= heat capacity of solution, J/mol-K
f_i	= fugacity of solute i , MPa
H_i	= Henry's constant for solute i , MPa
H_i^*	= the "solubility form" of the Henry's constant for solute i , MPa ⁻¹
ΔH_{sol}	= enthalpy of solution, J/mol
ΔH_{vap}	= enthalpy of vaporization, J/mol
p_i^{sat}	= vapor pressure of pure component i at the temperature of the solution, MPa
R	= molar gas constant = 8.314472 J/mol-K
T	= temperature, K
T_c	= critical temperature of the solute, K
T_0, T_1	= initial and final temperatures for an extrapolation of H_i , K
x_i	= mole fraction of solute i
x_i^{aq}	= mole fraction of the organic solute in the aqueous phase
x_w^{org}	= mole fraction of water dissolved in the organic phase
Greek Letters	
γ_i^{inf}	= infinite-dilution value for the activity coefficient of solute i in the solvent, dimensionless

Where do Henry's constants come from?

A review of the many data sources for Henry's constants is beyond the scope of this article. However, it is helpful to understand how these data are obtained. Henry's constants cannot be measured simply by placing a meter into a solution. Rather, they are derived indirectly from experiment via Eq. 1.

For a sparingly soluble gaseous solute, the determination of H_i is straightforward from Eq. 1 (although the experiments may be difficult). Measurements of the solubility x_i at low gas partial pressures yield H_i directly (perhaps after small corrections for gas nonideality to improve the value of f_i).

For a liquid solute that is nearly immiscible with the solvent, such as toluene with water, use of Eq. 1 is again straightforward. For the case where component i forms an organic-rich phase that is nearly immiscible with an aqueous phase, the solute fugacity in the solute-rich phase (which must be equal to that in the solvent-rich phase) can be approximated by Raoult's law:

$$H_i = \frac{(1 - x_w^{org}) p_i^{sat}}{x_i^{aq}} \quad (2)$$

where x_w^{org} is the mole fraction of water in the organic phase, x_i^{aq} is the mole fraction of the organic solute in the

aqueous phase, and p_i^{sat} is the vapor pressure of pure component i at the temperature of the solution. A comprehensive collection of mutual solubility data for hydrocarbons with water and seawater is available in Ref. 7.

For solutes with large or complete miscibility with the solvent (such as lower alcohols with water), the determination of Henry's constant must again come from Eq. 1, but full analysis of the phase equilibrium is typically required. This usually involves fitting a liquid-activity model to experimental data and extrapolating the solute fugacity back to infinite dilution with the model. Equation 1 ultimately reduces to:

$$H_i = \gamma_i^{inf} p_i^{sat} \quad (3)$$

where γ_i^{inf} is the infinite-dilution value for the activity coefficient of solute i in the solvent.

An engineer who cannot find a tabulated Henry's constant is not necessarily stymied. If good phase-equilibrium data exist for the solute-solvent pair at the temperature of interest, a reliable value of Henry's constant can be derived.

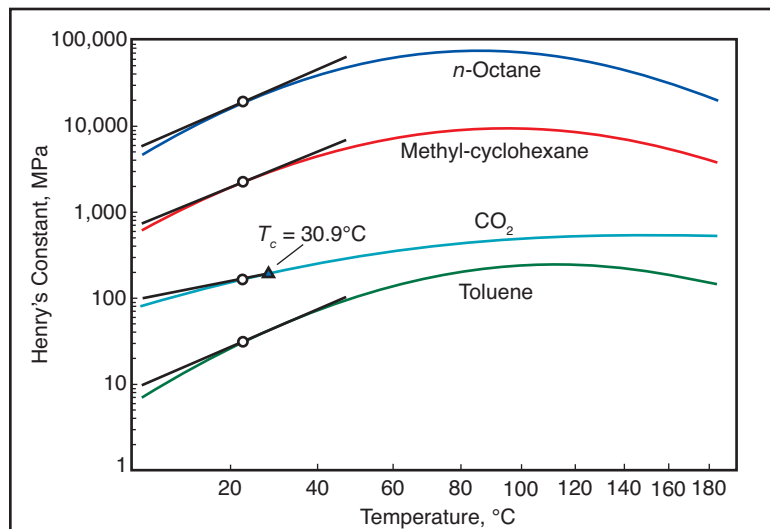
Temperature dependence

As stated earlier, the Henry's "constant" is not constant with respect to temperature. Figure 1 illustrates some typical behavior of $H_i(T)$ for several solutes in water. (Other aspects of Figure 1 will be discussed later.) The values for CO₂ are taken from the correlation of Fernández-Prini, *et al.* (8), while those for other solutes come from the correlating equations used by de Hemptinne, *et al.* (9). These are not necessarily the best values in the range plotted, but only the qualitative behavior is important for this discussion.

The Henry's constant typically increases with temperature at low temperatures, reaches a maximum, and then decreases at higher temperatures. The temperature at which the maximum occurs depends on the specific solute-solvent pair. As a rule of thumb, the maximum tends to increase with increasing solute critical temperature for a given solvent and with increasing solvent critical temperature for a given solute.

Clearly, the use of a Henry's constant that was derived at 25°C at a different temperature could lead to serious design errors. Even a variation as small as 10 K can cause the Henry's constant to change by a factor of two, which could have a serious impact on many designs.

In some cases, reliable values for Henry's constants are available over the entire temperature range of interest. For example, for common gases in water, the correlation of Fernández-Prini, *et al.* (8) extends from 0°C to the critical point of water. In other cases, solubility data are available so that Henry's constants can be derived by the methods described in the previous section. But in many cases, only a



■ Figure 1. Temperature dependence of Henry's constant for several solutes in water, showing the performance of the vapor-pressure extrapolation method starting at 25°C. The horizontal axis is linear in reciprocal absolute temperature.

few data, or perhaps only a single measurement, will be available, often at or near 25°C.

Sometimes no data at all will have been measured. If measuring it (or contracting for its measurement) are not options, one must rely on predictive schemes that estimate a Henry's constant from molecular structure (and perhaps other properties such as solute chromatographic parameters). These methods (10–14), which are beyond the scope of this article, typically provide a value at a single temperature, such as 25°C.

The following sections discuss how to extrapolate Henry's constants from a single data point at a given temperature (*e.g.*, 25°C) when temperature-dependent data are lacking.

Estimating temperature dependence using vapor pressure

The starting point for intelligent extrapolation of Henry's constants is Eq. 3. When extrapolating from a known value of H_i at temperature T_0 to temperature T_1 , Eq. 3 becomes:

$$\frac{H_i(T_1)}{H_i(T_0)} \approx \frac{\gamma_i^{inf}(T_1)}{\gamma_i^{inf}(T_0)} \times \frac{p_i^{sat}(T_1)}{p_i^{sat}(T_0)} \quad (4)$$

The interrelated temperature dependencies of Henry's constant H_i , infinite-dilution activity coefficient γ_i^{inf} , and solute vapor pressure p_i^{sat} can be demonstrated by plotting them together. Figure 2 shows these variables for a typical solute (toluene) on a logarithmic scale; note that while the hori-

zontal axis has units of degrees Celsius, it is actually linear in inverse absolute temperature (but reversed, so that temperature increases along the axis from left to right).

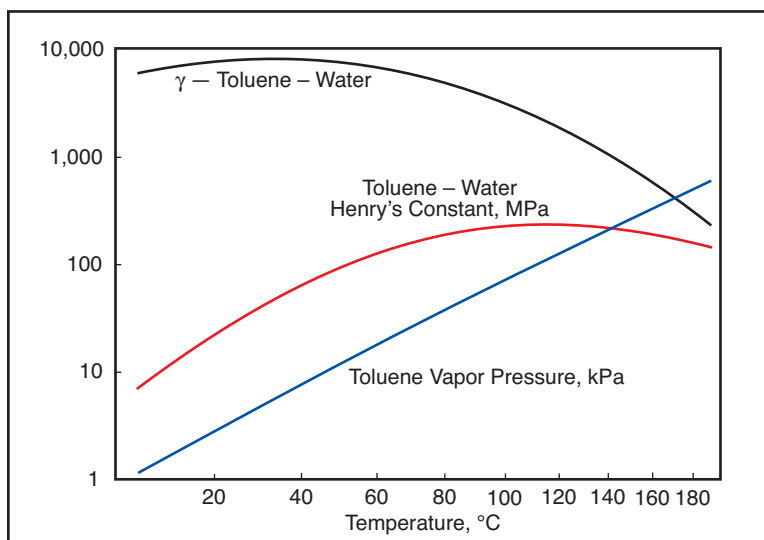
As expected from the Clausius-Clapeyron equation, $\log_{10} p_i^{sat}$ is nearly linear in inverse temperature. The temperature dependence of γ_i^{inf} is modest near ambient temperature, so that the temperature variation of H_i is primarily a consequence of the variation in p_i^{sat} . At higher temperatures, γ_i^{inf} varies much more rapidly, so that the temperature variation of H_i becomes more strongly dependent on the combined variations of both p_i^{sat} and γ_i^{inf} .

The behavior noted in Figure 2 suggests an extrapolation procedure. Especially for small temperature intervals near ambient conditions, the relatively minor contribution of $\gamma_i^{inf}(T)$ in Eq. 4 can be ignored and a reasonable extrapolation obtained from:

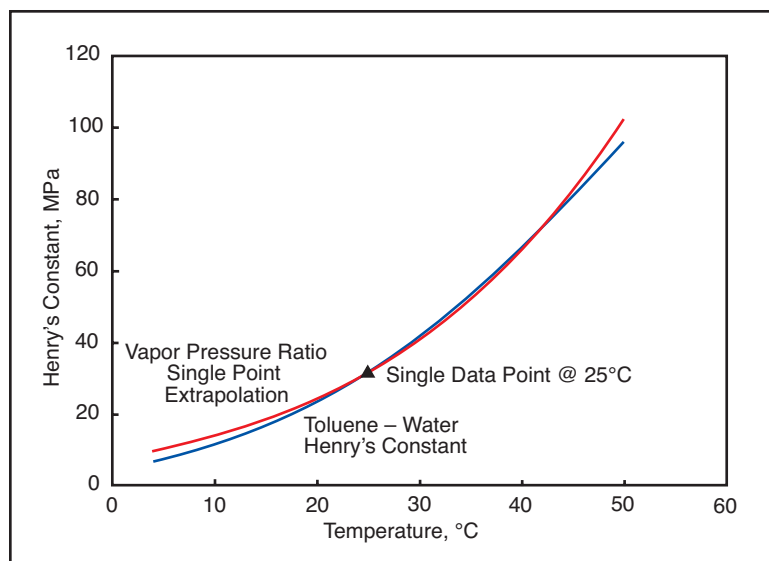
$$\frac{H_i(T_1)}{H_i(T_0)} \approx \frac{p_i^{sat}(T_1)}{p_i^{sat}(T_0)} \quad (5)$$

Equation 5 is particularly convenient because the vapor-pressure function $p_i^{sat}(T)$ is known for many solutes of interest, while temperature-dependent values of γ_i^{inf} are seldom available.

Figure 3 shows the performance of this vapor-pressure-ratio extrapolation method, Eq. 5, for toluene in water with a single value at 25°C as the starting point. Equation 5 provides an excellent extrapolation for this temperature range — much better than if H_i had been assumed to be constant.



■ Figure 2. Interdependence of Henry's constant, solute vapor pressure and infinite-dilution activity coefficient (Eq. 3) for toluene in water. Note the different pressure units on the Henry's constant and the vapor pressure.



■ Figure 3. Illustration of vapor-pressure extrapolation technique (Eq. 4) for the Henry's constant of toluene in water.

In Figure 1, the vapor-pressure-ratio extrapolation is plotted for four compounds over a wider temperature range. Because the horizontal scale is linear in reciprocal absolute temperature, the extrapolations are nearly linear on these coordinates. The accuracy of the extrapolation from 25°C with Eq. 5 deteriorates at higher temperatures, but it is quite good up to 50°C and not unreasonable up to perhaps 80°C.

Note that the vapor pressure of CO₂ does not exist above its critical temperature ($T_c = 30.9^\circ\text{C}$), so Eq. 5 cannot be used directly for the extrapolation of H_i above this temperature. However, the critical temperature of solute i does not introduce any irregularities into the behavior of $H_i(T)$, so H_i can still be extrapolated to some extent above the solute critical temperature by visual or graphical means based on the vapor pressure data below T_c .

For some less-common solutes, the vapor-pressure data needed for Eq. 5 may not be known at the temperatures of interest. In such cases, estimation techniques for $p_i^{sat}(T)$ (15) can be used to obtain the vapor-pressure ratio for Eq. 5.

Enhancing extrapolation with infinite-dilution activity coefficients

Equation 5 can be improved upon if one can estimate the temperature dependence of the infinite-dilution activity coefficient γ_i^{inf} ; in such cases, Eq. 4 would be used. This is only a small correction for short extrapolations near ambient temperature, but becomes a major factor for larger extrapolations, especially to higher temperatures such as those used in steam stripping.

In the absence of experimental data, predictive models for activity coefficients can be used to estimate

$\gamma_i^{inf}(T_1)/\gamma_i^{inf}(T_0)$ for use in Eq. 4. It is important to use a model that is designed to include temperature dependence; some predictive models are designed only for 25°C and therefore are inappropriate for this purpose. The modified UNIFAC model (16) yields the temperature variation of γ_i^{inf} ; the COSMO-RS method (17) might also be useful, although its use in this context has not been documented in the literature.

Hwang, *et al.* (18) studied the infinite-dilution vapor-liquid partition constant (which is closely related to the Henry's constant) in the context of steam stripping for organic pollutants in water. They established a databank for 404 common organic pollutants, including many EPA-designated priority pollutants, at 100°C and 25°C. In cases where high-temperature data were lacking, they used the vapor-pressure extrapolation method, supplementing it with activity coefficients estimated with UNIFAC. They tabulated

suggested values for $\log_{10}[\gamma_i^{inf}(100^\circ\text{C})/\gamma_i^{inf}(25^\circ\text{C})]$ for several different classes of organic compounds.

Van't Hoff extrapolation

An alternative method for extrapolation of single values for Henry's constants uses the solute enthalpy of solution, ΔH_{sol} , over a modest temperature range. A thermodynamic expression, usually associated with the name van't Hoff, relates the Henry's constant at the two absolute temperatures T_0 and T_1 :

$$\frac{H_i(T_1)}{H_i(T_0)} \approx \exp \left[\left(\frac{\Delta H_{sol}}{R} \right) \left(\frac{1}{T_1} - \frac{1}{T_0} \right) \right] \quad (6)$$

where R is the molar gas constant. Equation 6 derives from a differential expression, so its use over a finite temperature range makes the implicit assumption that ΔH_{sol} remains constant with temperature (so it cannot reproduce the curvature and maximum shown in Figure 1). This is usually a fair approximation for modest temperature differences of perhaps 20 K, making the van't Hoff approach reasonable for systems near ambient temperature, such as groundwater, where the temperature variations are not large (19). If available, data for the heat capacity of solution, $\Delta C_{p,sol}$, can be used to increase the range of reasonable extrapolation by providing a temperature dependence for ΔH_{sol} .

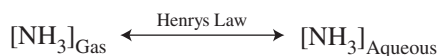
Data for ΔH_{sol} (and $\Delta C_{p,sol}$) for solutes in water are difficult to measure experimentally. Published values are limited and (as can be seen in tabulations such as that in Ref. 20) can vary substantially. Often, tabulated values of ΔH_{sol} are merely derived from values of H_i measured over a range of

temperatures. If such data for $H_i(T)$ already exist, it is a waste of effort and sacrifices accuracy to translate them into ΔH_{sol} and then use Eq. 6 — it is better to use the measured $H_i(T)$ directly. (It is reasonable, though, to use Eq. 6 to interpolate measured data for $H_i(T)$ over small temperature ranges, which was done by Washington (19)). However, if independent values of ΔH_{sol} exist at the desired temperature, either from calorimetric data or from a reliable estimation technique, Eq. 6 provides a reasonable method for extrapolating Henry's constants over modest temperature intervals. Note that ΔH_{sol} can be either negative or positive, depending on whether the temperature of interest is below or above the maximum of $H_i(T)$ (Figure 1).

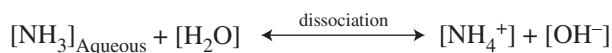
Occasionally (21), one sees an equation similar in form to Eq. 6, but with the negative of the pure-solute enthalpy of vaporization, $-\Delta H_{vap}$, in place of ΔH_{sol} . Such a substitution has little basis in thermodynamics, but it can provide an adequate estimate in some cases. This is because the Clapeyron equation relates ΔH_{vap} to the temperature dependence of the vapor pressure, so that the use of ΔH_{vap} in Eq. 6 becomes nearly equivalent to the vapor-pressure extrapolation method, Eq. 5. However, ΔH_{vap} is almost never measured independently, but is typically derived from data for $p_i^{sat}(T)$. Consequently, it is preferable to use Eq. 5 directly, in order to avoid loss of accuracy when $p_i^{sat}(T)$ is differentiated. Note also that the vapor-pressure extrapolation method, unlike the van't Hoff type methods, implicitly corrects for the temperature dependence of ΔH_{vap} over the range of the extrapolation.

Pitfalls with chemically reacting systems

Some substances (NH_3 , Cl_2 , organic acids, etc.) partition within the aqueous phase, due to reversible equilibrium processes such as dissociation. Henry's law describes only the equilibrium of a single neutral species of the substance between the two phases:



However, within the aqueous phase, partitioning of the aqueous form of a substance may occur and would, therefore, need to be accounted for and described. This is done using one or more additional equilibrium expressions, such as:



The consequence of such partitioning (2, 22, 23) is that, for a given gas-phase concentration, a larger quantity of the substance may actually exist within the aqueous phase at equilibrium than would be predicted by Henry's law. This can be especially significant if a dissociated species participates in an additional reaction, such as an acid-base reaction that

would consume OH^- . Similarly, a much smaller amount may actually exist in the gas phase at equilibrium than would be predicted by Henry's law if a quantitative analytical method that measures the sum of the associated and dissociated forms of the solute were used to determine the total quantity of the partitioned substance in the aqueous phase.

Pitfalls with units

A common problem with Henry's constants is caused by the wide variety of possible units of measure. Because Henry's law is used in many different disciplines, many different usages and conventions have developed. If proper care is not taken, it can be easy to use a reported Henry's constant in a way that does not match the way in which the original value was defined — leading to serious errors. Because Henry's constants vary over many orders of magnitude (Figure 1), errors due to units are more difficult to detect by inspection in this case than in many other engineering situations (for example, calculation of pure-component vapor pressures, where an engineer would have a good idea of the correct order of magnitude).

The definition in Eq. 1 (fugacity divided by mole fraction) implies units of pressure for H_i . This is the most common usage for chemical engineers. However, in various contexts one sees gas-phase composition described by partial pressure, mass concentration, molar concentration, etc., while units for liquid-phase composition can include molality, molarity and weight fraction. When composition is used for the gas phase, it is important to note what the implied total pressure is. When mole or weight fraction is used for the liquid phase, it is not always obvious which is meant from the units of Henry's constant, since fractions are dimensionless by convention. If the concentration units applied for both phases are the same, then the Henry's constant itself becomes dimensionless. This is unfortunate — because depending on which units were used, different dimensionless Henry's constants, with different values, exist for the same solute.

Another source of confusion is that some practitioners (for example, Ref. 20) use Henry's law in a "solubility" form, such as $C_i = H_i^* p_i$, where C_i is some measure of composition in the liquid phase and H_i^* is effectively the reciprocal of the "volatility form" of the Henry's constant (which has been used throughout this article). This means that the Henry's constant for any solute has two different values, depending on whether Henry's law took the solubility form or the volatility form.

Therefore, two things are imperative. First, those who report Henry's constants in the literature (both from original measurements or in compiling data from others) must be very clear about definitions. Second, those who use

Henry's constants must pay close attention to be sure they understand how the numbers they are using were defined.

Conversion among different units for Henry's constant is possible, but can be complicated by the need to convert between mass and molar concentration units. Therefore, factors such as the molar mass of the solute and the density of water are employed. Some calculators for this purpose are available on the Internet (24, 25). When using such calculators, it is essential to be clear about the definition associated with each unit, especially dimensionless units.

Finally, note that the expressions given above for estimating the temperature dependence of Henry's constant are for the definition of H_i in Eq. 1. A subtle but signifi-

cant point is that the ratio $H_i(T_1)/H_i(T_0)$ is not the same in all sets of units. In particular, if units of volumetric concentration (such as moles per liter) are used, an additional temperature dependence is introduced by the variation of fluid-phase density with temperature. This can be on the order of 10% for a 30 K change near room temperature when such units are used for the vapor; the change of liquid density with temperature is usually small enough to neglect. If one is using Eq. 4 or Eq. 5 with such density-dependent composition units, the preferred procedure is to convert to the units of Eq. 1, perform the $H_i(T)$ extrapolation in those units, and then convert back to the density-dependent units.

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Conclusions

It is important to recognize that the Henry's "constant" is actually a strong, nonlinear function of temperature. For accurate design, it is preferable to have temperature-dependent data for $H_i(T)$. Such data can be interpolated with a simple van't Hoff equation (such as Eq. 6) over small temperature ranges or a more complex expression (such as those in Ref. 8 or Ref. 9) if a larger range is needed; these correlations can be extrapolated slightly over temperature if necessary. If temperature-dependent data are not available, Eq. 5 can be used to extrapolate for modest distances near ambient temperatures; this can be augmented by the use of infinite-dilution activity coefficients (Eq. 4), which become more important at higher temperatures.

Additional pitfalls include failing to distinguish between the "solubility" and the "volatility" form of Henry's law, failing to consider the implications of liquid-phase solute partitioning, and failing to be careful about units of measure, especially dimensionless units. If one avoids these pitfalls, Henry's law can be a useful tool in many engineering applications.

CEP

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