THERMODYNAMICS

A Structure for Teaching and Learning About Much of Reality

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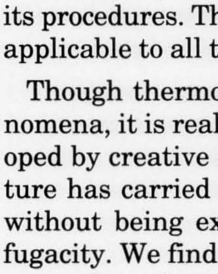
Thermodynamics is an amazing discipline. Its two brief laws contain the complete basis for establishing the states of pure and mixed systems and their tendencies for change. The foundation for scientific investigations into all forms of matter lie in its rigor. Constraints on engineers to interconvert heat and work, separate components from solutions, and obtain ultimate yields from chemical reaction arise with its symbolic manipulation. Reliable screening for feasibility and optimization of nearly every type of process can be guided by its procedures. Thermodynamics is fundamental and applicable to all technical endeavors.

Though thermodynamics focuses on natural phenomena, it is really just a deductive structure developed by creative and systematic human minds. Nature has carried out her diverse processes for eons without being explicit about energy, entropy, and fugacity. We find these mental constructs useful because they give us a chance to assimilate extensive amounts of real behavior, rather than being overwhelmed by its totality or misguided by less general alternatives. Further, we can use "always true" thermodynamics with appropriate information and approximation to effectively describe and predict multitudes of reality.

Modern thermodynamic ideas originated over 150 years ago, but the subject still evolves. Although some scholars claim that "there is nothing new in thermodynamics," a few still find challenges in its abstractness, rigor, and universality as well as in debating the "best" way to phrase the principles and their limits of application. But most current engineering work deals with the practical uses of thermodynamics—predominantly with models of reality. Modern computers enable testing of quantitative expressions for phenomena at every level of complexity. As a result, we find thermodynamics being used to an unprecedented extent to mimic and predict Nature's behavior more easily (and often more reliably) than experiment—especially for mixtures.



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Unfortunately, the word "thermodynamics" provokes uneasiness or frustration in many well-educated people, especially in alumni of engineering thermodynamics courses. This often arises from an incomplete or insecure classroom experience combined with insufficient background in assimilating all the basics. Becoming really comfortable with thermodynamic concepts and proficient in their use requires a comprehensive appreciation of the subject in addition to care, maturity, and intelligence. Thus, major objectives of thermodynamics education should include overcoming confusion and antipathy while fully integrating the concepts, knowledge, and procedures. The process, though quite demanding, must guide students to appreciate the structure and relevance of thermodynamics and to become effective in its use. It should also enrich their vision of Nature's unity and diversity.

What follows is one teacher's view of fundamental thermodynamic structure and how it leads to applications that could foster a useful and satisfying learning experience for chemical engineering students. While integration and connection require terms of study and often years of practice, the ideas presented here may be valuable for others in enhancing learning.*

STRUCTURE

Because thermodynamics is a logical construct, there are many ways that the subject can be developed. That is why there are so many textbooks. One extreme approach is to begin with axiomatics and mathematics, which then lead through formalisms to applications (the most elegant and difficult treatise on this is by Truesdell[1]). The other extreme is to note common observations, followed by generalizations and applications (Fenn has cleverly shown this technique with a cartoon character called "Charlie the Caveman"[2]).

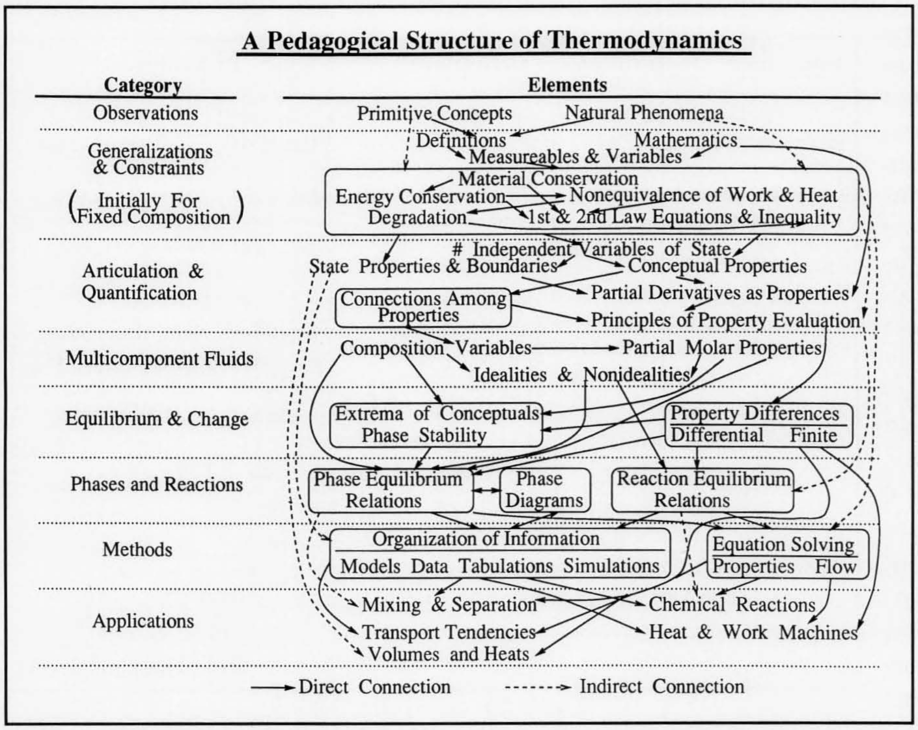

Figure 1. *A structure of chemical engineering thermodynamics.*

PRIMITIVE CONCEPTS MEASURABLES			NATURAL PHENOMENA HAPPENINGS		
Things	*Properties & State*	*Changes*			
System	Force	Input	Thermal and mechanical effects on fluids and solids	Material transfer of substances via various mechanisms	Reactive conversion with regular changes in form and amount
Surroundings	Length	Output			
Boundaries	Pressure	Accumulation			
	Volume	Generation			
		Consumption			

Table 1. *Observations*

	Definitions	Mathematics
Identity	Chemical species	Algebraic equations and variables
	System-surrounding interactions	Functions of several variables
Quality	Extensive and intensive	Independent and dependent variables
	Reversible and irreversible	Calculus derivatives and integrals
Quantities	Mass	Differential equations
	Temperature	Exact and inexact differentials
	Work	Balance equations
	Kinetic energy	Path dependence of integration
	Potential energy	

Table 2a. *Generalizations I*

Present-day students tend to be inexperienced in "the way things work," so I find that discussing observations first can be motivational, informative, and organizational. The flow diagram I generally follow is shown in Figure 1.

The way basics are initiated is through primitive concepts and natural phenomena, as listed in Table 1. The key to the concepts is a high level of precision that will lead easily to later mathematical descriptions of the phenomena. These initial elements should be phrased and illustrated in whatever terms that will make the group of learners relate to them. Years ago, references to cars and farming worked. Nowadays it needs to be connected to television, sports, music, environment, and the materials and goods of affluence.

The next step is generalizations and constraints, beginning with definitions related to physics and chemistry as well as to mathematics. Table 2a shows the kinds of things I define in familiar terms, in addition to the mathematical tools that must be used with facility in the study and implementation of thermodynamics. One point that I usually make is that we do not know what temperature (hotness) really is—we only know it can make a difference to a system, although not always. This uncertainty of what a property "really is" often makes the later conceptual quantities of energy, entropy, and fugacity less threatening since

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* *Jim Haile (Clemson) contributed much to these beginning thoughts.*

something as familiar as temperature is really unknown yet easily utilized with experience. Another device I have used to deal with the unfamiliar properties is to read the story of 37 sugar cubes, a small boy, and his mother.[3] (Some students, however, find that these challenges make the whole process even *less* appealing!)

Table 2b lists a set of "convenient" observations, definitions and equations which encompasses the conservation of mass, the number of variables needed to completely describe a system, the definition and conservation of energy, and the definition and generation of entropy. These particular choices are made because they lead directly to the most widely used statements of the laws and open system results, even though at this stage only systems of fixed composition are discussed. The level and amount of time on this part depends on the students' prior exposure—obviously, less is done with graduate students.

Because the fundamentals given to this point are often alien and abstract, they are articulated further, as shown in Table 3. The objectives are understandings, procedures, and recognitions that users must assimilate. It is essential that learners understand at this point that people invented state properties and conceptuals for their generality and directness, even if they were not measurable like the things we prefer to (and ultimately must) deal with.

The next step separates chemical engineers from the rest because the development is extended to multicomponent systems (see Tables 4a,b). This leads to a morass of definitions and complexities as the dimensionality of the system grows, and I know of no way to simplify this. By this time I have begun to insist that students have a notebook of definitions and I give the first part of each exam as a closed-book set of definitions, asking both word and equation answers for the quantities previously defined. I also always use the ≡ symbol for the definitions to distinguish them from mere equalities.

Particularly troublesome is fugacity. Students must recognize it is not a "corrected partial pressure"; it is a practical substitute for the chemical potential. Also, fugacity must be connected to temperature, pressure, and composition. The "Four Famous Fugacity Formulae" (FFFF) of Mike Abbott[4] (I use Five FFF) assures students that there are only a few options for every problem of phase and reaction equilibria. Also, they should be aware that it is now routine, though complicated, to connect complex composition behavior of activity co-

Convenient Observations	Definitions	Equations
Mass conserved (except in nuclear changes)	Atomic and molecular "weights"	Mass balance $M_{In} - M_{Out} = M_{Accumulated}$
# independent variables is # interactions	Heat, work, and material interactions	(#Ind) = (#Work) + (# Species) + 1 $P = P(T,V,x)$ $V^t = V^t(T,P,N^t) = N^tV(T,P,x)$
Work depends on path except if no thermal interactions (Joule)	Closed system $\Delta E \equiv W_{Adiabatic}$ $Q \equiv \Delta E - W$ $U \equiv E - E_K - E_P$	Energy balance E_{In}(Work,Heat,Material) − E_{Out}(Work,Heat,Material) = $E_{Accumulated}$
Work and heat are not equivalent even in reversible changes	Closed system $dS \equiv \delta Q_{Rev} / T$ T is integrating factor (Born and Caratheodory)	Closed system $dE = TdS + \delta W_{Rev}$
Work can be degraded to heat, but not *vice versa*	$dS_{Gen} \equiv dS - \frac{\delta Q}{T} \ge 0$	Entropy balance S_{In}(Heat,Material) − S_{Out}(Heat,Material) = $S_{Accumulated}$

Table 2b. *Generalizations II*

Objective	Example Mechanisms and Equations
Proper # variables for describing system	Determine total # variables; Count # equations Difference is # independent variables ⇒ # dependent (solved-for) variables is # equations
Replace boundary-crossing quantities with changes of system state properties	$dU_{Sys} = \delta Q_{Surroundings} + \delta W_{Surroundings}$ $= dQ_{Rev} + dW_{Rev}$ $= T_{Sys}dS_{Sys} - P_{Sys}dV_{Sys}$
Conceptual properties and their "natural" variables	$H \equiv U + PV \qquad G \equiv H - TS$ $dH = TdS + VdP \qquad dG = -SdT + VdP$
Connections among properties via partial derivatives	Maxwell relations $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$ Gibbs-Helmholtz relations $\partial(G/T)/\partial(1/T)\|_P = H$
Partial derivatives as properties	$T \equiv (\partial U / \partial S)_V \qquad P = -(\partial U / \partial V)_S$ $C_P(T,P) \equiv (\delta Q_{Rev} / dT)_P = T(\partial S / \partial T)_P = (\partial H / \partial T)_P$
Property evaluation from integration of partial derivatives	$\underbrace{\Delta H}_{\text{Path independent}} = \underbrace{\int(\partial H / \partial T)_P dT}_{\text{Path dependent}} + \underbrace{\int(\partial H / \partial P)_T dP}_{\text{Path dependent}}$

Table 3. *Articulation*

efficients to parameter mixing rules for PVTx equations of state (*e.g.*, Heidemann and Kokal[5]).

By this point in the course, there has been a tremendous amount of abstractness and it is time to get to applications which can be addressed via change and equilibrium, as shown in Tables 5a and 5b. This is where the generalizations can be made real with characterizations of driving forces and entropy generation in interesting systems undergoing change as well as in equilibrium (and metastable!) cases. A key is to make sure students overcome the myth about entropy always being maximized.

The next section (Table 6) shows the sets of relations that apply to phase and reaction equilibria as well as some of the physics of what Nature can do when it settles down. I use many plots of different variables for different kinds of substances and mixtures. The message is that "Nature does all things easily; ain't Nature grand!" I also insist that students recognize that "for every equation there is a graph, and for every graph there is an equation." If they are not sure of what an equation really means, they should draw its graph and vice versa.

At this point, the fundamentals are done. It's time to *use* thermodynamics. Table 7 shows the elemental methodology. The ultimate goal is a quantitative result that is reliable

Composition Variations

Amounts or fractions of species affect system

$N_i^t \equiv [N]_i^t$ n variables

$x_i \equiv [x]_i$ n − 1 variables

Independent variables
Extensive = n + 2
Intensive = n + 1
Mass fractions, volume fractions, molarity, molality, etc.
Chemical potential

$$\mu_i(S,V,x) \equiv \partial U^t / \partial N_i^t \Big|_{S^t,V^t,N^t_{j\neq i}}$$

Partial Molar Properties

$$\overline{F}_i \equiv \partial F^t / \partial N_i^t \Big|_{T,P,N^t_{j\neq i}}$$

$$F_i = \sum_i x_i \overline{F}_i$$

Gibbs-Duhem equation shows how n+2 intensive variables ($\overline{F}_i, T, P$) are related by one equation

$$(\partial F/\partial T)_{P,x}\, dT + (\partial F/\partial P)_{T,x}\, dP = \sum x_i d\overline{F}_i$$

to give n+1 independent variables

Partial Molar Gibbs Energy

$$\overline{G}_i = \partial G^t / \partial N_i^t \Big|_{T,P,N^t_{j\neq i}} = \mu_i(T,P,x)$$

Table 4a. *Multicomponent systems I*

Fluid Mixtures	Nonidealities and Idealities
Gases	
Compressibility factor	$PV^t = zN^t\mathbf{R}T$ $\quad \lim_{IG} z = 1$
Residual properties	$F^R \equiv F - F^{IG}$
Fugacity and fugacity coefficient	$\hat{f}_i \equiv x_i\hat{\phi}_i P$ $\quad \lim_{IG} \hat{\phi}_i = 1$
$d\overline{G}_i \equiv \mathbf{R}T\, d\ln \hat{f}_i$ (Fixed T)	Real $z, \hat{\phi}_i$ from EOS
Condensed Phase Solutions	
Excess properties	$F(T,P,x) \equiv \sum_i x_i F_i^o(T,P) + F^E(T,P,x)$ Ideal Solution $F^E = 0$
Reference fugacities and activity coefficients	$f_i(T,P,x) = x_i\gamma_i f_i^o$ $\quad$ Ideal Solution $\gamma_i = 1$
Lewis-Randall (**LR**) reference	$f_i^o = f_i^{pure}$ $\quad \lim_{x_i \to 1} \gamma_i = 1$
Henry's Law (**HL**) reference	$f_i^o = H_i$ $\quad \lim_{x_i \to 0} \gamma_i = 1$
Famous Fugacity Formulae (**FFF**)	#2 $\hat{f}_i(T,P,x) = x_i\gamma_i(T,P,x) f_i^o(T,P)$
Have P in various terms Use Poynting correction	#3 $\hat{f}_i(T,P,x) = x_i\gamma_i(T,P,x) f_i^o(T) \exp\left[\int \left(\overline{V}_i^o / \mathbf{R}T\right) dP\right]$
	#4 $\hat{f}_i(T,P,x) = x_i\gamma_i(T,x) f_i^o(T) \exp\left[\int \left(\overline{V}_i / \mathbf{R}T\right) dP\right]$
	#5 $\hat{f}_i(T,P,x) = x_i\gamma_i(T,P,x) f_i^o(T)$
Connections of residual to excess properties	FFF #2 $\quad \hat{f}_i^o(T,P) = \phi_i^o(T,P)P$ $\gamma_i(T,P,x) = \hat{\phi}_i(T,P,x) / \phi_i^o(T,P)$

Table 4b. *Multicomponent systems II*

Change

Driving forces for change
- Heat flows from high to low temperature
- Work flows from high to low "force" (*e.g.*, PV work from high to low P)
- Material diffuses from high to low chemical potential (fugacity)

Reversible changes ~ Equilibrium changes ($S_{Gen} \equiv 0$)
- Only differential differences in T, P, $\overline{G}_i$

Spontaneous changes ~ Real changes ($S_{Gen} > 0$)
- Finite differences in T, P, $\overline{G}_i$
- S_{Gen} increases with property difference
  Greatest for heat flow with T difference

Table 5a. *Change*

Criteria for Stability—What is Observed

Systems
- Only in isolated systems is entropy maximized
- All others—minimization of an energy function
  e.g., Minimum G if T,P fixed while varying x, phase, reaction
  (Entropy not minimized for ambient 2-liquid oil/water!)

Phases
- Differential criteria
  Pure fluids—Proposed phase unstable if $(\partial P / \partial V)_T > 0$
  Mixtures—Proposed phase unstable if stability matrix of $\partial \overline{G}_i / \partial N_i^t \Big|_{T,P,N^t_{j\neq i}}$ not positive definite
- Metastability satisfies differential but not global criteria
  Can occur in solids, microstructured fluids (polymer, bio, surfactant, colloid)

Table 5b. *Equilibrium*

and appropriately accurate for the case at hand. This requires organization of thermodynamic knowledge and introduction of models at the proper stage. Since with models "where there's a way, there's a will," the latter requires decisions. While students feel unprepared and/or unmotivated to choose among the myriad of options, "life's like that," so the practice is good. Modeling consists of a mathematical relation used to connect certain properties to measurables that will allow calculation of values for unknown measureables. Generalized thermodynamic models contain parameters that depend on the substance(s) of interest. The kinds of choices are suggested in Table 7. Teachers must make sure that students are given the tools to make these decisions, including the common choices and the usual rules of thumb.

The final requirement is to solve a set of nonlinear algebraic equations. With current computers and model software, students can now solve numerically more "realistic" problems, though the "black box syndrome" can arise if the only student input consists of numbers and "run."

PEDAGOGY

This process can be formalized in different ways; I prefer the concept of problem solving.[6] Table 8 shows a method developed with Jim Haile (Clemson University) called "PSALMS". It is a step-by-step technique that works well for typical chemical engineering thermodynamic problems. The two initial steps of "**P**roblem" and "**S**ystem" are the same as in essentially all "PS" methodologies. The next uses the power of thermodynamics that declares certain relations to be "**AL**ways true" so users can initiate something valid and relevant rather than stare at a blank piece of paper or make an assumption too early. The fourth step of "**M**odel" is an essential part of contemporary thermodynamics (the table suggests some of the choices to be made). The final step is "**S**olve and check," which is again a part of all PS methods.

By now this article has either lulled you to sleep because all of this seems so straightforward, or made you extremely

Phase Equilibrium Relations	**Reaction Equilibrium Relations**
Chemical Potentials	**Minimum Gibbs Energy**
$\overline{G}_i\left(T,P,x'\right)=\overline{G}_i\left(T,P,x''\right)=\ldots$	$\sum_i \nu_{ik}\overline{G}_i = 0$ (Independent Reactions k)
Fugacities	**Equilibrium Constant and Standard State (°)**
$\hat{f}_i\left(T,P,x'\right)=\hat{f}_i\left(T,P,x''\right)=\ldots$	$K_k(T) \equiv \exp\left(-\sum_i \nu_{ik}\overline{G}_i^o / \mathbf{R}T\right)$ $= \exp\left(-\sum_i \nu_{ik}\Delta G_{if}^o / \mathbf{R}T\right)$ $= \prod\left[x_i\hat{\phi}_i(T,P,x)P\right]^{\nu_{ik}}$ (FFF#1) Ref.(°) is pure IG at P = 1 $= \prod\left[\hat{f}_i(T,P,x)/f_i^o(T)\right]^{\nu_{ik}}$ (FFF#3-5) Ref.(°) is pure real (LR) or hypothetical (HL) substance

Phase Diagrams

- Pure P - T
  - 2-phase boundaries (S/V, L/V, S/L, S/S)
  - Fixed points (V/L, L/L criticals; triple points)
- Mixed multiphase systems
  - PTxy (multidimensional and projections)
    - Azeotropes, criticals, 3- and 4-phases

Enthalpies ("Heats") of Vaporizing, Melting, Subliming

- Related to P - T 2-phase lines by Clapeyron equation

$$\left(\frac{d\left(\ell n P^S\right)}{d(1/T)}\right)_{2-\text{phase}} = -\frac{\left(H''-H'\right)}{R\left(z''-z'\right)}$$

- Clausius approximation for gases (″) and liquids/solids (′)

$$z'' \approx 1 >> z'$$

Table 6. *Phases and reactions*

Organization of Information

Models and Data

Mathematical relations for
PROPERTIES $\left(z, C_P^{IG}, G^E, \hat{f}_i^o\right)$ in terms of
MEASURABLES (T, P, x, V) for manipulation to get
ALL properties (*e.g.,* conceptuals) (H, S, $\hat{f}_i$, etc.) needed for
SOLVING EQUATIONS for dependents (x, P, T, V, W, Q, etc) containing
PARAMETERS depending on molecular constitution

COMMON EXPRESSIONS requiring decisions

- PVTx equations of state
- $G^E \Rightarrow$ activity coefficients
- Reference fugacities, f_i^o
- Mixing rules for pseudopure parameters of mixtures
- Combining rules for unlike parameters from likes (often via k_{ij})

Solve Nonlinear Algebraic Equations for

- Intensive variables (T, P, x, etc.) in phases
- Material flows (flash, etc.)
- Phase existence and amounts

Table 7. *Methods*

agitated because of how unrealistic it might seem to be. Certainly, it's not easy—but much of it *is* possible to achieve.

PSALMS

Problem	Desired quantity, other variables
System	Physical and chemical situation Contents and constraints Boundaries, work modes, species Total variables, specified variables
ALways True	Relevant generalized relations for specified system Balances on mass, energy, entropy Property differences Fugacity, reaction equilibrium constant equations
Model	Approximations to generalized relations Choice of **F**amous **F**ugacity **F**ormula If FFF #1, EOS Type Ideal, Virial, CSP, "Full"; P or V Independent If FFF #2-5, Reference State, Pressure Effect Specific choices, *e.g.*, CSP parameterization; Cubic EOS; f_i^0 values; G^E correlation, group contribution method Data (new or literature)
Solve and check	Analytic, graphical, tabular, numerical

Table 8. *A thermodynamics problem-solving strategy.*

The Dilemmas of Beginners

There's a lot of material!
I've never done deduction before!
It's mostly abstract.
It's incredibly detailed!
It's a long way before real applications appear!
If I get started wrong, it takes a lot of work to get to the answer!

Table 9. *How students respond to thermodynamics.*

Suggestions to Keep Students Focussed

Stress procedure more than results, particularly in the beginning.
  "Any fool, even a computer, can do a calculation."
Articulate that the goal is to quantitatively describe the richness of nature.
  "Nature does all things and without any difficulty."
Emphasize exponential pattern of learning the subject.
  "Hang in there. When things begin to click, you take off. The question is whether the end of the term happens first."
Connect equations to observable phenomena and pictures (graphs).
  Student inexperience with natural behavior is pervasive and growing.
Insist upon precision of expression and thought, expecially definitions.
  "You gotta know what you're talking about!"
Minimize "understanding" and maximize "doing."
  "I don't know what entropy and fugacity are, but I can tell you when to use them and how they go."
Give practice problems involving only the setup steps (PSAL) of problem solving.
  Assist students to develop their own PS style.
Have students read and report on the literature of physical properties.
  "Hey guys! They actually use fugacity out there!"
Have students code a VLE program for real substances:
  Forces decision-making and precision.
  "Computers are unforgiving; they do all and only what they're told."
Undergraduates hard to teach fundamentals to; are not used to deduction, precision.
  They want to "do" something immediately.
Hard to get graduates to unlearn old errors; they are reluctant to change old ways.
  "They got me a B+!"

Table 10. *Suggestions to keep students focussed.*

Table 9 shows how I think the beginner in this subject reacts. Of course, self-recognition is vital to making progress, so I confront students with this soon after I begin to get the "glazed-eyes syndrome" somewhere in the multicomponent section. I also tell them that I only became fully comfortable with thermodynamics after the third time I taught it. But that does not mean they can cop out—it merely declares that progress is tough.

Finally, I have given in Table 10 a list of some suggestions that seem to help keep us on track. They are phrased as admonitions, followed by salient quotes from instructors and students.

My success as a teacher has fluctuated with the class, my own distractions, the ions in the air, and who knows what else. But it has been tremendously satisfying when things have clicked with students (the number in class ranging from one to nearly all). Interestingly, I think there is less a correlation with intelligence than with commitment, attentiveness, and willingness to move ahead without being completely satisfied.

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