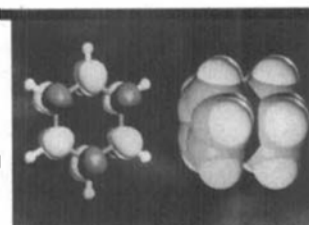


COMPUTATIONAL CHEMISTRY COLUMN

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Some Rules Are Better than Others

(Three Educational Computer Programs [1])

Ernst Schumacher*

Chemistry has an awesome set of rules handed down from master to apprentice. Some of them are communicable. Are they better than the rest? Chemists are known to be pragmatic. If something works, then why bother whether it is correct or even true? If it is not (always) true it still can serve as a handy piece of jargon for everyday life, perhaps for transmitting noncommunicable knowledge.

Take *Lewis*' rules for a starter: We all know they work well (if they do at all). They are not true, though. However, we usually know when they are applicable and teach them to students, wisely excluding cases where they fail. Who would dare to expose the innocent mind to all scruples at once?

Let's do it: The program FORMGEN [2] allows you to input some atom symbols and a lower and upper limit for the number of atoms to use. It then generates quite stubbornly all possible combinations of those atoms (with or without isomers), most of which pertain to nonexistent compounds. Now you, the scientific adventurer, introduce your valency rules, e.g. those

of *G.N. Lewis* if you have a taste for them, and immediately observe the effect of this filter: Many combinations drop out. Those retained are the *canonical Lewis set*. Do you know them as stable, isolable compounds? Well, some do exist, others do not, the synthesis of many has not even been attempted. Moreover, you have to rescue a few dropouts. A remedy for this disappointing result is to invent additional rules: Putting them into the program creates a more reliable 'Chemical Universe' ... until you are satisfied. You then have a better set of rules than most chemists know of and you are able to communicate it!

Now look into the folklore concerned with chemical reactions: Is *Transition State Theory* (TST) true, applicable, sound? How do I know? I make an *Arrhenius* plot and interpret the two constants extracted as an activation enthalpy and entropy. If the numbers are reasonable I reckon the theory is validated? A reaction dynamicist gets goose flesh about this naïveté. He is fully aware of the atrocious assumptions of TST and does not expect it to apply anywhere.

Try LEPS [3]! This program lets you choose among (simple) chemical reactions. It then walks you *completely and transparently* through the steps of TST until you have a rate constant, an activation energy, and a preexponential factor. Compare the result with experimental data. Perhaps you want to modify the ingredi-

ents of TST and follow the change in the outcome. You never have to rely on some obscure rules anymore...

Finally, some real work: In chemistry we talk about and discuss molecules. We never have those, however. It is a vast ensemble, some 10^{20} of them in a gas, a liquid or crystal. How many of what we observe are *molecular*, how many are *ensemble properties*? Since we attempt to manipulate molecules this distinction is quite essential. Here enters GASSIM [4] that models the simplest *many-body* system, a gas. It is really a two-dimensional gas, an adsorbed submonomolecular layer on a smooth, but confined crystal surface. After you start the program a screen similar to *Fig. 1* appears. The 'experiment' is on the left side. To manipulate it we use the commands on the right. The upper left 'cylinder' contains 255 molecules that are in constant motion at finite temperature. Every one of them obeys not more but not less than the simplest set of physical laws: *Newton's*. We model them as hard spheres. They reflect elastically from the 'walls' and from each other. Collisions conserve kinetic energy and linear momentum. Forces between molecules other than those necessary for elastic collisions do not exist. Gravitation can be toggled on or off. Do we agree that this seems to be about all that counts for an 'Ideal (perfect) Gas'? Fine! Then let's manipulate the system:

1) We want to find out what collisions do to the ensemble. With the command '=' (or its equivalent mouse click) we start with a highly artificial situation: All molecules have the same speed of 2 km/s but random positions and directions in the cylinder. Now Go! After 17 time steps of ca. 10^{-13} s we look at the distribution of velocities. There is still a prominent peak at 2 km/s but we make out populations between nearly 0 and 4 km/s. After several hundred steps a perfectly regular distribution develops known as the *Maxwell-Boltzmann* speed distribution that remains unaltered. That is an important ensemble equilibrium property of any molecular system at finite temperature that we often use to promote chemical reactions. We rely on the fact that a fast partial popula-

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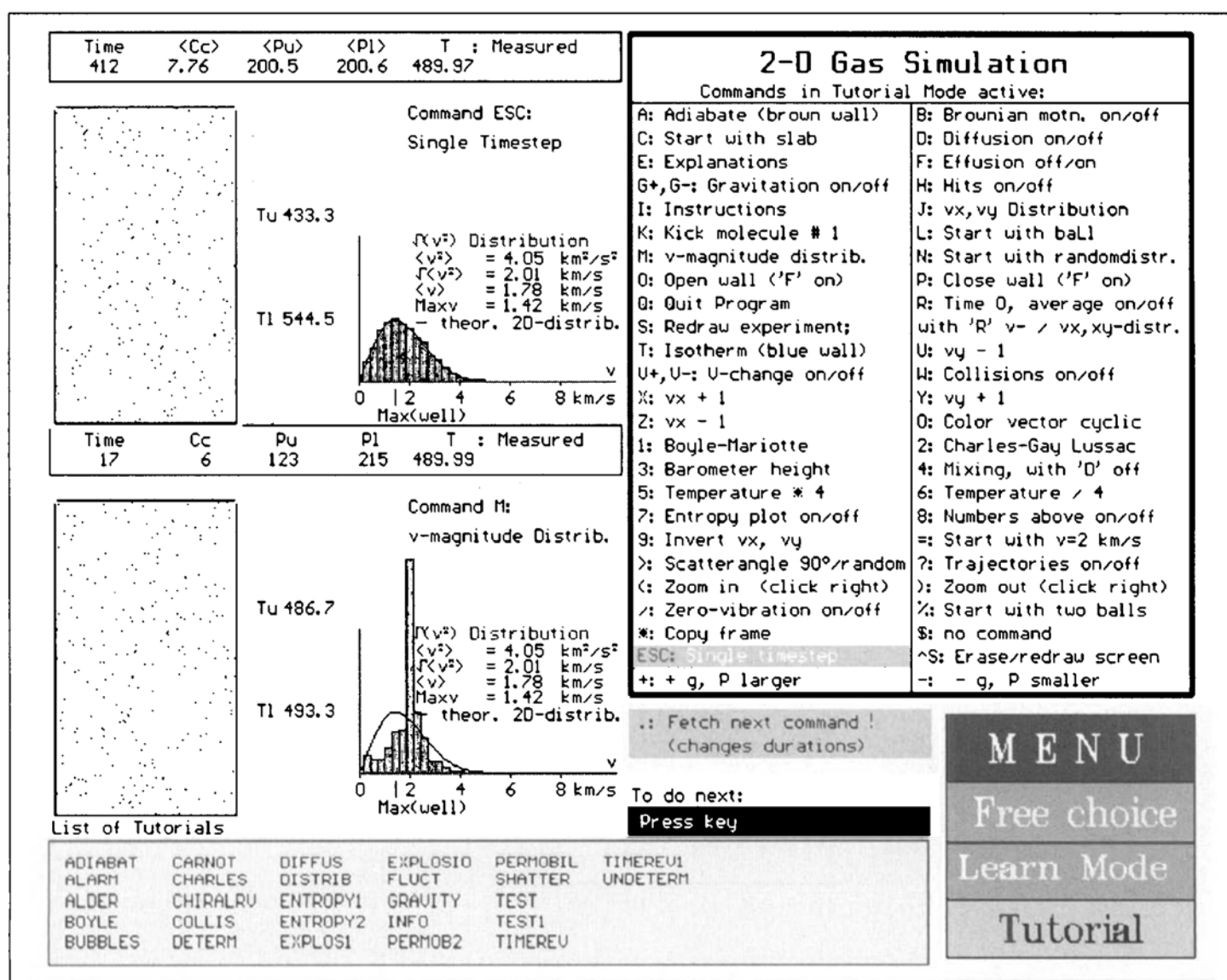


Fig. 1

tion that is ready for a chemical reaction, is constantly replenished from the rest by collisional reshuffling. The model does not assume the *Maxwell-Boltzmann* law nor its mathematical form to exist! The ensemble just produces this distribution as a thermal equilibrium property. Since from Kinetic Gas Theory we know the law, we can superimpose the theoretical curve over the histogram of speed classes. Of course, you should really see the program in action. Still pictures cannot convey the impression of the fast decay of the impossible single spike of 255 molecules at 2 km/s. Note the numbers above the experiment: They show the clock, the Collisioncounter per frame, the Pressure exerted by the reflecting molecules at the top (Pu) and bottom (Pl) wall, and the temperature as a measure of the average kinetic energy per particle. The upper experiment is a time average over the last 412 time steps, the lower is a single frame showing large fluctuations caused by the small sample of

GASSIM is distributed by SFIB (Schweizerische Fachstelle für Informationstechnologien im Bildungswesen, Erlachstr. 21, CH-3000 Bern 9). It is available with or without source code (Turbo Pascal Vers. 7). It is applicable at gymnasium, HTL, and university level.

The other packages can be ordered directly from the author, E. Schumacher, Kalchackerstr. 69, CH-3047 Bremgarten; EM: schumacher@iac.unibe.ch, Tel./Fax. +41(0)31 302 63 07.

A package *Statistical Thermodynamics* (170 programs, MathCad required, 160 page manual) is also available.

Two computer *notebooks* offer symbolic manipulations and explanations for:

1) *Group Theory applied to Chemistry*;

2) the derivation of all or of the chiral subset of (substitution)isomers: POLYA.

The programs run on MS-DOS machines, preferentially with a 80486DX CPU, at least 640 kB RAM, VGA graphic card and mouse. Versions for Apple Macintosh are in preparation.

molecules, visible with the instantaneous Pu and Pl compared to the average <Pu>, <Pl> in the upper frame. Of course, average and instantaneous Temperature are equal since the system conserves kinetic energy (the walls are adiabatic).

2) The simple laws of the Ideal Gas are equilibrium ensemble properties. We demonstrate them as in Fig. 2 by isothermal compression of the gas. We see *Boyle-Mariotte's* law confirmed. The cylinder is now diabolic.

3) We really can demonstrate most of the Thermodynamics of a gas. Fig. 3 shows a Carnot cycle whose last leg was an isothermal expansion. The SV-diagram is superimposed on the pV-plot. The adiabatic parts show constant entropy and rapid change in pressure. The isothermal parts decrease and increase in entropy (this is the cycle of a heat pump). The cycle is not precisely closed: The simulator does not work reversibly and a student can immedi-

ately perceive the cause for it, the same as in actual life.

4) We enclose the gas at ca. 250 K in the lower half of the cylinder. The upper half is empty. Now we open a tiny hole in the middle and watch the effusion into vacuum. The plot to the right in Fig. 4 gives the instantaneous number of effused molecules as a function of time. Its logarithm is proportional to the entropy gain of the effusion that drives this process.

5) We toggle gravitation on and produce a perfect barometric density distribution when we average over many hundred single frames, Fig. 5. The simulator produces ca. 25–50 frames per second (MS-DOS machine, 486/25 MHz, with coprocessor).

The list of commands, right side of Fig. 1, contains about 50 items covering most of the physical chemistry of gases. Moreover, a sequence of commands can be recorded in 'Learnmode' and later reproduced in 'Tutorialmode'. Some titles of demonstrations are in the list at the bottom of Fig. 1. Choose one by mouse click. A short description of background information and purpose appears on the screen. In addition a number of carefully edited explanation texts introduce such topics as deterministic vs. random behavior, time reversal symmetry in mechanical systems, the ergodic theorem, the micro-reversibility argument in H-function theory, collision physics, chirality in time reversed systems. You can call these texts in the middle of an experiment if something happens that raises questions.

We leave the program and return to the rules. For GASSIM the rules consist of Newton's laws applied to point masses. Ensemble properties like the distribution functions do not need additional rules. They emerge as attributes of a many-body system. A student who has obtained a basic introduction into physics understands gases and their thermal equilibrium properties. He just needs to tell a computer to manipulate many particles at a time, something that is hardly feasible with pen and paper but a simple algorithm in GASSIM (or, more abstractly, in Kinetic Gas Theory). There is much more to it yet: The model illustrates the convergence of a nonequilibrium situation into its final equilibrium. We even get an impression about the time scale of such processes. The small ensemble shows fluctuations about the macroscopic mean values that are of paramount importance for chemical and biochemical reactions.

Where is the limit? The rules may be extended: Introduce *van der Waals* interaction between the point masses as in the program COLLISIO [4] and watch the formation of dimers, their rotations, vibrations and dissociation by collision or at a wall. Remove thermal energy and observe the condensation to a liquid phase and finally to a crystalline assembly. This is all being done today. We call it *Molecular Dynamics*. It gobbles up supercomputer time with really large ensembles. From these studies we learn how to distinguish between molecular and ensemble proper-

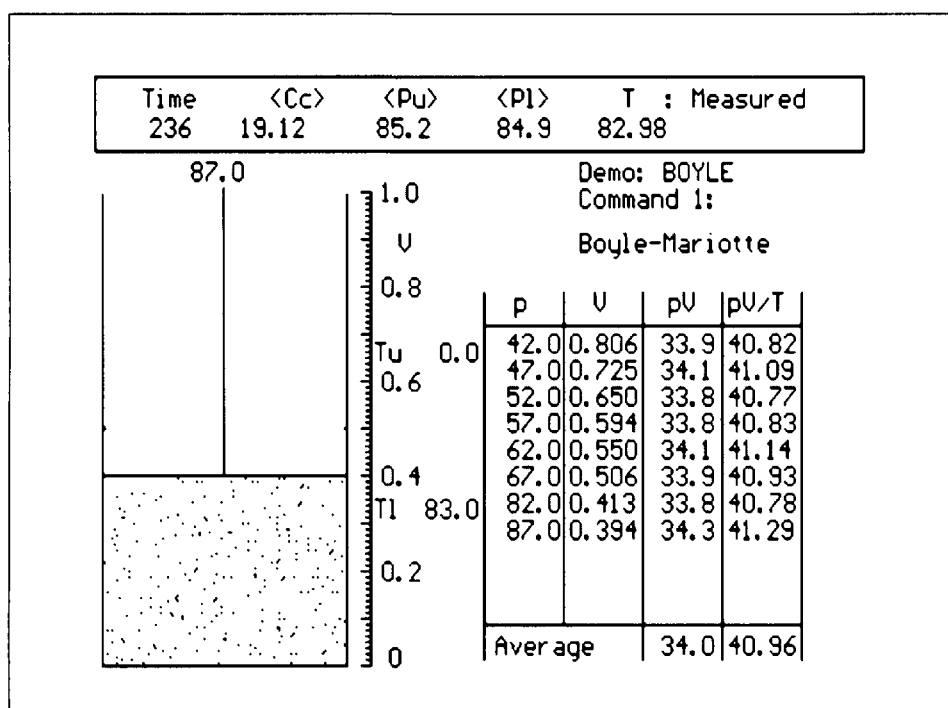


Fig. 2

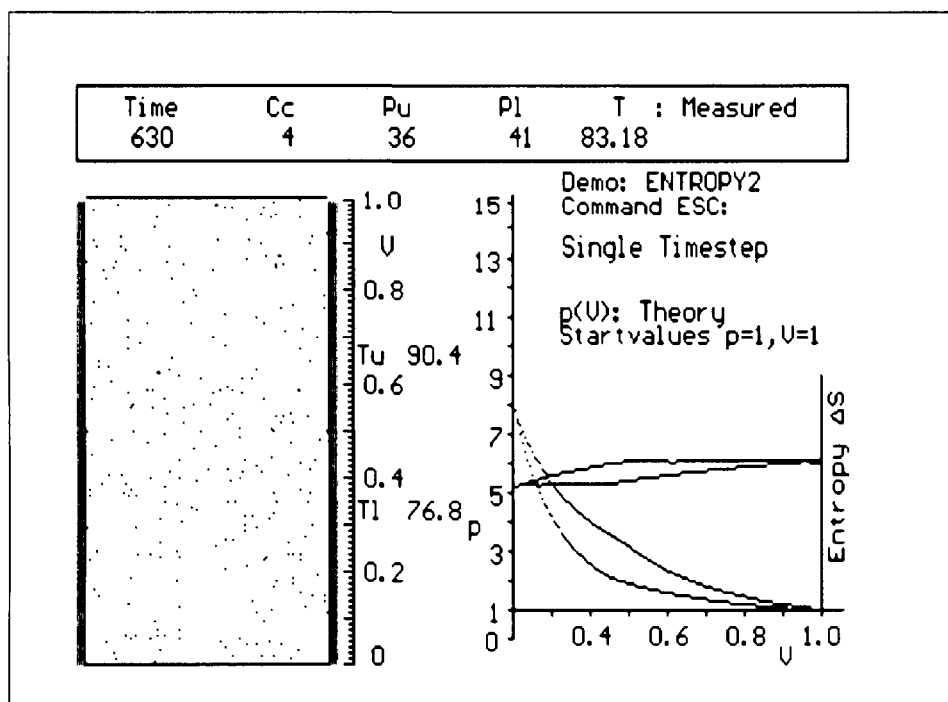


Fig. 3

ties just in case we have to have better rules for manipulating molecules in the real world of new materials and biological processes.

However, progress has many faces: Do not demolish the chemists intuitive concept of molecules too early. It has much more content than the poor skeleton of the quantum chemist. It is already 'dressed' with much of what we would call solvent, medium, or matrix effects. It conveys odor, flavor, and color. It even bears the characteristics of transition states suggesting specific reactivity. All this is part of what we called 'noncommunicable' knowledge. It is not transparent in the formulae we write on the blackboard. A fine chemist just 'feels' these properties in his 'guts', a fact, physicists never understand (because we failed to explain to them, what we do).

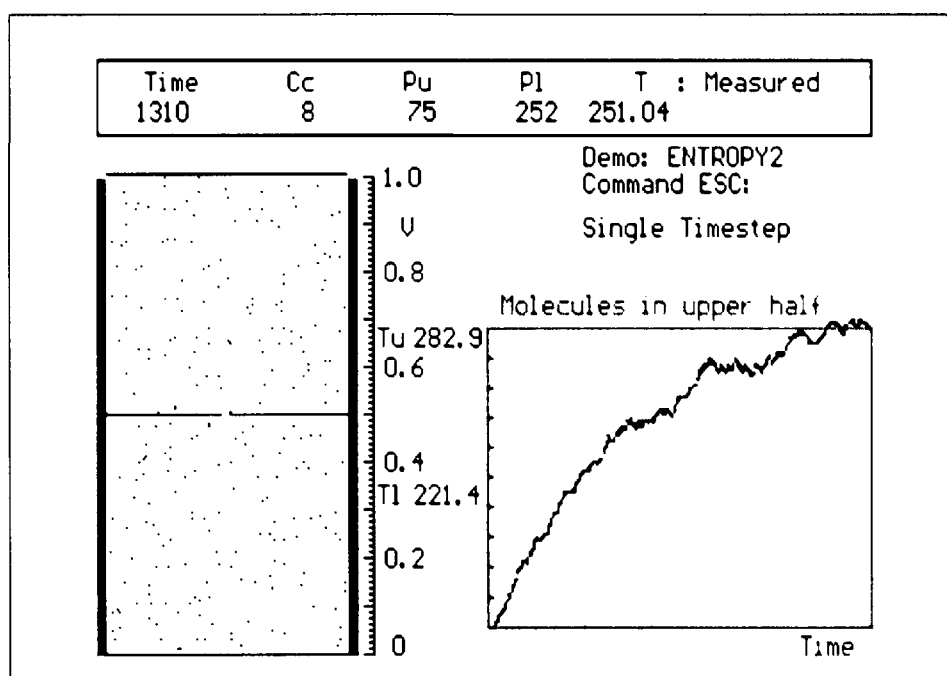


Fig. 4

[1] Citations refer to the information box

Availability of the Programs reviewed:

- [2] FORMGEN is part of a package CHEMUNT, a collection of more than 50 programs for chemical education. An 80-page manual offers introductions, explanations, and a practical guide for the user.
- [3] LEPS is part of the package KINETICS, a collection of dozens of programs which treat chemical kinematics, chemical dynamics, and an introduction into nonlinear and chaotic chemical behavior. A 162-page manual accompanies the material.
- [4] GASSIM is the main program of a package GASSIM which simulates gases. It is also an introduction with active participation of the student into the mechanical theory of heat, thermodynamics, and kinetic gas theory. Several smaller programs illustrate every aspect of the algorithmic background. A 94 page manual and many screen texts offer explanations. German and English versions exist. COLLISIO demonstrates the interaction of two *van der Waals* molecules in real time (solving *Hamilton's* equations of motion).

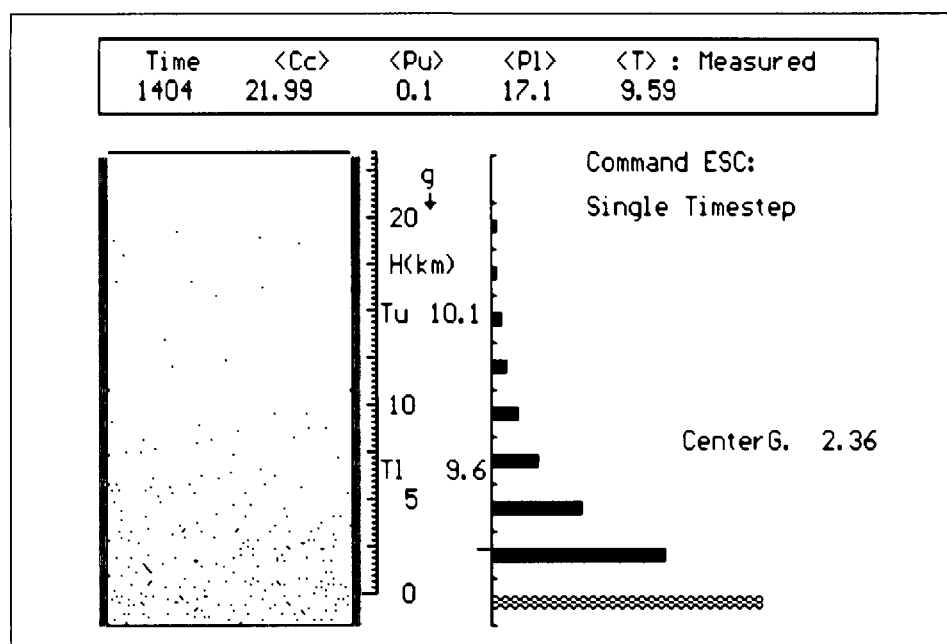


Fig. 5

ANNOUNCEMENT

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