

Our intuitive sense of how liquids behave is no doubt based on our widespread contact with the most common liquid, water. Swimming, bathing, cooking, and gardening, we come to know water's density, viscosity, surface tension, and thermal conductivity intimately. Nothing in our everyday experience would suggest that water, or any other liquid, could be effective as the thermodynamic working medium of a heat engine or refrigerator, expanding when heated, cooling when expanded, etc. And our formal training as scientists and engineers reinforces this misconception: In college, examples and homework problems use gases to teach the principles of thermodynamics, while fluid-mechanics courses begin with the simplifying assumption that liquids may be treated as incompressible and thermodynamically inert.

The discovery of the thermodynamic usefulness of liquids was made by someone unencumbered with any such traditional academic education. John Fox Jennens Malone (1880-1959) completed his formal education in his 18th year, with an apprenticeship at John Penn and Sons, where British Navy engineers often gained experience before going to sea. He then joined the merchant marine, suffering 17 wounds in assorted Middle-East and Latin-American conflicts during the next 14 years. Leaving the merchant marine, Malone founded the Sentinel Instrument Company and, later, the Fox Instrument Company, and began experimenting with liquid engines in the 1920s. He measured compressibility and thermal expansion of many liquids, including hydrocarbons, mercury, carbon dioxide, and sulfur dioxide. His first complete liquid engine burned coal, used high-pressure liquid water as working medium, and produced 50 hp in 1925. In 1927, a more compact and versatile 50-hp water engine was completed, and an extensive program of experimentation ensued.

In 1931, Malone published his results, including "Trials by three different independent engineers gave 27% indicated efficiency. Thus, after allowing for furnace and mechanical losses in a commercial engine, 20% overall efficiency between the heat in the coal and the shaft horsepower can be expected." (The steam engines that powered ships at the time were 9%-12% efficient, and those of locomotives 5%-7% efficient.) His cycle had features of both Stirling and Brayton engines. As in a Stirling machine, the pressure oscillations were spatially uniform throughout the engine (except for viscous effects). At the same time, as in a Brayton machine, the regenerator/recuperator, which Malone called the "thermodynamic pile," consisted of two interwoven sets of passages, fitted with check valves in opposite directions, so fluid flowed in one direction through one set of passages during the hot blow (i.e., hotward displacement) and in the other direction through the other set of passages during the cold blow. Some of his heat-exchanger heat-transfer surface area was also involved in this unidirectional, pulsatile flow, allowing useful heat transfer in a heat exchanger whose fluid volume was greater than the displacement stroke.

But with liquid water, how did it work at all? In a 1939 letter to a colleague, Malone wrote "A study of liquids as mediums in thermodynamics will teach an engineer more about the art of thermodynamics than all the universities on earth..." Indeed, those of us who have worked with non-ideal gases or with liquids in Stirling machines know how these working fluids stretch our understanding beyond undergraduate coursework.

The most obvious quality that any heat-engine working fluid must have is an adequately large thermal expansion coefficient, to convert heat to work. The dimensionless thermal expansion coefficient

$$\frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

is exactly 1 for ideal gases. (All variables are defined at the end of this note.) For liquid water near room temperature, this is only about 0.1, but, at the temperatures where Malone's engines operated, it reaches and exceeds 1, as shown in the Figure.

Van der Waals's law of corresponding states suggests that all fluids might have similar properties, if everything is normalized by values at the critical point. Examining the Figure, readers can judge for themselves how well this holds among three common fluids.

Using a Maxwell relation to relate entropy and volume changes shows that the heat absorbed per unit volume in a pressure reduction actually depends on the same derivative as the work done per unit volume in a thermal expansion:

$$\frac{1}{V} \left(\frac{\partial Q}{\partial p} \right)_T = \frac{T}{V} \left(\frac{\partial S}{\partial p} \right)_T = \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p.$$

Thus, hot liquid water would be a good working medium in a refrigerator, if there were any reason to refrigerate something at such temperatures. With a lower critical temperature, liquid carbon dioxide has been considered for Malone refrigeration just below room temperature.

Meanwhile, the compressibility of liquids remains low, matching our intuition. The dimensionless compressibility,

$$\frac{p}{V} \left(\frac{\partial V}{\partial p} \right)_T,$$

which is 1 for an ideal gas, is typically about one-tenth of the dimensionless expansion coefficient. This unfamiliar combination of properties—gas-like thermal expansion, yet low compressibility—gives liquids an advantage over gases in Stirling machines: Low compressibility lets the engineer spend void volume more freely, without costing too much power-piston stroke.

Next, consider the adiabatic temperature change with pressure. Making it dimensionless, and again using a Maxwell relation, we have

$$\frac{p}{T} \left(\frac{\partial T}{\partial p} \right)_S = \frac{p}{T} \left(\frac{\partial V}{\partial S} \right)_p = \frac{p}{T} \frac{(\partial V/\partial T)_p}{(\partial S/\partial T)_p} = \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p / \frac{c_p/V}{p/T},$$

which depends on the isobaric heat capacity per unit volume, c_p/V . For an ideal gas, the right-hand side is $(\gamma-1)/\gamma$, where γ is 1.67 for monatomic gases (e.g., helium) and 1.4 for diatomic gases (e.g., air or hydrogen). In liquids, c_p/V is larger, so adiabatic temperature changes in liquids are smaller. Thus, a recuperative or regenerative cycle is needed when using a liquid to span a large temperature difference without a very high pressure change, to decouple the machine's temperature span from the adiabatic temperature change.

Finally, while requiring a recuperative or regenerative cycle, liquids seem to be stuck with an inherent irreversibility in such a cycle. In anything worthy of the name "cycle," equal mass must pass through the regenerator in the hot and cold blows, which occur at different pressures. With an ideal gas, the heat capacity per unit mass c_p is $\gamma R_{\text{uni}}/(\gamma-1)m$, which is independent of pressure, so the heat deposited in each differential length of solid regenerator during the hot blow can be precisely removed during the cold blow, leaving the solid in time-averaged steady state. But if the fluid has a different heat capacity during the cold blow than during the hot blow, how can it let each place in the regenerator stay at the same temperature from one cycle to the next? Any non-ideal gas must suffer from this problem, which leaves me wondering exactly what happens in the regenerator of a Stirling refrigerator that uses helium near 5 Kelvin. Is this only the least of many worries under such challenging conditions?

John Malone's 1931 J. Soc. Arts article emphatically expressed his desire to commercialize liquid engines for propulsion of cargo ships, locomotives, and large trucks, and shaft and electric power generation for factories, mines, plantations, and isolated communities. According to Malone's son, "at one time a project was actually started to develop [sic] the street-end power station to eliminate the enormous capital outlay of the wires and pylons which form the 'grid'." But by late 1931 Malone was bankrupt. We can imagine why his work ended. The worldwide economic depression of the 1930s must have made venture capital scarce. Large coal-fired steam turbines with 20% efficiency were in ascendancy for applications above 10,000 hp. The development of the internal combustion engine was already well underway, and its incomparable power-to-weight ratio made it seem the only practical choice for airplanes and automobiles.

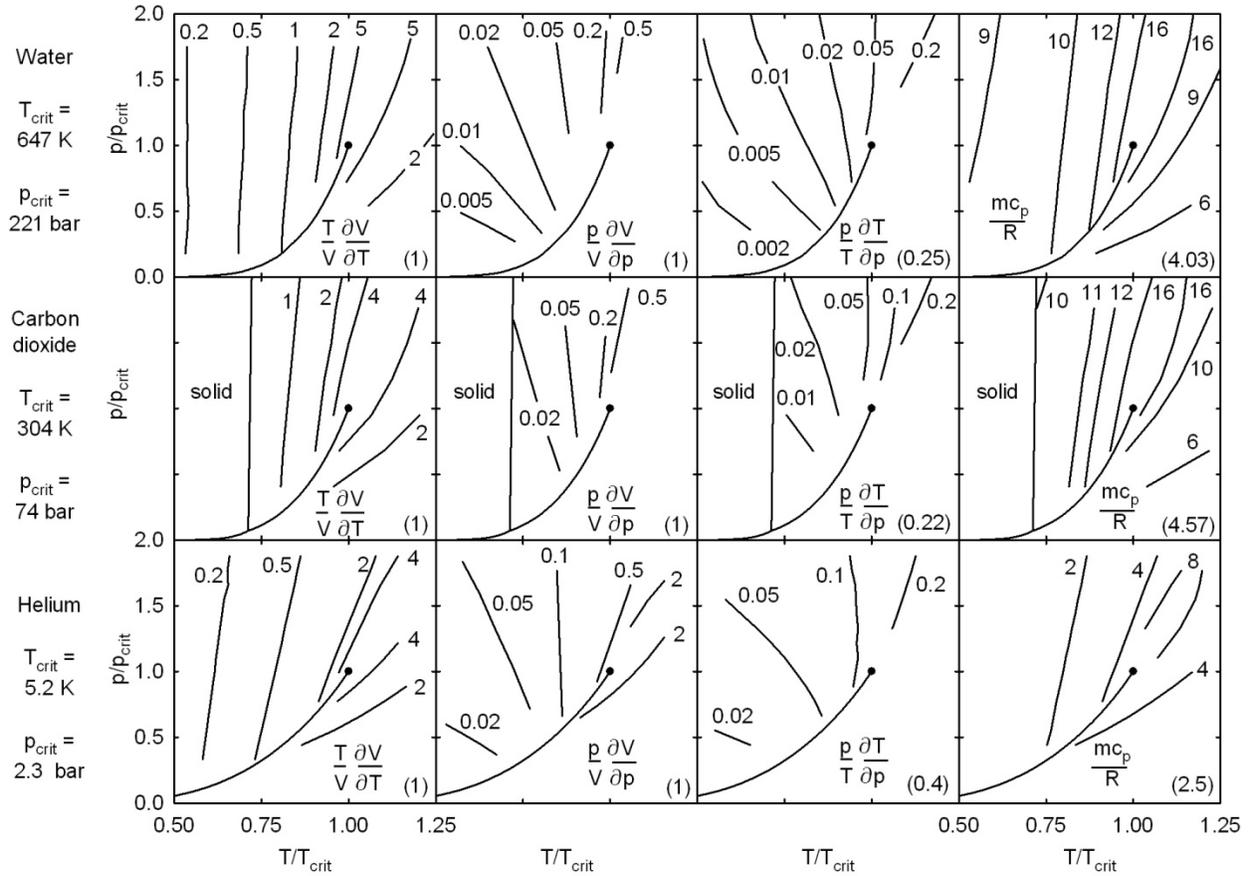
References:

Biographical information from personal correspondence with Malone's son Ray. For some interesting background information about marine engineering at the time, see the wikipedia.org article on "John Penn (engineer)."

J. F. J. Malone, "Heat engine," U.S. Patent No. 1,487,664 (1924); "Heat engine operated by the expansion of liquids," U.S. Patent No. 1,717,161 (1929).

J. F. J. Malone, "A new prime mover," J. Roy. Soc. Arts (London) 79, 680-709 (1931); reprinted by R. A. Ford, "Secrets of the Malone heat engine" (Lindsay Publications, Bradley IL, 1983). A shorter version appeared as "A new prime mover," The Engineer, 97-101 (1931).

Variables used here: T = absolute temperature; p = pressure; V = volume per unit mass; S = entropy per unit mass; Q = heat per unit mass; c_p = isobaric heat capacity per unit mass; m = molar mass; R_{uni} = universal gas constant; γ = ratio of isobaric to isochoric heat capacities.



Some thermophysical properties for water (used in Malone's engines), carbon dioxide (a candidate for refrigeration near ambient temperatures), and helium (for cryogenic refrigeration) in the liquid-like and non-ideal regions of their phase diagrams. The axes of all 12 plots are identical. The liquid-vapor equilibrium curve, ending at the critical point, appears in all plots. Ideal-gas values are given in parentheses in the low- p , high- T corner of each plot. Curves are derived from data at webbook.nist.gov/chemistry/fluid, with the addition of carbon dioxide's melting and sublimation data from *International Thermodynamic Tables of the Fluid State: Carbon Dioxide* (Angus, Armstrong, and de Reuck, eds.; Pergamon, 1976).