Principles of liquids working in heat engines

(thermodynamics/Stirling/Malone)

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ABSTRACT   The thermodynamic and thermophysical properties of liquids suggest that they should be powerful working fluids in heat engines. Their use requires heat engines based conceptually on the Stirling and Malone principles. The principles are explained, and then experiments on propylene are presented that demonstrate the principles and confirm the thermodynamic analysis.

Thermal properties of liquids

Fluids may be characterized thermodynamically by heat flow and work for isothermal processes and by temperature change for adiabatic processes. For an incremental pressure change dp of a fluid occupying volume V and at constant temperature T, the incremental heat flow to the fluid is

$$dQ_T = -(T\beta)Vdp, \tag{1}$$

whereas the incremental work done on the fluid is

$$dW_T = (p\kappa_T)Vdp; \tag{2}$$

where $\beta \equiv (\partial \ln V/\partial T)_p$ is the isobaric expansion coefficient and $\kappa_T \equiv -(\partial \ln V/\partial p)_T$ is the isothermal compressibility. For an incremental adiabatic change of pressure, the incremental temperature change is

$$dT_a = (\partial T/\partial p)_S\, dp = (T\beta/\rho c_p)dp, \tag{3}$$

where ρc_p, the specific heat per unit volume, is the product of the mass density, ρ, and the specific heat at constant pressure per unit mass, c_p. For an ideal gas, $T\beta$ and $p\kappa_T$ are unity. For real gases, $T\beta$ and $p\kappa_T$ are very close to 1 at moderate pressures and at temperatures well above the critical temperature.

The critical point of a fluid at temperature T_c and pressure p_c determines the equation of state rather well in its general vicinity in the sense that $T_c\beta$ and $p_c\kappa_T$ do not depend strongly on fluid (1) when the temperature and pressure are expressed in reduced coordinates $T_r \equiv T/T_c$ and $p_r \equiv p/p_c$. Hence, understanding the behavior of one fluid may be quantitatively useful in understanding that of another.

The quantity $T\beta$ determines how active a fluid is thermodynamically because, for a given geometry and pressure change, it determines the heat flow. As T and p approach the critical point, $T\beta$ approaches infinity. For a very large region of the T,p plane about T_c,p_c, one finds $T\beta > 1$. In this region the fluid is more active thermodynamically than the ideal gas. At low enough temperature $T\beta$ becomes less than 1.

The quantity $p\kappa_T$ reflects the elastic properties of the fluid. As T and p approach the critical point, $p\kappa_T$ approaches infinity. For a region of the T,p plane about T_c,p_c, this quantity is also significantly greater than 1. At low temperatures, κ_T approaches

a constant value. The quantity $p\kappa_T$ is a largely irrelevant quantity with respect to the principles of heat engines. It determines the relationship between the pressure range and the volume range of the fluid and, hence, relates primarily to the configuration of the engine. It is closely related to the elastic energy stored in the fluid and, hence, to the explosive hazard.

We are concerned primarily with fluids having T/T_c somewhat less than 1. Such fluids will display "liquid-like" behavior. A convenient substance for the present purposes is propylene, whose critical temperature (364.9 K), critical pressure (46.2 bar; 1 bar = 1.00 × 10⁵ pascals), relatively low molecular mass and ρc_p, and moderate thermal diffusivity make it a good medium for experimentally studying the essential qualities of heat engines operating within a moderate temperature span above and below an ambient temperature of about 300 K. Smoothed experimental measurements on propylene by N. Dave, G. Fisher, M. Fleisher, and M. Metcalf (unpublished work) of this laboratory are shown in Fig. 1, where contours of equal $T\beta$ and $p\kappa_T$ are shown on the plane of reduced pressure and temperature. In the entire range of the measurements, $T\beta$ is comparable to 1. A very large region of the p_r, T_r plane lies within the gas-like contour $T\beta = 1$ and has $T\beta > 1$. Hence, in the range of T and p shown, propylene is quite active thermodynamically. Because $p\kappa_T \ll 1$, in the same region the compressibility is much less than p^{-1}. This quality is characteristic of a "liquid." For the region of T,p shown in Fig. 1, propylene is a thermodynamically powerful liquid.

Other quantities of importance in a heat engine are ρc_p, the thermal conductivity K, the thermal diffusivity $\kappa \equiv K/\rho c_p$, the viscosity η, and the kinematic viscosity $\nu \equiv \eta/\rho$. Of the above, the quantity ρc_p thermodynamically distinguishes liquids from gases via the adiabatic temperature change (Eq. 3). Though $T\beta$ is comparable to that for gases, the ρc_p is usually orders of magnitude greater for liquids than for gases, so that for reasonable pressure changes the adiabatic temperature change in liquids is not large. Carnot (2) considered the use of liquids in heat engines but rejected them for this reason.

In Fig. 2 we show (3–5) by means of a set of logarithmic line graphs some of the diversity as well as uniformity of a number of fluids. Aside from the critical parameters, the quantities shown are valid for 300 K and saturated vapor pressure. We also include ⁴He and normal H_2 gas for comparison. Whereas the liquid properties are not strongly pressure dependent well below T_c, gaseous properties like ρc_p, κ, and ν do depend on pressure. The values given for the gases in Fig. 2 are for a pressure of 3 bar. This is the pressure at which the elastic stored energy per unit volume in the gas is the same as that in propylene at a pressure of $\approx 2.5\, p_c$ or 115 bar, near the average pressure in some of our experiments. The liquids shown include the liquid metals and arbitrarily exclude fluids with T_c closer to 300 K than propylene. The metals Hg and NaK are liquid at 300 K. Though they are not powerful thermodynamically at room
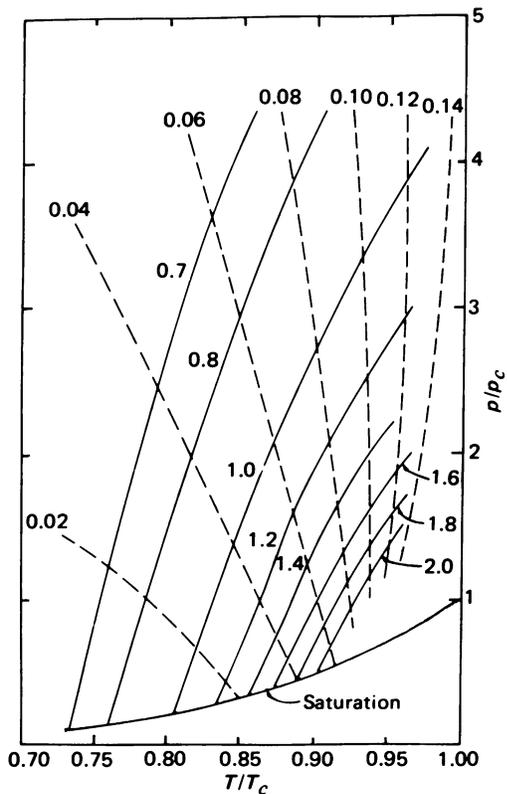
FIG. 1.   Contours of constant $T\beta$ (——) and $p\kappa_T$ (- - -) for propylene on reduced pressure and temperature scales. "Saturation" is the reduced vapor pressure curve. $p_c = 46.2$ bar; $T_c = 364.9$ K.

temperature, the value of $T\beta$ can be 0.2–0.3 at temperatures where steel still has strength. Their large thermal diffusivity compensates in part for thermodynamic deficiencies.

In Fig. 2 the values of T_c and p_c cover a broad range. T_c is selected according to application. A high p_c is generally desirable for heat engine work, other qualities being equal, because this implies a lower κ_T and larger pressure changes in isochoric and isothermal processes. The ρc_p line shows the large difference between the liquids as a whole and the gases. The thermal conductivity line shows that the liquid metals conduct heat qualitatively better than the other fluids as a whole. The thermal diffusivity is orders of magnitude greater for the gases than for the liquids as a whole, excepting the liquid metals, especially NaK. The viscosity coefficient and kinematic viscosity for the liquids also tend to cluster in a relatively small range. The gases have a high ν and a low η. A general inspection of Fig. 2 suggests that, aside from the high K and κ of liquid metals, a truly dramatic change of performance as determined by the above properties is unlikely to be achieved by changing from one insulating liquid to another.

Summary of qualities of liquids as related to heat engines

(*i*) From Eq. 1 and Fig. 1, liquids are more powerful thermodynamically than ideal gases over a large region of the p,T plane and comparable to them over a *very large region*. (*ii*) Owing to the small κ_T, the large heat flows associated with a large Δp can be effected in a liquid without explosive hazard. (*iii*) Owing to a relatively large value of ρc_p for liquids, possible reversible adiabatic temperature changes, Eq. 3, will be much smaller for liquids than for gases, including the much larger pressure changes possible with liquids. (*iv*) For liquids, c_p depends on pressure:

$$(\partial c_p / \partial p)_T = -T(\partial^2 v / \partial T^2)_p, \qquad [4]$$

where v is volume per unit mass. This will decrease the intrinsic thermodynamic efficiency of regenerative heat engines but may favorably affect the regeneration itself. (*v*) The values of both $T\beta$ and $p\kappa_T$ may vary significantly over the temperature range spanned by the engine. (*vi*) Heat engines using liquids will use small volume changes and large pressure changes relative to gases, which tend to favor the opposite. This allows liquid flow in narrow passages with a consequent improvement in heat transfer to the fluid but without a concomitant excessive increase in fluid friction. (*vii*) Because the density does not change greatly over the T range spanned by the engine, the size of the heat exchangers can be the same at the hot and cold temperatures. Hence, reversibility of the engine is favored.

Heat engine cycles in which liquid can work

The small adiabatic temperature difference possible with liquids requires a special quality of the heat engines in which they work in order to span a practical temperature difference. Two types of engine are particularly important: that of Stirling (6) put forward in 1816 and that of Malone (7) described in 1931. Schematic drawings showing the essence of Stirling and Malone heat engines are shown in Fig. 3.

The Stirling Principle. A second thermodynamic medium is introduced for the dual purposes of facilitating the cycle for the primary medium and of expanding the temperature range spanned by the machine to a value in excess of that which can be achieved by purely adiabatic processes. The schematic Stirling engine shown has two moving parts, a piston P and a displacer D. The end of the engine labeled A is at ambient temperature T_A; the remote end, labeled R, has temperature $T_R \gtrsim T_A$. The piston and the displacer can be moved separately. The material in D and the adjacent cylinder walls constitutes the second thermodynamic medium. Ideally it has an infinite heat capacity so that it can absorb heat essentially isothermally. Further, it should have low longitudinal thermal conductance to eliminate heat leak and high transverse conductance to promote thermal equilibrium with the fluid. The heat capacity quality is easy to achieve for a gas as primary medium since ρc_p for gases is so much less than that typical for metals. The second medium in the above context is called a regenerator.

As D reciprocates, there is a reciprocating fluid flow in the regenerator. Ideally, fluid moving toward R exits from the regenerator at T_R; fluid moving toward A exits at T_A. Motion of D alone produces a pressure variation. If the motion of P is phased with respect to that of D so that when the fluid volume at the remote end is large the pressure is falling and when this volume is small the pressure is rising, then the engine is a prime mover ($T_R > T_A$) or a refrigerator ($T_R < T_A$). For the opposite phasing, the engine is a heat pump.

The Malone Principle. In 1931, J. F. J. Malone described "a new prime mover," which used liquids as primary media. For liquids, ρc_p is quite comparable to that for metals. Therefore, the ratio of regenerator volume to liquid volume would have to be very large if the Stirling arrangement were used.

In Fig. 3 the essential difference between the Stirling and Malone arrangements is displayed. According to Malone's principle, the reciprocating flow of the Stirling engine is replaced by pulsating unidirectional flow with counterflowing streams in good thermal contact with one another. Malone called his replacement for the displacer a "thermodynamic pile" to distinguish it from a regenerator. Most of the liquid in the engine is in the thermodynamic pile. As the thermodynamic pile reciprocates, fluid flows alternately toward and away from the remote end. At any instant, half the fluid in the thermodynamic pile is essentially static. In one stroke the fluid moves only a fraction of the length of the thermodynamic pile. In the limit of small displacements, Malone's thermodynamic pile
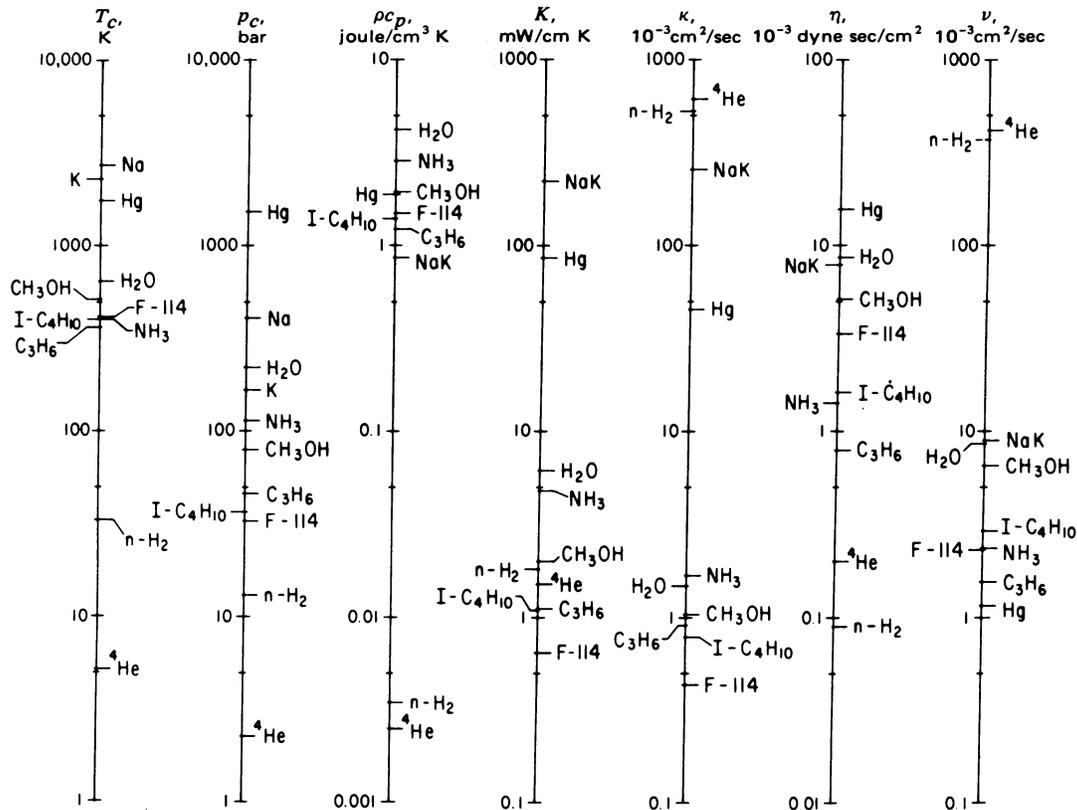
FIG. 2. Properties of selected liquids at 300 K and saturation pressure, excepting the critical properties. Symbols are defined in the text. F-114 is $C_2Cl_2F_4$, I-C_4H_{10} is isobutane, and NaK is sodium-potassium eutectic. Data on insulating fluids were from ref. 13; data on Hg were from ref. 4; data on NaK were from ref. 5.

approximates a counterflow heat exchanger. Its essential quality is that *at constant pressure* no nonfluid heat capacity is needed in the thermodynamic pile to change the temperature longitudinally of the oppositely flowing streams. In the heat engine the pressure does change and a second thermodynamic medium is needed to reject (absorb) the heat of expansion (compression). This heat, proportional to $T\beta$, may be much smaller than that, proportional to ρc_p, needed to change the temperature between T_A and T_R. Hence, the heat load on the second medium is dramatically reduced. The thermodynamic pile as a counterflow heat exchanger is a strange one; the fluid flowing from the remote end can have a different pressure and, hence, different enthalpy from that flowing toward the remote end.

Thermodynamic qualities of liquids working in heat engines that use the Malone principle

Malone's original engine was practically and intrinsically irreversible. However, when the temperature difference spanned by a Malone engine is not large, the engine is practically reversible, transferring heat either to or from a reservoir at T_R most effectively when $T_R - T_A = 0$. As the temperature dif-

FIG. 3. Schematic Stirling and Malone mechanisms. →denotes a check valve. T.D. pile, thermodynamic pile.

ference increases, the engine will become ever more irreversible, even under ideal conditions. This intrinsic irreversibility depends on the liquid and on the temperature spanned.

The engine is complex. An accurate description would be very complicated, would be different for each liquid, and would lead to little intuition. We develop here an approximate intuitive approach based on the essential qualities of the engine. We assume for simplicity that the piston and the thermodynamic pile are articulated separately. First, even rather close to T_c the liquid is rather incompressible so that there is little difference between the heat flow to a constant mass or to a constant volume of fluid. Thus, we can replace the isothermal heat flow formula $Q_T = (\overline{T\beta})V_D\Delta p$ from Eq. 1, where V_D is the displaced volume, Δp the pressure change, and $\overline{T\beta}$ the averaged value of this quantity with respect to pressure, by $Q_T' = T(\partial v/\partial T)_p \, \delta m \, \Delta p$, where v is the volume per unit mass and δm is the mass circulated per cycle. This substitution ignores the fact that when the pressure is reduced in a fixed volume some of the fluid will leave the volume. The error is of order $\overline{\kappa_T}\Delta p$, where $\overline{\kappa_T}$ is an average compressibility. Second, at least for small displacements, the Malone thermodynamic pile is rather like a counterflow heat exchanger, but with the special quality that fluid flowing toward the remote end has a different pressure from that flowing away from it. Because fluid enthalpy is pressure dependent, it follows from conservation of energy that even under ideal heat transfer conditions each fluid stream cannot be forced by heat exchange to change its temperature by $T_R - T_A$. The fluid stream with the greater enthalpy will transfer heat directly from R to A to the extent of the enthalpy difference and with no resulting useful work. From the pressure dependence of the specific heat, Eq. 4, it is straightforward to show that the heat loss per cycle is
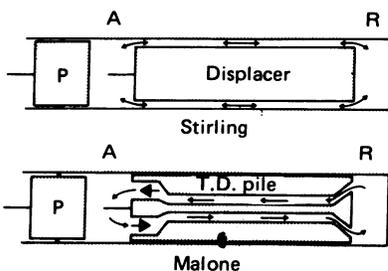
$$Q_{loss} = \delta m \int_{T_A}^{T_R} dT \int_{p_{low}}^{p_{high}} T \left(\frac{\partial^2 v}{\partial T^2}\right)_p dp. \qquad [5]$$

To obtain a simple formula, assume that the pressure averaged value of $(\partial v/\partial T)_p$ changes linearly over the temperature range. Then one has

$$Q_{loss} \approx \tfrac{1}{2}\, \delta m (T_R + T_A)[(\overline{\partial v/\partial T})_R - (\overline{\partial v/\partial T})_A]\Delta p. \quad [6]$$

Consequently, with $T_R > T_A$ and the engine phased to do work, heat $\delta m[T(\overline{\partial v/\partial T})]_R\,\Delta p$ will be absorbed at R; heat given by Eq. 6 will flow directly from R to A; and heat $\delta m[T(\overline{\partial v/\partial T})]_A\,\Delta p$ will be rejected at A. The work done per unit mass circulated is then

$$\frac{\delta W}{\delta m} \simeq \left[T\left(\frac{\partial v}{\partial T}\right)\right]_R \Delta p - \left[T\left(\frac{\partial v}{\partial T}\right)\right]_A \Delta p$$
$$- \frac{T_R + T_A}{2}\left[\left(\frac{\partial v}{\partial T}\right)_R - \left(\frac{\partial v}{\partial T}\right)_A\right]\Delta p. \quad [7]$$

The ideal thermal efficiency η is obtained by dividing Eq. 7 by the heat per unit circulated mass absorbed at T_R:

$$\eta \simeq \frac{(\overline{\partial v/\partial T})_R + (\overline{\partial v/\partial T})_A}{2(\overline{\partial v/\partial T})_R}\left(1 - \frac{T_A}{T_R}\right). \quad [8]$$

The second factor is Carnot's efficiency. Reduction of efficiency is related to the temperature dependence of $(\partial v/\partial T)_p$. In the above formulas, one can also replace $\delta W/\delta m$ by W/V_D, where W is the work per cycle and V_D the volumetric displacement of the thermodynamic pile, provided the expansion coefficient β is substituted for $(\partial v/\partial T)_p$:

$$W \simeq [(\overline{T\beta})_R - (\overline{T\beta})_A -$$
$$\tfrac{1}{2}(T_A + T_R)(\bar\beta_R - \bar\beta_A)]V_D\Delta p, \quad [7']$$

and

$$\eta \simeq [(\beta_R + \beta_A)/2\beta_R](1 - T_A/T_R). \quad [8']$$

Experiments with liquid propylene

Motivation for selecting propylene as working substance for experiments near room temperature has been discussed. Measurements were made by use of a heat engine designed according to Malone's principle and driven by a powerful external means. The apparatus (Fig. 4) has a fixed thermodynamic pile and a separate moving displacer that can be given any motion desired. There are 30 parallel plate flow channels in the thermodynamic pile, each 0.025 cm thick with flow in alternate

FIG. 4.   Schematic of experimental heat engine. T.D. pile, thermodynamic pile.

channels in opposite directions. The length is approximately 60 cm and total volume is 338 cm^3. An ambient heat exchanger of 48 cm^3 volume allows T_A to be controlled by cooling water; a remote heat exchanger volume of 49 cm^3 permits electrical power $\dot Q_{ext}$ to be added to the remote end to control T_R. The displacer has a maximum displaceable volume of about 100 cm^3; total fluid volume in this element is about 178 cm^3. Mercury in a U-tube separates the propylene or other working fluid from the hydraulic oil in the hydraulic ram. Lines, valves, and dead volume in the U-tube combine to give a total average working fluid volume of 920 cm^3. Experiments have been performed with ram-displaced volumes of both 40.2 and 67.8 cm^3. The pressure in the engine is nearly uniform at any instant. We have studied the engine over a broad range of periods τ; the results presented here were obtained for $\tau \simeq 3.0$ sec. This period refers to harmonic motions of both ram and displacer, which are phased at 90°.

Most quantitative experiments were performed with refrigerator/prime mover phasing because the heat absorbed from the remote end can be compensated by electrical heating at rate $\dot Q_{ext}$. As the pressure changes, the temperatures indicated as T_A and T_R change significantly because the thermocouples are in open channels and the fluid responds to pressure changes quasiadiabatically. In the measurements, the average values of T_A and T_R are maintained essentially constant by adjusting $\dot Q_{ext}$ and the cooling water; in the course of a run the total displaced volume V_D is varied. Measurements are also made of the pressure-ram and pressure-displacer indicator diagrams and of the overall pressure change Δp. The pressure-ram indicator diagram is measured with the displacer both moving and not moving. By taking the difference in the enclosed areas, we can eliminate some of the sources of work not associated with primary thermodynamic processes.

Typical results of experiments to test the validity of the approximate work formula [7'] for a Malone engine are shown in Fig. 5. The quantity W is the *net* measured indicated work done by the fluid per cycle obtained, at a given $T_R - T_A$, by subtracting from the difference in indicated work between displacer moving and not moving the same quantity for $T_R - T_A = 0$. The symbol, ✕, shows the value of $W/\Delta p$ calculated from [7'], multiplied by $\pi/4$ to account for the 90° phased harmonic motion and using experimental measurements of β. The symbol, +, gives $W/\Delta p$ calculated by multiplying a heat per cycle of $(\pi/4)(\overline{T\beta})_R V_D \Delta p$ absorbed at the remote end by the Carnot efficiency. Our assessment of the precision of the measurements of work and of β together with the accuracy of [7'] suggests that these measurements are in reasonable agreement with expectations.

The results of a typical study of $\dot Q_{ext}$ as a function of V_D/τ are shown in Fig. 6, in which the calculated components of $\dot Q_{ext}$ based on other measurements are also shown. The largest component of the total is the thermodynamic heating rate

$$\dot Q_R = \frac{\pi}{4}(\overline{T\beta})_R\,(V_D/\tau)\Delta p, \quad [9]$$

valid for 90° phasing. All the quantities on the right side are measured. In the absence of ram motions, and so at nearly constant pressure, we measured the external power needed for equilibrium as a function of $\Delta T = T_R - T_A$ and of V_D/τ. The results have the form, in which the quantities a, b, and c are evaluated experimentally,

$$\dot Q = a\Delta T + b\Delta T\,(V_D/\tau)^2 + c\Delta T(V_D/\tau). \quad [10]$$

Here, a is associated with thermal conduction or heat leak, b reflects ideal regenerative losses, and c depends on imperfections in the geometry of the thermodynamic pile. During full heat-engine operation, the fluid flowing toward R has a higher
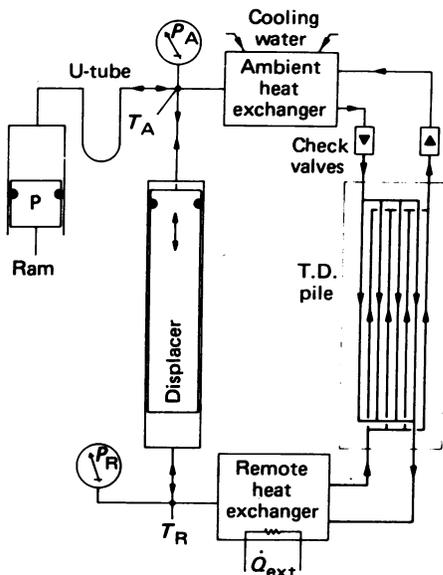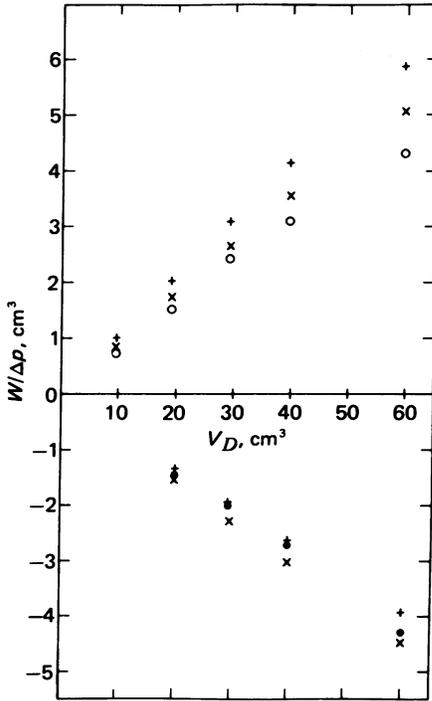
FIG. 5. Net work per unit maximum pressure change and per cycle as a function of displaced volume for two temperature spans for propylene. V_p = 67.8 cm^3. X, Calculated by the theory of the Malone engine; +, calculated assuming Carnot efficiency. O and ●, Measured values using the following engine parameters: (O) $\overline{T_R - T_A}$ = + 37.9 K, $\overline{T_A}$ = 301 K, $\bar{p}$ = 133.4 bar, $\overline{\Delta p}$ = 143.3 bar; (●) $\overline{T_R - T_A}$ = −39.7 K, $\overline{T_A}$ = 301 K, $\bar{p}$ = 111.6 bar, $\overline{\Delta p}$ = 193.6 bar.

pressure and lower specific heat than that flowing away from R. It follows from the "counterflow heat exchanger" model that the ideal regenerative loss, proportional to b, is *reduced* for refrigerator/prime mover phasing by the factor

$$f = \frac{(1 + \alpha)(k - 1) \exp[-\alpha(k - 1)/k]}{k - \exp[-\alpha(k - 1)/k]},$$ [11]

where $1 + \alpha = \rho c_p/b(V_D/\tau)$ and k is the ratio of the average heat capacity for fluid flowing away from R to that flowing toward R. The effect represented by f significantly reduces the ideal regenerative loss. The ΔT to be used in Eq. 10 for full engine operation is $T_R - T_A + \Delta T_i$, where ΔT_i reflects the fact that the heating and cooling effects in the displacer take place adiabatically. There is also a heat loss $\dot{Q}_0$ in the limit $V_D/\tau \rightarrow$ 0 due to ram motion alone. It is evaluated empirically. The above components of the heating rate are shown on Fig. 6. The agreement of their sum with experiments suggests that all major effects have been accounted for.

Applications

The principles demonstrated here may have wide application from very low to moderately high temperatures and from very small cryocoolers to large prime movers. Malone's principle properly applied should solve a major problem in the production of temperatures of a few degrees absolute. Liquid working substances should play an important role in work-operated and heat-operated refrigerators and heat pumps operating near room temperature, and studies of heat engines using liquid metals such as NaK may lead to the development of new efficient prime movers.
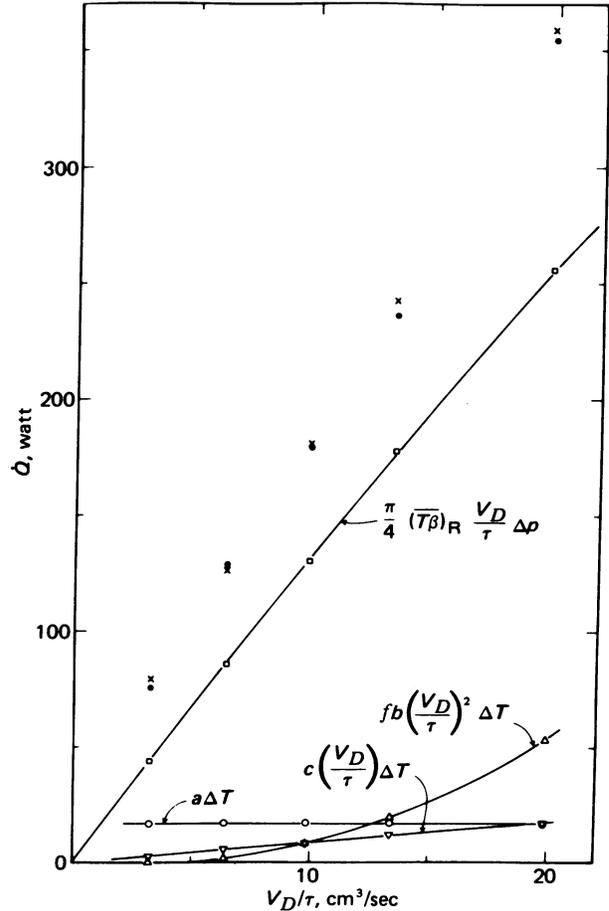

FIG. 6. Comparison of measured (●) and calculated (X) power required to stabilize the remote end temperature as a function of the ratio of displaced volume to period, for one temperature span with propylene for the following engine parameters: V_p = 67.8 cm^3, $\overline{T_R - T_A}$ = +37.9 K, $\overline{T_A}$ = 301 K, $\bar{p}$ = 133.4 bar, $\overline{\Delta p}$ = 143.3 bar, τ = 3.0 sec, $\overline{\Delta T_i}$ = 8.0 K, $\dot{Q}_0$ = +15.7 watt. Various components of the calculated values are shown on the figure and explained in the text.

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