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We will provide only an outline here.

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Since the initial and final states of the working substance are the same in a cyclic process, and internal energy is a function of state, *the internal energy of the working substance is unchanged in a cyclic process*.

Therefore, the net heat absorbed by the working substance is equal to the external work that it does in the cycle.

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If during one cycle of an engine a quantity of heat Q_1 is absorbed and heat Q_2 is rejected, the amount of work done by the engine is $Q_1 - Q_2$ and its *efficiency* η is defined as

$$\eta = \frac{\textbf{Work done by the engine}}{\textbf{Heat absorbed by the working substance}} = \frac{Q_1 - Q_2}{Q_1}$$

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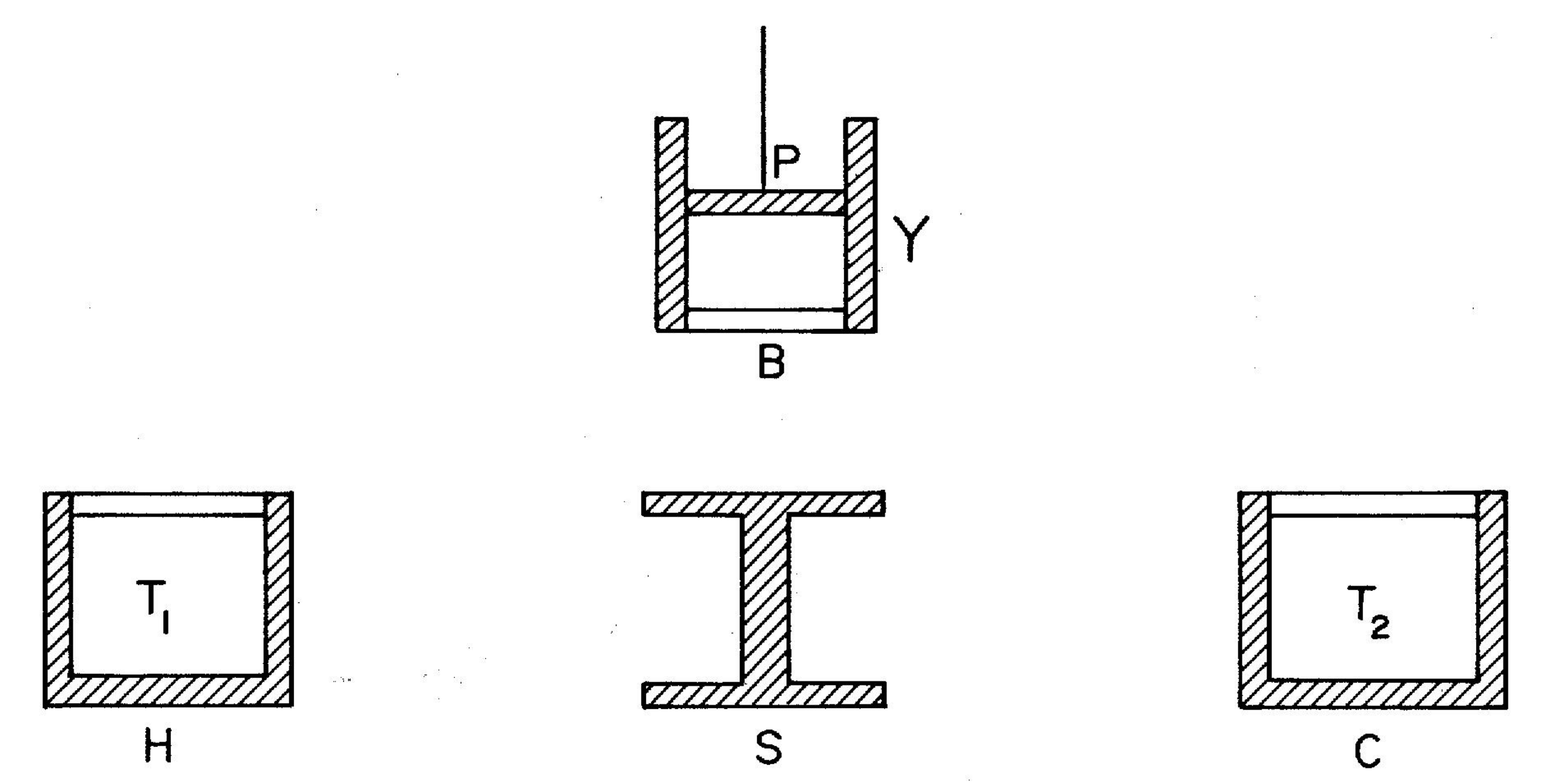
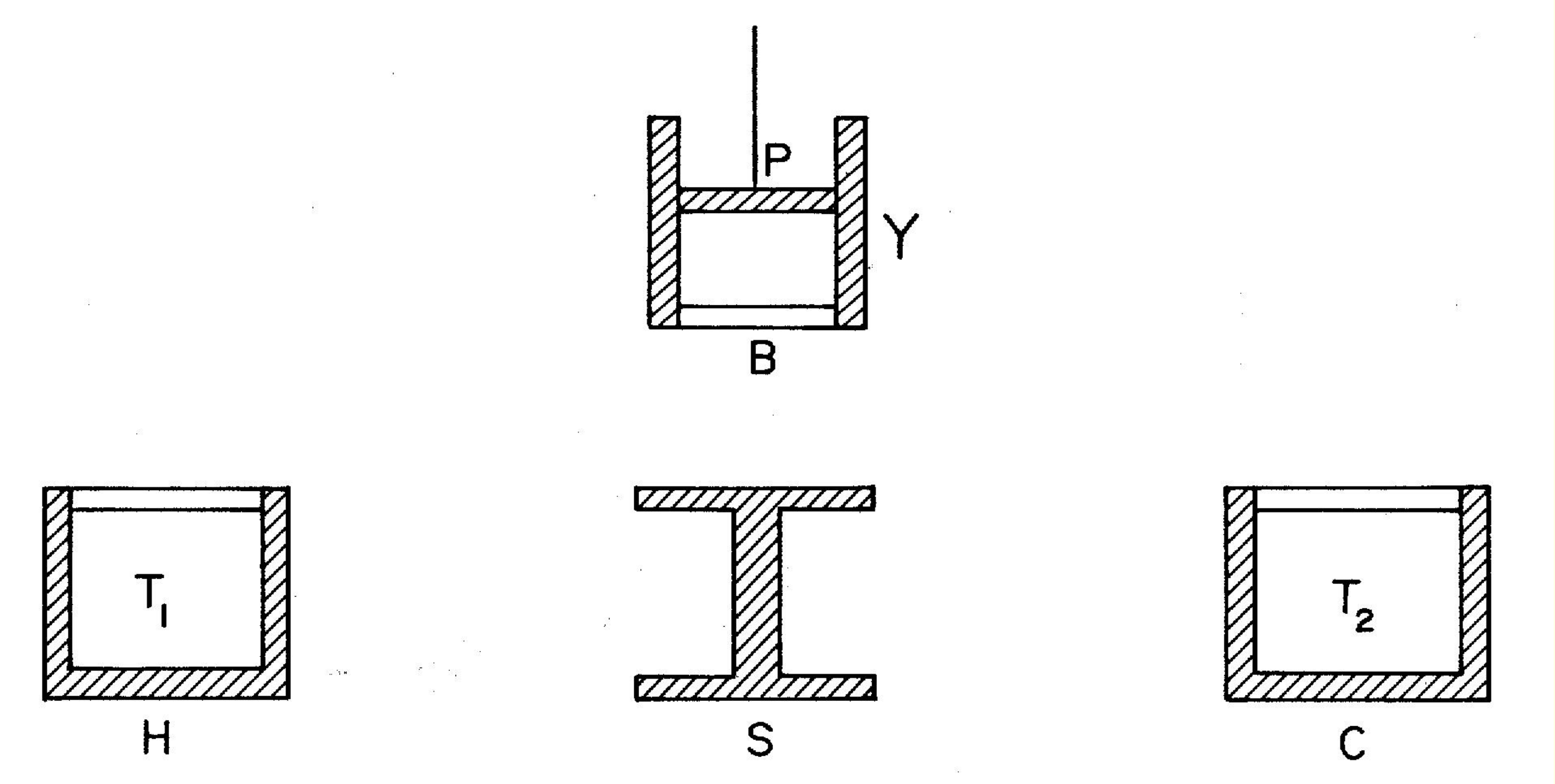
Carnot was concerned with the efficiency with which heat engines can do useful mechanical work. He envisaged an ideal heat engine consisting of a working substance contained in a cylinder (figure follows).



The components of Carnot's ideal heat engine.



The components of Carnot's ideal heat engine.

By means of this contraption, we can induce the working substance to undergo transformations which are either adiabatic or isothermal.

An infinite warm reservoir of heat (H) at constant temperature T_1, and an infinite cold reservoir for heat (C) at constant temperature T_2 (where $T_1 > T_2$) are available.

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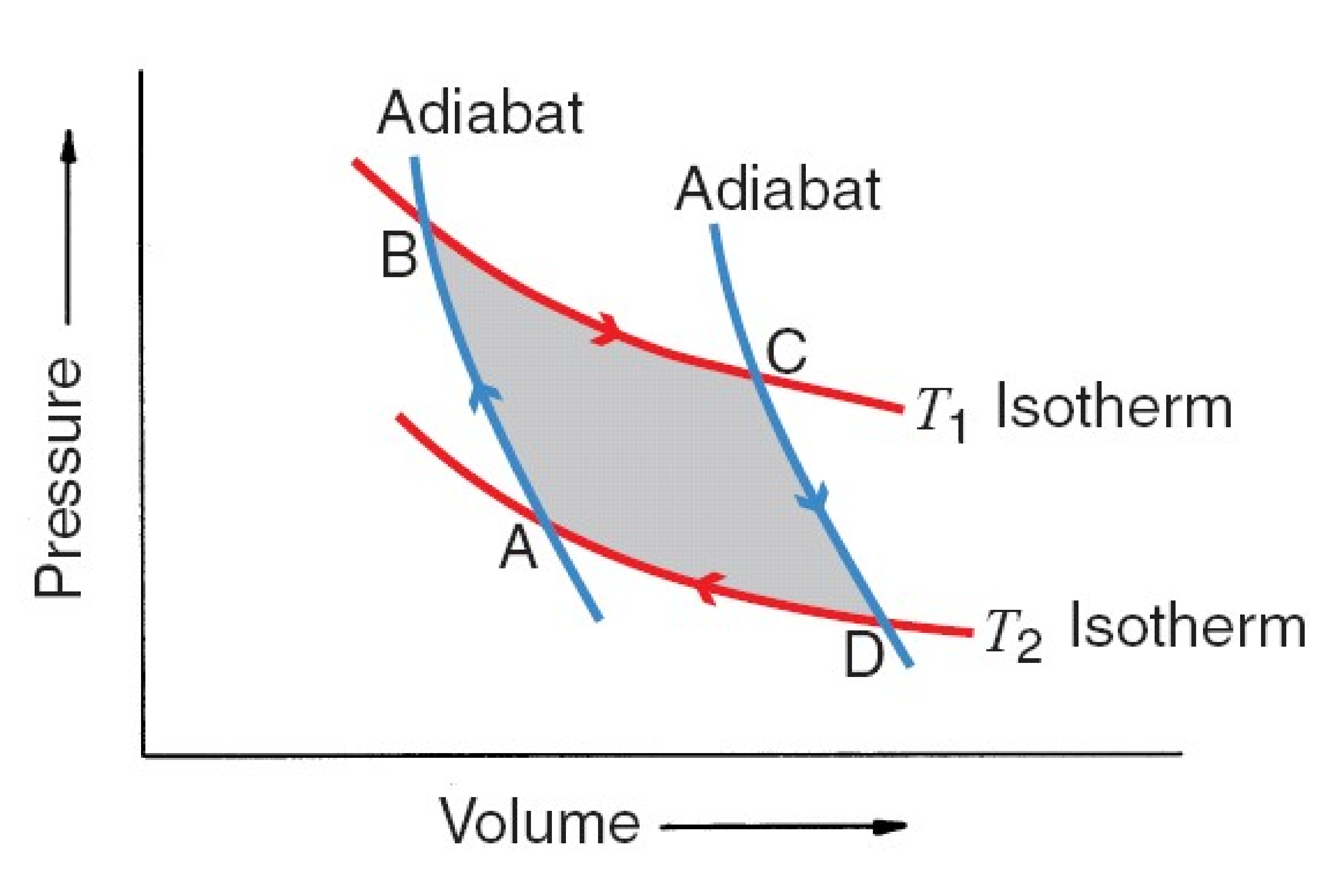
As the working substance expands, the piston moves outward and external work is done by the working substance.

As the working substance contracts, the piston moves inward and work is done *on* the working substance.



Representations of a Carnot cycle on a $p - V$ diagram. The red lines are isotherms and the blue lines adiabats.

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3. The working substance undergoes an adiabatic expansion to point D and its temperature falls to T_2. Again the working substance does work against the force applied to the piston.

4. Finally, the working substance is compressed isothermally back to its original state A. In this transformation the working substance gives up a quantity of heat Q_2 to the cold reservoir.

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In this cyclic operation the engine has done work by transferring a certain quantity of heat from a warmer (H) **to a cooler** (C) **body.**

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Exercise: Show that in a Carnot cycle the ratio of the heat $Q_!$ absorbed from the warm reservoir at temperature T_1 to the heat Q_2 rejected to the cold reservoir at temperature T_2 is equal to T_1/T_2.
Solution: See *Wallace & Hobbs*.

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The warm and cold reservoirs for a steam engine are the boiler and the condenser. The warm and cold reservoirs for a nuclear power plant are the nuclear reactor and the cooling tower.

In both cases, water (in liquid and vapour forms) is the working substance that expands when it absorbs heat and thereby does work by pushing a piston or turning a turbine blade.

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We can apply the principles of thermodynamic engines to the atmosphere and discuss concepts such as its efficiency.

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Another statement of the Second Law is:

`Heat cannot of itself pass from a colder to a warmer body in a cyclic process.`

That is, the "uphill" heat-flow cannot happen without the performance of work by some external agency.

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The First Law of Thermodynamics for a reversible transformation may be written as

$$dq = c_p\, dT - \alpha\, dp\,,$$

Therefore,

$$ds = \frac{dq}{T} = c_p \frac{dT}{T} - \frac{\alpha}{T} dp = \left(c_p \frac{dT}{T} - R \frac{dp}{p} \right)$$

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Integrating, we have

$$s = c_p \log \theta + s_0$$

where s_0 is a reference value for the entropy.

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The potential temperature can be used as a surrogate for entropy, and this is generally done in atmospheric science.

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The Clausius-Clapeyron Equation

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The Clausius-Clapeyron equation describes how the saturated vapour pressure above a liquid changes with temperature. [Details will not be given here. See *Wallace & Hobbs*.]

In approximate form, the Clausius-Clapeyron Equation may be written

$$\frac{de_s}{dT} \approx \frac{L_v}{T\alpha}$$

where α is the specific volume of water vapour that is in equilibrium with liquid water at temperature T.

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Taking the exponential of both sides,

$$e_s = e_s(T_0)\exp\left[\frac{L_v}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

Since $e_s = 6.11\,\mathbf{hPa}$ at $273\,\mathbf{K}$ $R_v = 461\,\mathbf{J\,K^{-1}kg^{-1}}$ and $L_v = 2.500 \times 10^6\,\mathbf{J\,kg^{-1}}$, the saturated vapour pressure e_s (in hPa) of water at temperature T (Kelvins) is given by

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Exercise: **Using MATLAB, draw a graph of e_s as a function of T for the range $-20°\mathrm{C} < T < +40°\mathrm{C}$.**

Generalized Statement of 2nd Law

The Second Law of Thermodynamics states that

- **for a *reversible transformation* there is no change in the entropy of the universe.**

In other words, if a system receives heat reversibly, the increase in its entropy is exactly equal in magnitude to the decrease in the entropy of its surroundings.

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The Second Law of Thermodynamics cannot be proved. It is believed to be valid because it leads to deductions that are in accord with observations and experience.

Evidence is overwhelming that the Second Law is true. Deny it at your peril!

Quotes Concerning the 2nd Law

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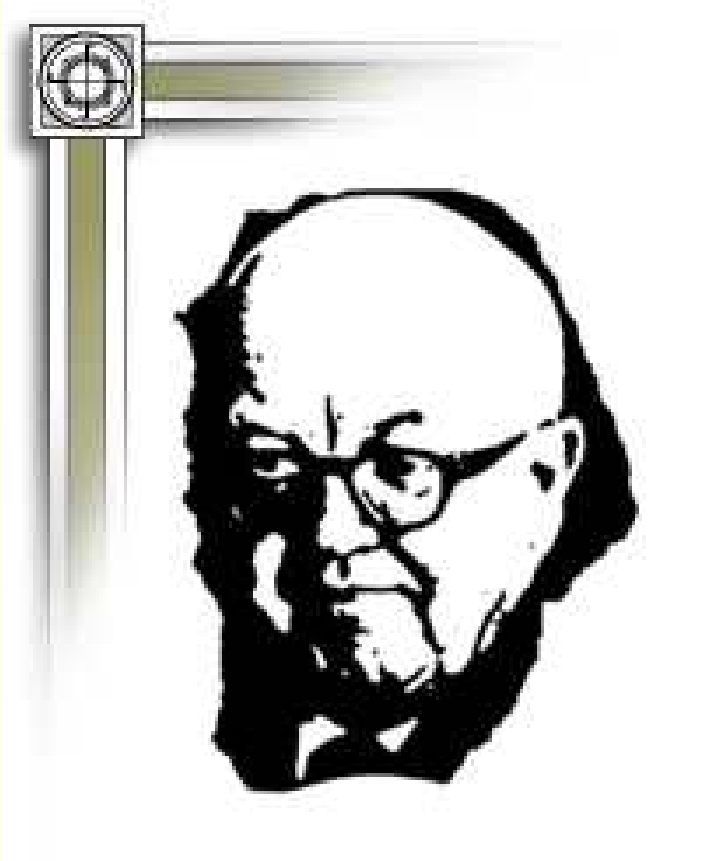
If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations, then so much the worse for Maxwell's equations. And if your theory contradicts the facts, well, sometimes these experimentalists make mistakes. But if your theory is found to be against the Second Law of Thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Charles Percy Snow (1905-1980) a scientist and novelist, most noted for his lectures and books regarding his concept of *The Two Cultures*.



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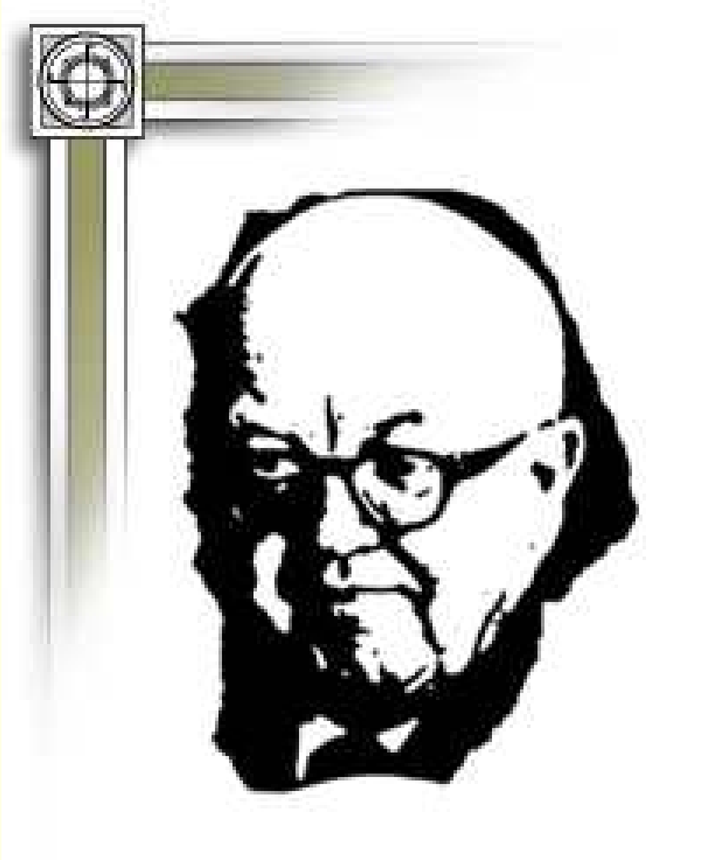

A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold: it was also negative.

Nothing in life is certain except death, taxes and the second law of thermodynamics. All three are processes in which useful or accessible forms of some quantity, such as energy or money, are transformed into useless, inaccessible forms of the same quantity. That is not to say that these three processes don't have fringe benefits: taxes pay for roads and schools; the second law of thermodynamics drives cars, computers and metabolism; and death, at the very least, opens up tenured faculty positions.

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Professor Seth Lloyd,
Dept. of Mech. Eng., MIT.

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They are sometimes parodied as follows:

- **(1) You can't win**
- **(2) You can't break even**
- **(3) You can't get out of the game.**

End of §2.7