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To discuss interactions among thermodynamic systems and the environment, we describe two types of idealized walls between such systems:

adiabatic = thermally insulating
diathermic = " conducting.

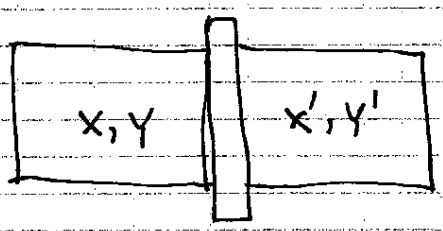
No real wall is truly adiabatic, so it is an idealization. Also, with diathermic walls we usually idealize them by assuming their heat capacity is so small it can be ignored.

The word "adiabatic" has different meanings in physics. In mechanics (classical or quantum), it refers to a system with time-dependent parameters, whose time dependence is much slower than any time scale of the motion. In thermodynamics, it has the meaning above. This is the original meaning of the word, as you can see from the Greek roots (a-dia-bat = not-through-go).

Now some definitions.

Def. An isolated system is in thermal equilibrium if its thermodynamic coordinates $(X_1,\ldots,X_n; Y_1,\ldots,Y_n)$ are constant in time. It is the experience that all isolated systems reach thermal equilibrium if you wait long enough.

Def. Two thermodynamic systems with coordinates (X,Y) and (X',Y') (each of which can be vectors, e.g. $X=(X_1,\ldots,X_n)$), in diathermic contact with each other are said to be in thermal equilibrium with each other if all the coordinates X, Y, X', Y' are constant in time.



↕ diathermic wall.

Of course, the X's are under experimental control, so we can hold them fixed by fiat.

Thermodynamics is axiomatized by a series of laws, whose justification is experimental.

The Zeroth Law of Thermodynamics says that if A, B, C are systems, and if A ⇔ B and B ⇔ C, where ⇔ means, "is in thermal equilibrium with," then A ⇔ C.

The 0th law allows us to define an empirical temperature scale. The example of the mercury thermometer will illustrate the idea.

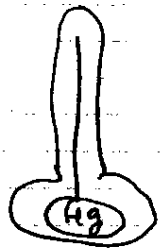
First note that, in view of the 0th law, if we choose some standard state of a standard system as a reference, then all other systems in thermal equil. with the standard are in thermal equil. with each other. Here are two standards:

1. ice + water at 1atm pressure
2. water + steam at 1atm pressure.

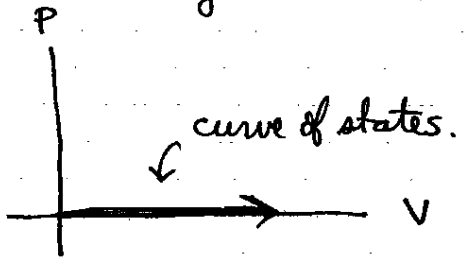
A thermometer is basically a thermodynamic system who states are constrained to lie on a 1-parameter family (a curve in the state space), which gives a 1-parameter family of standard state. An empirical temperature is then any labelling of states along this curve, which should be smooth and montonic but otherwise is arbitrary.

The mercury thermometer is a device to hold a given mass of

mercury under a fixed pressure $P = 0$, in which the volume is variable. Small changes in volume are made visible by the thin capillary tube. The vacuum above the mercury guarantees $P = 0$.

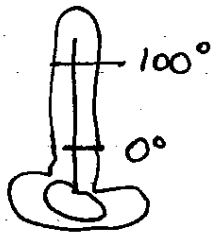


Here the curve of states in the state space of the mercury, represented as the PV plane, runs along the V-axis (where $P = 0$).



There is nothing special about this; any (almost) curve would work.

The thermometer is brought into thermal equilibrium with the freezing and boiling water standards, which are assigned the values 0° and 100°.



Values in between are marked off linearly, and the result is declared to be the mercury temperature scale. What is really being measured is the volume of the mercury, and we are effectively declaring a linear relationship between T and V,

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$$T = T_0 + aV,$$

a = const.

If we carry out the same procedure with another fluid (e.g., alcohol), temperatures 0° and 100° will agree by definition, but values ~~xxxx~~ in between will not, at least if you measure them accurately enough, because the expansivities of mercury and alcohol (as functions of T) are not proportional. So we have no unique empirical temperature scale, and none has any claim to any universal meaning.

Later we will see that there is a universal (or absolute) temperature scale, which is defined to with a scale factor (the choice of unit). This was first realized in the 1850's.

Some remarks about the ideal gas temperature scale. We will write the ideal gas equation of state in the form

$$PV = nRT,$$

where n = # of moles of the gas and R = the gas constant = 8.6 J/mole-deg K. This can also be written,

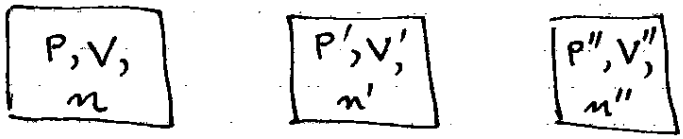
$$PV = NkT,$$

where N = # of molecules of the gas and k = Boltzmann constant. In this form we are making explicit reference to a microscopic model of the gas (we are counting molecules), so the first form is preferable in a purely macroscopic treatment such as thermodynamics. Also, the gas constant R can be measured by purely macroscopic measurements. It is related to microscopic quantities by $R = N_A k$,

where N_A is the Avogadro number, but in fact R was known accurately for a long time before there were accurate measurements of N_A or k.

The ideal gas law is only an approximation, not too bad for ordinary gases but not perfect, so we are not talking about any real system. However at low pressures all gases approach the ideal gas eqn. of state.

The ideal gas eqn. of state uses the absolute (Kelvin) temperature scale on the right hand side, so how could we state this ~~law~~ eqn. of state if we wished to play dumb and pretend that we only knew about empirical temperature scales? Here is an answer. Consider various systems of ideal (low pressure) gases,



The P,V, and n values of the different gas systems need not be equal, and they might also be different gases. Then we can take it as an experimental fact that two such systems are in thermal equilibrium if and only if

$$\frac{PV}{n} = \frac{P'V'}{n'} .$$

Since the quantity indicated characterizes the ~~states of these systems~~ families of states in thermal equilibrium, ~~then~~ we can simply define it as a temperature, the ideal-gas temperature scale. This can be regarded as yet another empirical temperature scale, although it has somewhat greater claim to universality than the others because

it does not depend on which gas is used (as long as the pressure is low). If we wish to adjust the unit of temperature, say, so that the difference between the freezing and boiling water standards comes out to be 100°, then we introduce a constant, call it R, and we have

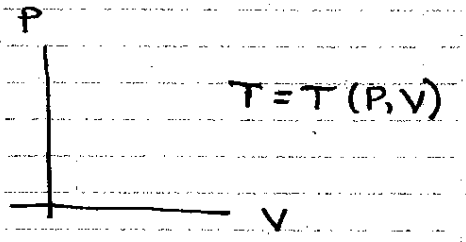
$$\frac{PV}{n} = RT.$$

← So we derive the ideal gas eqn of state, partly by definition.

It turns out that the ideal gas temperature scale is identical to the absolute temperature scale, but this has to be proven.

Now we comment on coordinates on the thermodynamic state space and geometric ways of representing that space.

Start with the example of an S.T.S. = Simple Thermodynamic System, in which $X = V$ and $Y = P$ $(n=1)$. As we have seen, the state space can be identified with the P-V plane. Given any state (= a point in the P-V plane) we can measure its empirical temperature with some thermometer to obtain the function $T = T(P,V)$.



This is an example of a <u>state function</u> (a function of the thermodynamic state of the system.) The function $T = T(P,V)$ is called the <u>equation of state</u> of the system.

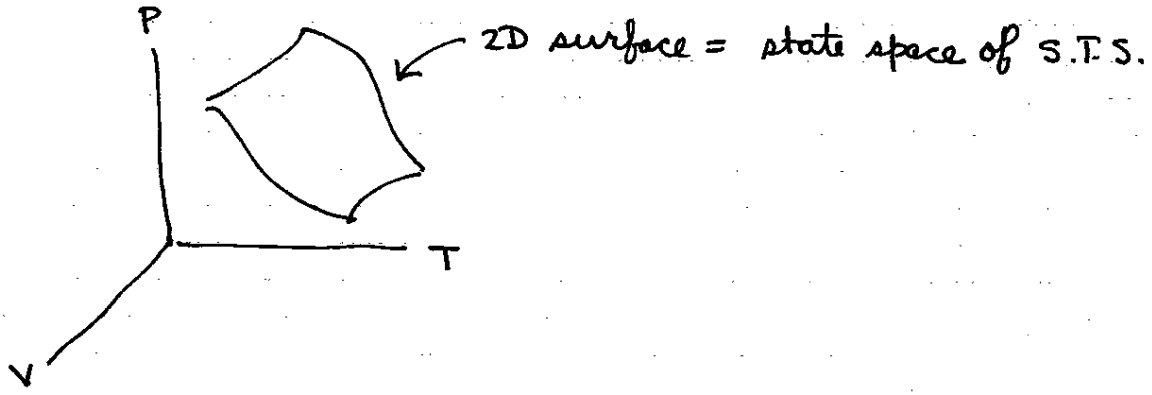
So we have three variables, (P,V,T) for an S.T.S., and they are related by one function. Assuming that this functional relation can be solved for any variable in terms of the other two, we can

obtain two more functions,

$$P = P(V,T)$$
$$V = V(P,T),$$

which are also considered to be (other versions of) the eqn. of state. Whether these inversions can be carried out and produce a unique solution (remember, some equations possess multiple roots or no roots at all) is a question we shall try to gloss over for now, but in fact in some interesting cases it cannot be done, at least in some regions of the state space. Let us just say for now, disregarding these concerns, that any pair of variables (P,V), (P,T), (V,T) can be used as coordinates on the thermodynamic state space of the S.T.S. The state space can be seen as the P-V plane, the P-T plane, or the V-T plane. Different choices are useful for different purposes.

Another possibility is to construct a 3-dimensional space with coordinates (P,V,T), and to say that the state space is a 2-D surface in this space specified by the eqn. of state. Then we get a picture like this:



This surface can be projected onto the various coordinate planes. See Zemansky Fig. 2.4 for a projection onto the P-T plane, and Fig. 2.5. for the state surface for water. In the latter case,

notice that the surface has ledges, corresponding to mixtures of different phases. The equation of state surface is continuous, but not smooth everywhere. 1/26/05

What about a system with >1 generalized coordinate? We guessed earlier that the state space had dimension n+1, which amounts to assuming that the specification of the $X_1, \ldots, X_n$ and T uniquely specifies an equilibrium state. That is, we can take $(X_1, \ldots, X_n, T)$ as coordinates on the state space. Then the conjugate forces $(Y_1, \ldots, Y_n)$ must be functions of these,

$$Y_i = f_i(X_1, \ldots, X_n, T)$$

where f_i, $i=1,\ldots,n$, are some functions. These functions are the <u>equations of state</u> of the system. There are n equations of state when there are n generalized coordinates.

Consider, for example, the dielectric slab, in which

$X_1 = V$	$Y_1 = P$
$X_2 = D = \sigma_f$	$Y_2 = -VE.$

Then the eqns of state are

$$P = f_1(V, D, T)$$
$$-VE = f_2(V, D, T).$$

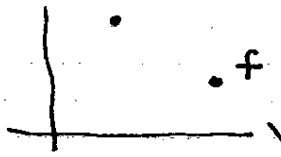
On the second eqn, we can divide by $-V$ and absorb that into the definition of f_2, so the second eqn of state has the form,

$$E = f_2(V, D, T).$$

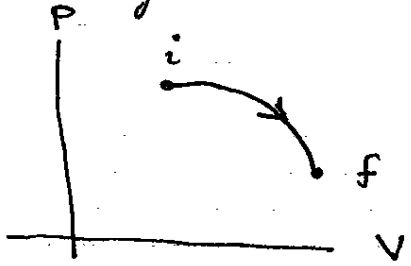
In these equations we have a certain amount of mass M in mind, so writing

$\rho = M/V$ for the density and eliminating V in favor of ρ, we obtain equations of state purely in terms of intensive variables. The first equ. of state $P = f_1(V, D, T)$ is a generalization of the E.O.S. for a S.T.S. The second, $E = f_2(V, D, T)$, gives the relation between E and D, as a fn. of the density and T. For a linear system, this would also be written $E = D/\varepsilon$, where ε is the dielectric function, which depends on ρ (or V) and T. We do not assume linearity here because we want to study general properties of matter (this is the strength of thermodynamics), not special systems. Also, nonlinear dielectrics are important in practice.

Now we discuss <u>transformations</u> of thermodynamic systems. Take an S.T.S. for example, and represent initial and final points on the P-V plane.



These are equilibrium states. Any transformation that changes i into f must be time-dependent, and so strictly speaking the intermediate states are not equilibrium states. But if the time dependence is <u>slow</u>, so that the time scale for the changes in the system are much longer than the equilibration time, then the intermediate states can be approximated by equilibrium states, and can be plotted in the state space as a curve connecting i and f.



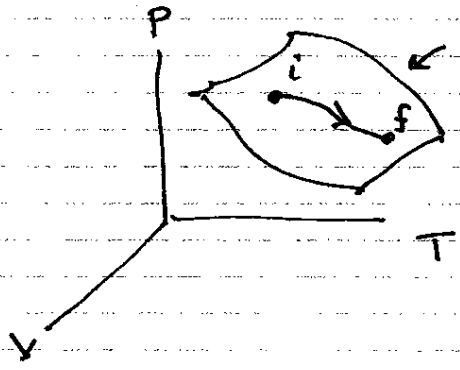
We will call such a transformation quasi-static. We will be mainly interested in quasi-static transformations, but others also occur, for example, the free expansion of a gas. The free expansion of a gas takes you from an initial to a final equilibrium state, but the intermediate states are not near equilibrium and cannot be plotted as a curve on the state space.

Two idealized kinds of quasi-static transformations are often of interest, the adiabatic and isothermal transformations. Assume these are familiar. The isothermal transformation requires a heat bath to maintain constant T.

The work done by a system on the environment during a quasi-static transformation is

$$\begin{pmatrix}\text{work done}\\ \text{by system}\end{pmatrix} = \int_{\text{path}} \sum_i Y_i\, dX_i$$

This is just a consequence of the definition of the Y_i. The path can be seen as a curve on the state space, for example, for an S.T.S.,



← 2D equ. of state surface.

For a system with 2 X's, like the dielectric system, the state space is 3D and can be seen as a 3D surface in a 5D space. For example, for the dielectric system it might be

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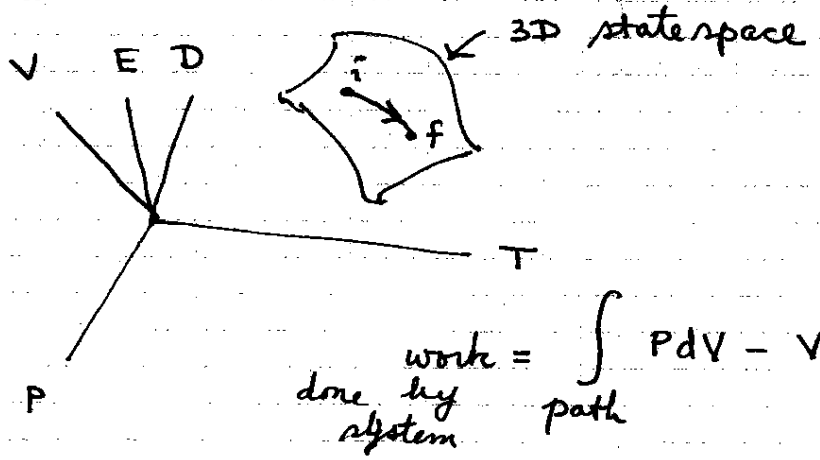
sketched as

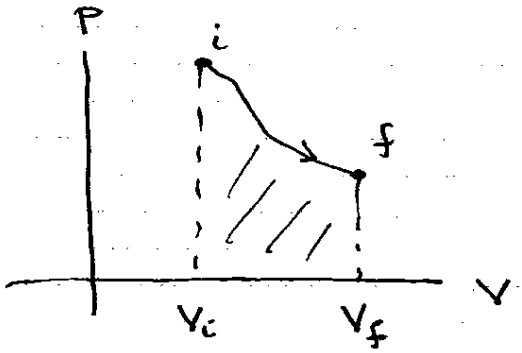


this is a combination of mechanical and electrical work.

$$\text{work} = \int_{\substack{\text{path} \\ \text{done by} \\ \text{system}}} P\,dV - V E\,dD$$

where a curve showing a quasi-static change is illustrated.

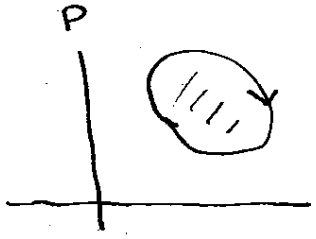
Note, for an S.T.S., if you identify the state space with the PV plane, then the work is interpreted geometrically as the area under the curve.



$$\text{work} = \int_i^f P\,dV = \text{area}.$$

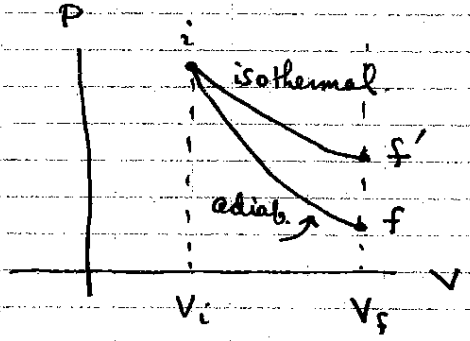
If the path is closed, taking you back to the initial state, then the work done is a loop integral,

$$\text{work} = \oint P\,dV \quad \text{or} \quad \oint \sum_i Y_i\,dX_i \text{ in the general case.}$$



$\text{area} = \oint P\,dV.$

By the way, note that in an S.T.S. in the PV plane, an adiabatic curve descends more rapidly than an isothermal one: 1/26/05



You can see why if you think about it physically. Next...

The First Law of Thermodynamics is basically conservation of energy, plus the notion that heat is a form of energy, applied to an infinitesimal, quasi-static transformation. It says:

1) There exists a state function U on any thermodynamic system, the internal energy of the system. U is defined up to an additive constant. U can be expressed as a function of any set of independent coordinates on the state space, for example, $U = U(X_1, \ldots, X_n, T)$.

2) In an infinitesimal, quasi-static ~~process~~ transformation,

$$dQ = dU + \sum_i Y_i \, dX_i ,$$

where dQ is the amount of heat absorbed during the transformation. This transformation connects ~~any~~ two nearby points on the state space.

Although the formula uses the notation dU and dQ, Q is different from U, because Q is not a state function. There is no meaning to the concept, "the amount of heat in the system," although one

can talk about the amount of energy in the form of heat (ΔQ or dQ) that enters the system during some transformation. U, on the other hand, is a state function. Its differential dU can be expanded by the chain rule,

$$dU = \sum_i \frac{\partial U}{\partial X_i} dX_i + \frac{\partial U}{\partial T} dT,$$

assuming we use $(X_1, \ldots, X_n, T)$ as coordinates. A similar formula for Q has no meaning. Because of this difference, we often write $đQ$ instead of dQ, and say that $đQ$ is an inexact differential (it is not the differential of a function).

Now a definition.

Def. A transformation is reversible if it can be reversed, restoring the system to its original state, with no change in the rest of the universe.

Quasistatic processes are reversible, if the system is in contact with a heat bath, the system will remain at the temperature of the heat bath (the process is isothermal), because the quasi-static (slow) condition guarantees that the system has time to reach and stay in thermal equil. with the bath.

In thermodynamics, the equation(s) of state of a substance are not (cannot be) computed, they must be measured. For example, suppose we know the equation of state of a S.T.S. Does this give us enough information to determine the function U? The answer is no, the determination of U requires the measurement of another

function (it must be measured).

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Now make two statements of the second law of thermodynamics.

Clausius version: A process whose only result is the transfer of heat from a colder to a hotter object is impossible.

Note: "only result" means that the rest of the universe is unchanged. You can transfer heat from a colder to a hotter object — a refrigerator does this — but you have to dump some extra heat into the environment in the process, and the rest of the universe has changed.

Kelvin version: A process whose only result is the conversion of heat into work is impossible.

Note: "only result" means the same as above.

Note also, it is easy to convert work into heat with no effect on the rest of the universe. Friction does this. It is the reverse that is impossible.