substance. Since the material is assumed to be compressible, its volume is not conserved. The volume changes due to creation (expansion of the gas) or destruction (compression) for which we introduce a production rate Π_V. Therefore:

$$\dot{V} = \Pi_V \tag{5.10}$$

We also have to consider the balance of energy—remember that we make energy responsible for the coupling of processes. Since a simple gas undergoes two types of processes we should expect two types of energy transfer, one associated with heating and the other with compression. Therefore, the law of balance of energy includes two expressions for energy fluxes:

$$\dot{E} = I_{E,th} + I_{E,comp} \tag{5.11}$$

Energy relations. $I_{E,th}$ denotes the energy flux that accompanies the entropy transfer in heating and cooling and $I_{E,comp}$ is the rate at which energy is transferred as a result of production of volume. According to Chapters 4 and 2, these fluxes are

$$I_{E,th} = T\,I_S \tag{5.12}$$

$$I_{E,comp} = -P\,\Pi_V \tag{5.13}$$

where T and P are the temperature and the pressure of the gas, respectively.[2] The negative sign in Equ.(5.13) tells us that the body of gas receives energy when it is compressed (negative Π_V) and it loses energy when it expands (positive Π_V).

This completes the generic laws and the generic energy relations. The rest of the model of the thermofluid processes of the ideal gas must come from constitutive relations.

5.2.2 Heating of an Ideal Fluid

As before, heating means absorption of entropy by a body; cooling means that the body loses entropy; the terms heating and cooling do not refer to any other circumstances. So the question we are dealing with is how a gas responds to entropy. Everyday experience tells us that a typical fluid either expands or gets warmer when its entropy increases.[3] The type of fluid considered will be an ideal one where ideal is defined by Equ.(5.8) and therefore by Equ.(5.9). There is no entropy production in the fluid, and the entropy current in heating or cooling equals the rate of change of entropy of the body.

Isothermal heating of an ideal fluid. Let us now turn to the constitutive problem of the heating of a fluid such as the ideal gas (whose other properties we will define in

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[2] The derivation of Equ.(5.13) suggests that we look upon compression and expansion of a body of gas as a fluid (hydraulic) process. We may just as well consider it a mechanical process where the transfer of momentum through the body is accompanied by the motion of its surface (Chapter 3). The result for energy transfer, Equ.(5.13), is the same.

[3] A fluid need not expand when it takes up entropy. A notable and most important exception to the rule is water which contracts if it is heated at temperatures between 0°C and 4°C. In this chapter we will consider only the ideal gas that expands upon heating.

Section 5.2.3). In Section 4.3.3 we discussed the problem of heating or cooling of a fluid at constant temperature. A fluid can be expanded or compressed isothermally if it is heated or cooled at the appropriate rate. The entropy therefore has the effect of changing the volume of the body. It does not do what we expect heat to do: it does not increase the temperature of the body. For this reason the term *latent heat* was coined to denote the heat absorbed in an isothermal process. It is instructive to hear how this name was used more than 180 years ago by J. Ivory:[4]

> The absolute heat which causes a given rise of temperature, or a given dilatation, is resolvable into two distinct parts; of which one is capable of producing the given rise of temperature, when the volume of the air remains constant; and the other enters into the air, and somehow unites with it while it is expanding … . The first may be called the heat of temperature; and the second might very properly be named the heat of expansion; but I shall use the well known term, latent heat, understanding by it the heat that accumulates in a mass of air when the volume increases, and is again extricated from it when the volume decreases.

Here we will formalize the definition of *latent entropy*. It is the factor Λ_V which relates rates of change of entropy content to rates of change of volume, i.e., it tells us how much entropy is needed to let a gas expand at constant temperature:

$$\dot{S} = \Lambda_V \dot{V} \tag{5.14}$$

We will call this new quantity the *latent entropy with respect to volume*. It tells us how much entropy we need to let a body expand by one unit of volume. Since we are considering ideal fluids, the rate of change of entropy equals the flux of entropy in heating which means that:

$$I_S = \Lambda_V \dot{V} \tag{5.15}$$

It is instructive and useful to exhibit the process of isothermal heating in the *TV* diagram (Fig. 5.7).[5]

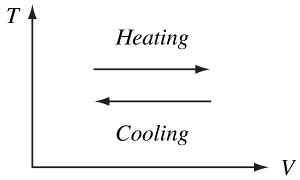

Figure 5.7: *TV* diagram of isothermal heating or cooling of a compressible fluid. In most cases, the volume of a fluid increases if it is heated at constant temperature (the latent entropy is positive). However, there are exceptions, such as water in the temperature range 0 – 4°C (here, the latent entropy is negative)..

We can easily calculate the amount of entropy exchanged in an isothermal process, or the change of the entropy content, by integrating the current of entropy from an initial point in time t_i to a final point t_f:

$$S_e = \int_{t_i}^{t_f} I_S \, dt = \int_{t_i}^{t_f} \Lambda_V \dot{V} \, dt \tag{5.16}$$

or

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[4] J. Ivory (1827), quoted by Truesdell (1980), p. 17. Much more information regarding the caloric theory may be found in Fox (1971).

[5] The use of *TV* diagrams was customary in the original development of thermodynamics. Today's custom of using *PV* diagrams does not make nearly as much sense. To use two fluid (or mechanical) variables, i.e., pressure and volume, for thermodynamics might give us the mistaken impression that a science of heat does not have to make use of thermal quantities. The old choice of temperature and volume was fortunate since it is the only one that allows for a complete mathematical theory of thermodynamics of fluids including water with its anomaly. See Truesdell (1979) and Truesdell and Bharatha (1977) for a detailed discussion of this matter.

$$S_e = \int_{V_i}^{V_f} \Lambda_V \, dV \tag{5.17}$$

We have not really solved the constitutive problem yet. The burden of calculating the current has been placed on the determination of a new quantity, namely the latent entropy. We can calculate the process of heating at constant temperature only if we know this constitutive quantity. We could try to measure it in a manner analogous to what we did for the entropy capacitance of incompressible materials (Section 4.5.3). In practice, however, it is very difficult to measure the latent entropy of gases since they take up very little entropy in comparison to measuring devices and containers. For this reason, it would be nice if we could find new ways of dealing with the constitutive problem. Fortunately, the relationship between entropy and the power of a fall of entropy through a temperature difference, which we have not exploited yet, introduces severe restrictions on the constitutive relations. These restrictions will reduce the burden of measurement: we will be able to determine the latent entropy of the ideal gas using theoretical arguments (see Section 5.2.6).

Heating of the ideal gas at constant volume. J. Ivory spoke of two effects of heating. If you add heat to a body, either the volume or the temperature (or both) will change. Here, we will investigate the second possibility, namely a change of temperature alone. This can happen only if the volume of the body is forcibly kept constant. With solids or liquids this condition is automatically satisfied to a high degree. Gases have to be put in an airtight container.

As in the case of heating of solids or liquids, we introduce the *entropy capacitance at constant volume*, i.e., the coefficient K_V which relates rates of change of the entropy content to rates of change of temperature:

$$\dot{S} = K_V \dot{T} \tag{5.18}$$

Here we refer explicitly to the condition of *heating at constant volume*, since the volume of a gas does not stay nearly constant as in the case of solids or liquids. Again, we assume we are dealing with an ideal fluid, so:

$$I_S = K_V \dot{T} \tag{5.19}$$

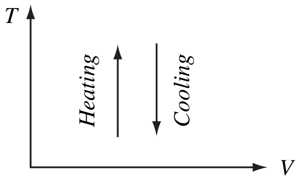

Figure 5.8: *TV* diagram of isochoric heating or cooling of a compressible fluid.

As in the case of isothermal heating, it is instructive to represent the process in a *TV* diagram (Fig. 5.8). In general the entropy capacitance is a function of both the volume and temperature of the body. We can determine the amount of entropy exchanged during heating at constant volume:

$$S_e = \int_{t_i}^{t_f} I_S \, dt = \int_{t_i}^{t_f} K_V \dot{T} \, dt \tag{5.20}$$

or

$$S_e = \int_{T_i}^{T_f} K_V \, dT \tag{5.21}$$

Direct measurements of the entropy capacitance at constant volume of gases are not so simple to do since the values are rather small compared to those for the measuring apparatus. We will be able to solve the constitutive problem in a combination of theoretical and experimental steps (Section 5.2.8). Theory allows us to relate the quantities we seek to others that might be simpler to measure.

The general process of heating of an ideal fluid. In general, a body which is heated undergoes changes of volume and of temperature simultaneously. For this reason, the entropy content must depend on both the volume and the temperature. Its rate of change must depend upon the rates of change of the independent variables. In other words,

$$\dot{S} = \Lambda_V \dot{V} + K_V \dot{T} \tag{5.22}$$

The coefficients are the latent entropy with respect to volume and the entropy capacitance at constant volume, respectively. For ideal fluids the rate of change of entropy equals the entropy current in heating or cooling, so we have:

$$I_S = \Lambda_V \dot{V} + K_V \dot{T} \tag{5.23}$$

We shall see in one of the following sections (Section 5.2.7) how this law can be exploited in the case of adiabatic processes undergone by the ideal gas, without us even knowing the form of the constitutive quantities. This will prove an important step in solving the constitutive problem of the ideal gas.

5.2.3 The Thermal Equation of State of the Ideal Gas

The ideal gas is a system which can change its volume and temperature. These two variables are related to a third property of the gas, namely its pressure. In Section 4.3.1, we encountered the *law of Gay-Lussac* which is obeyed by dilute gases. It states that the pressure of the fluid is a linear function of temperature if it is heated at constant volume. One finds that such gases have another simple property. Experiments demonstrate that the pressure and volume of a gas such as air at room temperature are inversely proportional if the temperature is kept constant (Fig. 5.9):

$$PV = constant \tag{5.24}$$

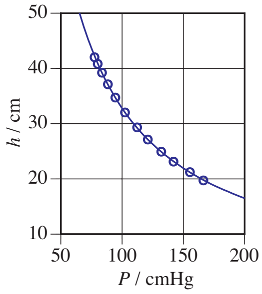

Figure 5.9: Relation between volume and pressure of air at constant temperature. The air is inside a cylinder with mercury as the piston. h is the height of the air column (proportional to volume) and P is measured in cm mercury column. The function fitted through the data points is the expected hyperbola (see Equ.(5.24)).

This relation is called the *law of Boyle and Mariotte*. The laws of Gay-Lussac and of Boyle and Mariotte together define the *ideal gas* as the fluid having the following *thermal equation of state*:[6]

$$PV = nRT \tag{5.25}$$

Here, $R = 8.314$ J/(mole · K) is the *universal gas constant*, and n is *the amount of substance* measured in moles.[7]

The *amount of substance* comes into the equation of state of the ideal gas in the following way. It is found that the law holds with a single (universal) value of the gas constant if certain mass ratios of different gases are used. For example, 16 g of oxygen gas turn out to be equivalent to 1 g of hydrogen gas. These amounts also turn out to be chemically equivalent in the sense that simple fractions or multiples of these numbers occur in chemical reactions using up all of the reactants. Since the amount of substance is the fundamental measure of how much stuff is participating in chemical reactions, the coefficient n appearing in the equation of state also measures the amount of substance.

Gases obeying both the laws of Gay-Lussac and of Boyle and Mariotte do not really exist in nature. Rather, a real gas approximates the behavior of an ideal fluid called the *ideal gas* if its temperature is high and its density low. What can be understood as sufficiently high or low needs to be determined by experience. Basically, gases follow the ideal law for temperatures which are high compared to the point at which they liquefy. The material at the center of the Sun behaves as an ideal gas despite its high density.

It is often useful to write the equation of state of the ideal gas in terms of density instead of volume. We express the volume of the body by its density and its mass: $V = m/\rho$. Further, we have the following relationship between the mass and the amount of substance of the fluid: $m = M_0 n$. Here, M_0 is the *molar mass* (mass per unit amount of substance) of the gas. Using these relationships, the equation of state of the ideal gas becomes

$$P = \frac{R}{M_0}\rho T \tag{5.26}$$

5.2.4 Transformation of the Constitutive Relation for Heating of the Ideal Gas

In Section 5.2.2, the constitutive relation for the response of an ideal fluid to entropy was formulated by considering the general case of a combination of heating at constant volume and at constant temperature. In other words, we used temperature and volume as the independent variables of the formulation. Since a fluid has a third important property, i.e., its pressure, we could write the constitutive relation with the help of pressure and temperature. Since we have a relation between P, V, and T for the ideal gas (Equ.(5.25)), we can solve the problem for this fluid.

We would like to introduce the expression for the heating (Equ.(5.23)) in a form involving pressure and temperature, instead of volume and temperature. In practice, heating often occurs at constant pressure, which makes the new form particularly use-

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[6] Proof of Equ.(5.25): Since P is proportional to $1/V$ at constant T (Boyle's relation), the product PV is a constant that depends only on the temperature of the gas:

$$PV = f(T)$$

Here, $f(T)$ is an unspecified function. Also, since P is proportional to T at constant volume, P/T is a constant which depends on the volume only. Therefore, P/T is some other function $g(V)$ of the volume:

$$P/T = g(V)$$

If we divide the first equation by T and multiply the second one by V we get

$$PV/T = f(T)/T$$
$$PV/T = Vg(V)$$

This implies that the quantity PV/T is a function of T alone and a function of V alone. Therefore, it cannot be a function of either T or V, which means that it is constant: $PV/T =$ constant.

[7] See Chapter 6 for more details on the subject of the amount of substance.

ful for some applications:

$$I_S = \Lambda_P \dot{P} + K_P \dot{T} \tag{5.27}$$

The new constitutive quantities are called the *latent entropy with respect to pressure* Λ_P, and the *entropy capacitance at constant pressure* K_P, respectively. For the ideal gas, it is simple to relate them to quantities involving the volume of the body. We derive this relationship with the help of the time derivative of the equation of state:

$$P\dot{V} + V\dot{P} = nR\dot{T} \tag{5.28}$$

This allows us to replace the time derivative of the volume in Equ.(5.23):

$$\begin{aligned} I_S &= \Lambda_V \frac{1}{P}\left(nR\dot{T} - V\dot{P}\right) + K_V \dot{T} \\ &= -\Lambda_V \frac{V}{P}\dot{P} + \left(\Lambda_V \frac{nR}{P} + K_V\right)\dot{T} \end{aligned} \tag{5.29}$$

If we compare this to the expression of the heating involving the pressure, Equ.(5.27), we find that

$$\Lambda_P = -\Lambda_V \frac{V}{P} \tag{5.30}$$

$$K_P = \frac{nR}{P}\Lambda_V + K_V \tag{5.31}$$

This result demonstrates that knowledge of both entropy capacitances is equivalent to knowing the capacitance at constant volume and the latent entropy with respect to volume. Since the measurement of the (ratio of the) entropy capacitances will prove simpler than that of the latent entropy in many cases, the relationships just derived are of particular importance.

5.2.5 Energy Exchanged in Isothermal Compression

There is one more important element of preparation before we can tackle the constitutive problem of the ideal gas in Section 5.2.6. We know from fluids and mechanics how to find the energy exchanged during compression or expansion of an ideal fluid. The general form is given by Equ.(5.13). From what we already know about the ideal gas we can find the energy exchanged in *isothermal* compression or expansion. We use the law of balance of volume (Equ.(5.10)) and the equation of state of the ideal gas (Equ.(5.25)) and insert both in Equ.(5.13):

$$I_{E,comp} = -\frac{nRT}{V}\dot{V}$$

This can be integrated over a period of time to yield

$$E_{comp} = -\int_{t_i}^{t_f} \frac{nRT}{V}\dot{V}\,dt = -nRT\int_{V_i}^{V_f} \frac{1}{V}dV$$

and finally

$$E_{comp} = -nRT \ln\left(\frac{V_f}{V_i}\right) \tag{5.32}$$

Note that the result does not depend on the absolute values of the volumes involved but rather on the ratio of final to initial volume. A doubling of the volume of one mole of a gas at room temperature means that about 1.7 kJ are emitted by the gas to the environment.

5.2.6 The Constitutive Problem of the Ideal Gas

The ideal gas is described by three functions, pressure (Equ.(5.25)), latent entropy (Equ.(5.14)), and entropy capacitance (Equ.(5.18)). We know the first of these three relations, but not the latter two. We can gain additional information on the latent entropy based upon theoretical considerations alone. In this subsection we shall give a brief account of the theory along the lines of what Carnot did some 180 years ago. The entropy capacitances will be found after considering adiabatic processes in Section 5.2.7. When we have finally solved the complete constitutive problem of the ideal gas, we will be able to discuss in detail the operations undergone by a fluid serving as the driving agent in a heat engine (Section 5.3).

By applying the relations developed up to this point to the operation of a Carnot engine (see Section 4.4.3 and Fig. 4.34), we will be able to determine the latent entropy of the ideal gas. For this purpose we have to discuss how the ideal gas is used as the driving agent of a Carnot engine. Absorbing entropy from a furnace at constant temperature is achieved by letting the ideal gas *expand isothermally* (step 1, from points 1 to 2 in Fig. 5.10). The second step must be an *adiabatic expansion*, which serves to lower the temperature of the gas to equal that of the cooler. During step 3 the entropy absorbed must be discharged. This is done by *compressing the fluid isothermally*. Finally, in step 4 (between points 4 and 1), the gas is *compressed adiabatically*. As a consequence, the temperature of the working agent is raised back to its initial value. The four-step cycle just outlined is called a *Carnot cycle*.

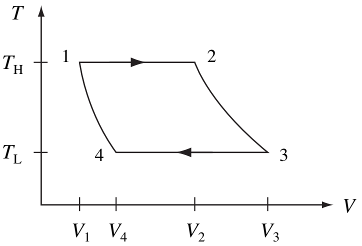

Figure 5.10: Carnot cycle of the ideal gas. The curved lines are the adiabats. The cycle runs between a furnace at high temperature T_H and a cooler at lower temperature T_L.

To obtain a restriction on the constitutive quantities of the ideal gas we proceed as follows. (This pretty much corresponds to what Carnot did in his theory of heat engines.) Consider a Carnot cycle operating with a very small difference of the temperatures between the furnace and the cooler:

$$\Delta T = T_H - T_L << T_H \tag{5.33}$$

In this case the adiabats of the ideal gas in Fig. 5.10 are very short, which means that they do not contribute to the exchange of energy in the *mechanical* process. For this reason we do not have to know more about adiabatic processes yet. The energy exchanged in compression and expansion in such a Carnot cycle is determined by the isotherms alone. According to Equ.(5.32), this quantity must be equal to

$$\begin{aligned} E_{comp} &= -nR(T+\Delta T)\ln\left(\frac{V_2}{V_1}\right) + nRT\ln\left(\frac{V_3}{V_4}\right) \\ &\approx -nR\Delta T\ln\left(\frac{V_2}{V_1}\right) \end{aligned} \tag{5.34}$$

The last step is a consequence of the fact that for a Carnot cycle having short adiabats the corresponding volumes must be nearly equal (Fig. 5.10), i.e., $V_3 = V_2$, and $V_4 = V_1$. From what we know about the motive power of a Carnot engine (Chapter 4) we can say that the energy released by the engine in one cycle is given by

$$E_{th} = -(T_L - T_H)S_e = -\Delta T\, S_e \tag{5.35}$$

If we combine Equations (5.34) and (5.35), we see that the entropy absorbed from the furnace must be

$$S_e = nR\ln\left(\frac{V_2}{V_1}\right) \tag{5.36}$$

On the other hand, the entropy absorbed in the isothermal expansion, S_e, is equal to the integral of the latent entropy over the volume, Equ.(5.17). This is possible only if the *latent entropy of the ideal gas* is given by

$$\Lambda_V = \frac{nR}{V} \tag{5.37}$$

In summary, the theory of thermodynamics—the relationship between entropy and energy—determines one of the constitutive quantities of the ideal gas. Note that Λ_V is proportional to the molar density (concentration) of the gas.

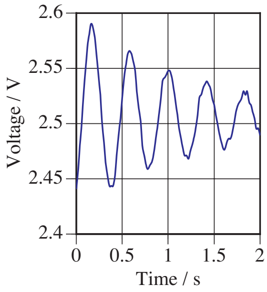

Figure 5.11: Voltage of a sensitive resistive thermometer as function of time. The thermometer is in air that is compressed and expanded rhythmically. A glass cylinder is fitted onto the neck of a large beaker and moves up and down on the air cushion inside the beaker. The motion is so fast that the air does not have time to be heated or cooled. The experiment is an example of Rueschardt's experiment (see Torzo et al., 2001).

5.2.7 Adiabatic Processes of the Ideal Gas

In Section 4.3.3 we saw that the temperature of a compressible fluid can be raised by compression alone without heating. Processes in which heating is absent are called *adiabatic*. They play a major role in natural and man-made phenomena such as the propagation of sound, the transport of heat by convection in the Earth's atmosphere, or cycles in heat engines and refrigerators. Since adiabatic processes allow us to measure a constitutive quantity of the ideal gas, namely, the ratio of its entropy capacitances, we will be able finally to compute all quantities determining its behavior (Section 5.2.8).

Description of adiabatic motion. If you suddenly compress air inside a cylinder, its temperature increases; if the air is expanded, its temperature decreases (Fig. 5.11). These changes occur without heating or cooling which can be achieved by insulating the cylinder against the flow of entropy.

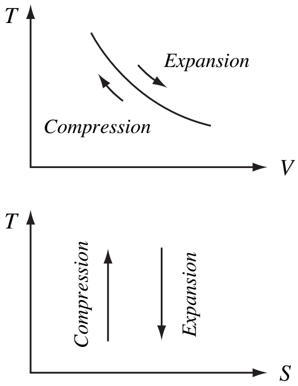

Figure 5.12: *TV* and *TS* diagrams of adiabatic compression and expansion. The term *adiabatic* means that entropy cannot be transmitted across the boundaries of the body. The temperature of most fluids, such as the ideal gas, decreases as a consequence of adiabatic expansion. The curve in the *TV* diagram is typical of the ideal gas.

The term *adiabatic* simply means that *no entropy has been exchanged* between the body and its surroundings. In other words, entropy currents across the surface of the system are equal to zero. It is convenient to display adiabatic processes in a *TV* diagram or in the *TS* diagram (Fig. 5.12, see also Chapter 4, Fig. 4.26). The temperature of the ideal gas rises if the fluid is compressed and it drops when the fluid is allowed to expand. Remember that the material can undergo reversible processes only. For this reason, the amount of entropy stored in the gas remains constant while the temperature changes. We have to conclude that the curve representing adiabatic compression in the *TS* diagram is a vertical arrow pointing up. The reverse, adiabatic expansion, results in a drop of temperature at constant entropy. Therefore, the representative curve in the *TS* diagram will be a vertical arrow pointing down.

How does this change arise? Our simple descriptions of isochoric and isothermal processes contain the seeds of an understanding of adiabatic operations. In real life, heating at constant volume and heating at constant temperature usually do not occur separately. The entropy content of a body changes when its volume and temperature change. Part of the added entropy increases the temperature, and part of it is changes the volume. In adiabatic changes, however, entropy does not cross the boundary of the body. Therefore the entropy normally emitted in the isothermal compression of the gas cannot leave the system. As a consequence, it raises the temperature. In somewhat oversimplified terms, we could say that in adiabatic compression some latent heat has been "converted" into sensible heat. (Do not take this literally; there only is one type of entropy inside a body!) A better way to explain the phenomenon graphically may be to say that *the entropy of the gas is squeezed into a smaller space*.

We can give a mathematical statement of the fact that heat does not cross the surface of the system under consideration. The current of entropy vanishes, which means that

$$I_S = 0 \tag{5.38}$$

which according to Equ.(5.23) is equivalent to

$$0 = \Lambda_V \dot{V} + K_V \dot{T} \tag{5.39}$$

or

$$\frac{dT}{dV} = -\frac{\Lambda_V}{K_V} \tag{5.40}$$

This is the fundamental equation of adiabatic change of ideal fluids including the ideal gas. In principle, we can solve the differential equation if we know the ratio of the latent entropy and the entropy capacitance of the fluid.

Solution to the problem of adiabatic motion of the ideal gas. We can derive the theory of adiabatic changes for the ideal gas. As a first step, the expression for the entropy current has to be transformed so that it contains the two entropy capacitances. The equation of state is used to eliminate the rate of change of temperature in Equ.(5.23). From Equ.(5.28) we obtain

$$\dot{T} = T\left(\frac{\dot{P}}{P} + \frac{\dot{V}}{V}\right) \tag{5.41}$$

Now, the entropy current takes the following form:

$$\begin{aligned} I_S &= \Lambda_V \dot{V} + K_V \dot{T} = \Lambda_V \dot{V} + K_V T\left(\frac{\dot{P}}{P} + \frac{\dot{V}}{V}\right) \\ &= T\left[K_V \frac{\dot{P}}{P} + \left(K_V + \Lambda_V \frac{V}{T}\right)\frac{\dot{V}}{V}\right] \end{aligned} \tag{5.42}$$

Using the relationship between K_P and K_V, Equations (5.30) and (5.31), we conclude that

$$I_S = T\left[K_V \frac{\dot{P}}{P} + K_P \frac{\dot{V}}{V}\right] \tag{5.43}$$

If we now apply the condition of adiabatic change, Equ.(5.38), we get a simple differential equation for pressure and volume. With the *ratio of the entropy capacitances* defined by

$$\gamma \equiv K_P / K_V \tag{5.44}$$

this equation takes the form

$$\frac{\dot{P}}{P} + \gamma \frac{\dot{V}}{V} = 0 \tag{5.45}$$

Naturally, the equation of adiabatic change can be integrated only if the constitutive quantities themselves, or their ratio γ, are known for the ideal gas. Fortunately, we have independent information concerning the ratio of the entropy capacitances. Different types of measurements, which do not involve measuring amounts of entropy, all indicate that *for the ideal gas this ratio must be constant*:

$$\gamma = constant \tag{5.46}$$

Also, this constant is larger than 1, which means that more entropy is needed to raise the temperature of the ideal gas by one degree in an isobaric process than in an isochoric one. An example of how to measure this important ratio is presented in Section 5.2.9. More important still is the propagation of sound in the ideal gas (Example 5.5) which gives the same result. Now the solution of the problem of *adiabatic motion of the ideal* gas is very simple. Integration of the differential equation gives the *law of Poisson and Laplace*:

$$PV^{\gamma} = constant \tag{5.47}$$

Using the thermal equation of state of the ideal gas, $PV = nRT$, this relation can be written with different variables:

$$P^{1-\gamma} T^{\gamma} = constant \tag{5.48}$$

or

$$TV^{\gamma-1} = constant \tag{5.49}$$

Remember that all of these equations hold *for the ideal gas only*. The curves representing adiabatic change in a pressure-volume (*PV*) diagram, which are usually found in books on thermodynamics, are derived from the form just calculated. For different types of fluids there may be completely different adiabats which do not even faintly resemble those for the ideal gas (Fig. 5.13). *Existence and form of the adiabats are constitutive properties*. Since the *adiabatic exponent* $\gamma > 1$, adiabats of the ideal gas in the *PV* diagram are steeper than isotherms.

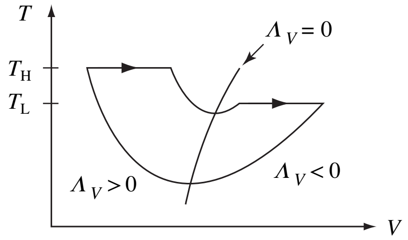

Figure 5.13: A strange Carnot cycle resulting for a fluid having an anomaly such as water (curved parts are adiabats). For water, the latent entropy is positive above 4°C and negative between 0°C and 4°C. At the maximum density at 4°C, $\Lambda_V = 0$. When $\Lambda_V < 0$, entropy is emitted when the body expands at constant temperature. See Thomsen and Hartka (1962).

5.2.8 Determining the Entropy Capacitances of the Ideal Gas

In Section 5.2.6 we determined the latent entropy of the ideal gas on the basis of theoretical considerations. The missing piece of information, i.e., the entropy capacitances of the ideal gas, can be calculated if we know their ratio. Above in Section 5.2.7, we have found that this ratio must be constant and that it can be measured in a number of ways. According to the results of Sections 5.2.4 and 5.2.6, Equations (5.30), (5.31) and (5.37), we obtain

$$K_V = n\frac{R}{\gamma - 1}\frac{1}{T} \tag{5.50}$$

$$K_P = n\frac{\gamma R}{\gamma - 1}\frac{1}{T} \tag{5.51}$$

From this the molar capacitances can be calculated. Note that the entropy capacitances of the ideal gas are inversely proportional to its temperature.[8] There is a simple relationship between the molar capacitances:

$$\bar{\kappa}_P = \bar{\kappa}_V + R/T \tag{5.52}$$

A proof of this relation is given in Example 5.7. Remember this holds for the ideal gas.

Temperature coefficients of energy and enthalpy. The product of an entropy capacitance and the temperature of the material is often used in place of the entropy capacitance. Here we have two such products:

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[8] This is one of the reasons why Carnot's thermodynamics met with resistance. According to common prejudice, the heat capacitance of the ideal gas should be constant since "…facts have lately become known which support the view that heat […] consists in a motion of the least parts of bodies." (R. Clausius, 1850). On the mechanical theory of heat where heat is (a form of) energy, and assuming a kinetic theory, the heat capacity of the ideal gas turns out to be constant.