

# 1. Principles of Thermodynamics

## 1.1 Introduction

Thermodynamics gives a phenomenological and very general description of matter – largely independent of models of microscopic structure (which were practically nonexistent at the time of foundation of thermodynamics in the 19th century). It is based on very few basic laws plus rules of calculus. Properties of matter or concrete systems are taken from outside (experiment, statistical mechanics).

■ **System.** Macrophysical entity under consideration, may interact with its *environment*. It is often homogeneous or consists of homogeneous *phases*. The usual classification according to the possibility of exchange of energy and matter between the two goes as follows: *Open system*: both energy and matter may be exchanged. *Closed system*: particle number(s) fixed, energy may be exchanged. *Isolated system*: no exchange of matter or energy.

■ **Thermodynamic equilibrium.** State of matter without any macroscopic changes or flows. A genuine equilibrium state is unambiguously determined by externally imposed state variables like pressure, volume, electric and magnetic fields. There are no memory effects like *hysteresis*. Traditionally, in the description of thermodynamic equilibrium there are three different equilibria:

- mechanical equilibrium: no changes of form or other processes accompanied by production of macroscopic mechanical (or electromagnetic) work;
- chemical equilibrium: no changes in the macroscopic chemical composition of the system;
- thermal equilibrium: no macroscopic energy flows in a system in mechanical and chemical equilibrium. In plain words: no heat flows.

In *local thermodynamic equilibrium* macroscopic subsets of the system are in equilibrium, but in neighbouring subsystems the equilibria are different, so that the system is not in equilibrium as a whole. Currents, heat flow etc. may occur; this is the realm of *hydrodynamics*. In most practically important cases local equilibrium is reached in macroscopically short time.

■ **State variables.** State variables are parameters needed for characterization of the equilibrium state. Usually there is only a handful of them,

in many cases like the prototypical one-component gas two is enough to determine the equilibrium state, in which the rest are then functions of these parameters, *state functions*. State variables are either *extensive* or *intensive*, the former being proportional to the number of particles (the volume  $V$ , particle number  $N$ , internal energy  $U$ , entropy  $S$ , magnetic moment  $m = \int d^3r M(r)$  etc.), whereas the latter (the temperature  $T$ , the pressure  $p$ , the chemical potential  $\mu$ , magnetic field strength  $H$ ) are independent of the number or particles. In thermodynamic differential forms these variables appear as conjugate pairs of extensive and intensive variables.

For quantities like energy and entropy the extensiveness requires weakness of interaction energy (or correlations) between macroscopic subsystems of the original system in comparison with the "bulk" quantities prescribable to the subsystems themselves. Gravity might cause problems in this respect at very large scales. Electromagnetic interaction is usually screened in matter and thus of short range.

■ **Process.** A change of state is called a *process* in thermodynamics. In a *reversible* process the direction may be inverted in the "whole universe" (system plus environment). These processes are always *quasistatic*, i.e. so slow that the state of the system is infinitesimally close to thermodynamic equilibrium. Not all quasistatic processes are reversible, however. An *irreversible* process is often a sudden or spontaneous change (e.g. mixing of gases, explosion), during which the system may be far from equilibrium and the description by the state variables is no sufficient. An irreversible process may occur quasistatically, though. A *cyclic* process (cycle) consists of repeating periods during which the system always returns to the initial state.

## 1.2 State variables and differential forms

State variables are macroscopic quantities related to the equilibrium. Not all of them are independent in equilibrium, though. Once independent variables are chosen, the rest are unambiguous functions of them, say  $p = p(T, V, N)$ ,  $U = U(T, V, N)$ ,  $S = S(T, V, N)$  etc.

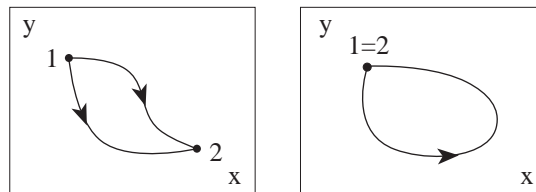


Figure 1-1: Examples of processes leading from state 1 to state 2.

When the change is infinitesimal, the rules of calculus yield the following relation between the differential of a function and the differentials of

independent variables:

$$dp = \left( \frac{\partial p}{\partial T} \right)_{V,N} dT + \left( \frac{\partial p}{\partial V} \right)_{T,N} dV + \left( \frac{\partial p}{\partial N} \right)_{V,T} dN.$$

This implies that in a cyclic process the net change vanishes:

$$\oint_{1 \rightarrow 1} dp = \oint_{1 \rightarrow 1} dU = \dots = 0.$$

■ **Differential and differential form.** Consider the *differential form*

$$dF \equiv F_1(x, y) dx + F_2(x, y) dy, \quad (1.1)$$

where  $F_1$  and  $F_2$  are given functions. An example familiar from mechanics is the differential form of work exerted by a force  $\mathbf{F}$  on a body:

$$dW = \mathbf{F} \cdot d\mathbf{r} = F_x dx + F_y dy + F_z dz.$$

The notation  $dF$  in (1.1) means that the differential form is not necessarily a differential, therefore  $\int_1^2 dF$  may depend on the integration path. If the condition  $\partial F_1/\partial y = \partial F_2/\partial x$  holds, then  $dF = dF(x, y)$  is a differential (often referred to as the exact differential in this context). Then the integral  $\int_1^2 dF = F(2) - F(1)$  is independent of the path and  $F_1(x, y) = \partial F(x, y)/\partial x$  ja  $F_2(x, y) = \partial F(x, y)/\partial y$  are coordinates of the gradient of some function  $F$ .

■ **Integrating factor.** If the form  $dF = F_1 dx + F_2 dy$  is not a differential, in case of two variables a function *integrating factor*  $\lambda(x, y)$  may be found such that, in a vicinity of the point  $(x, y)$  the condition

$$\lambda dF \equiv \lambda F_1 dx + \lambda F_2 dy = df$$

holds, which implies  $\partial(\lambda F_1)/\partial y = \partial(\lambda F_2)/\partial x$ . Both the integrating factor  $\lambda$  and the function  $f$  are then state variables.

In case of three or more variables the integrating factor may not exist, in general. In thermodynamics, however, the integrating factor of the differential form of heat always exists, this is partially the content of the second law.

■ **Legendre transform.** *Legendre transform* generates changes of variables between conjugate variable pairs. Consider, for simplicity, the function  $f(x)$  and define the variable conjugate to  $x$  as

$$y \equiv \frac{df(x)}{dx}. \quad (1.2)$$

The Legendre transform of  $f$  is the following function of  $y$ :

$$g(y) \equiv f(x) - yx, \quad (1.3)$$

where on the right-hand side  $x$  is expressed as a function of  $y$  from relation (1.2). Direct calculation yields

$$\frac{dg(y)}{dy} = -x, \quad (1.4)$$

so that  $df = ydx$  and  $dg = -xdy$ .

■ **Mathematical identities.** In thermodynamics, fixed variables are usually indicated explicitly when calculating partial derivatives. This is because several sets of independent variables are in wide use and infer different physical meaning for partial derivatives in different sets. Examples of useful relations for various changes of variables are listed below.

■ **Jacobi determinants.** The use of Jacobi determinants

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$

is often convenient when carrying out changes of variables in differential relations. This is due to the properties

$$\frac{\partial(u, y)}{\partial(x, y)} = \left( \frac{\partial u}{\partial x} \right)_y, \quad \frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(s, t)} \frac{\partial(s, t)}{\partial(x, y)},$$

valid for Jacobians of arbitrary order and easily checkable by direct calculation for  $2 \times 2$  determinants.

**Example 1.1.** Consider the function of two variables  $F(x, y)$ . If by some reason we want to use the pair  $(x, z)$  as independent variables, we may write

$$F(x, y) = F(x, y(x, z)).$$

The chain rule then yields

$$\begin{aligned} \left( \frac{\partial F}{\partial x} \right)_z &= \left( \frac{\partial F}{\partial x} \right)_y + \left( \frac{\partial F}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z, \\ \left( \frac{\partial F}{\partial z} \right)_x &= \left( \frac{\partial F}{\partial y} \right)_x \left( \frac{\partial y}{\partial z} \right)_x. \end{aligned}$$

### 1.3 Equation of state

Equation of state expresses the relation of state variables of the system in equilibrium. It is usually written in a form involving "mechanical" variables and the temperature. Equation of state does not usually include internal energy or other extensive variables of dimensions of energy, and in this sense the equation of state does not give a complete thermodynamic description of the system. A few widely used equations of state are listed below.

■ **Classical ideal gas.** The equation of state of classical ideal gas is

$$pV = NT. \quad (1.5)$$

Here,  $p$  = pressure,  $V$  = volume,  $N$  = number of molecules and  $T$  = absolute temperature.

■ **Mixture of ideal gases:** Equation of state remains the same  $pV = NT$ , with  $N = \sum_i N_i$ . The total pressure may be expressed as  $p = \sum_i p_i$ , where  $p_i = N_i T / V =$  *partial pressure* of the  $i$ th component.

■ **Virial expansion of real gas.** The equation of state of the ideal gas may be amended so that the intermolecular interaction is taken into account. Denote the (particle) *number density* by  $n \equiv N/V$ . In the limit of small density the pressure may be expanded in powers of the density (the *virial expansion*)

$$p = T [n + n^2 B_2(T) + n^3 B_3(T) + \dots], \quad (1.6)$$

where the *virial coefficients*  $B_n$  depend on the temperature only.

■ **Curie's law.** Magnetic field strength  $H$ , magnetic induction  $B$  and *magnetization*  $M$  are related as.

$$B = \mu_0(H + M).$$

Further the magnetic moment of the system shall often be denoted by  $m$ ; in case of homogeneous field then  $m = VM$ .

The magnetic equation of state expresses the dependence of magnetization  $M$  on the field strength  $H$ . Many *paramagnetic materials* (no spontaneous magnetic ordering) obey Curie's law

$$M = \frac{C}{T} H, \quad (1.7)$$

where  $C$  is a material constant proportional to the number density of paramagnetic atoms.

■ **Responses.** Thermodynamic responses describe the reaction of state variables to the change of other state variables. They usually are easily measurable quantities. The equation of state determines "mechanical" responses like *thermal expansion coefficient*

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p,N}, \quad (1.8)$$

*isothermal compressibility*

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,N} = \frac{1}{n} \left( \frac{\partial n}{\partial p} \right)_T, \quad (1.9)$$

or *isothermal susceptibility*

$$\chi_T = \left( \frac{\partial M}{\partial H} \right)_T \quad (1.10)$$

of magnetic material.

Under an adiabatic (thermally isolated) change the responses are *adiabatic compressibility*

$$\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{S,N} = \frac{1}{n} \left( \frac{\partial n}{\partial p} \right)_S \quad (1.11)$$

and *adiabatic susceptibility*

$$\chi_S = \left( \frac{\partial M}{\partial H} \right)_S. \quad (1.12)$$

## 1.4 Zeroth law

Zeroth law of thermodynamics is the observation that there is a quantity called *temperature* characterizing the thermal equilibrium and a *thermometer* to measure and compare temperatures. This comparison is transitive: *if two bodies are separately in equilibrium with a third one they are in equilibrium with each other.*

## 1.5 Internal energy

In thermodynamics *internal energy* is the total energy of the system at rest. Usually the potential energy of the system in an external field is excluded. Then internal energy consists of the kinetic energy of relative motion of particles, energy of their interaction and structural energy of the particles.

Due to interaction between the system and its environment care has to be taken in dividing the world in the system and the environment, especially when long-ranged interactions occur.

At the present state of our knowledge of the structure of matter it is quite obvious that the internal energy of the system is a state variable and thus an unambiguous function of the state. It is also clear that internal energy may be determined even in systems which are not in a state of thermodynamic equilibrium.

## 1.6 Work

*Work* is energy exchange between the system and environment which may be described in terms of work of macroscopic mechanics and electromagnetic theory.

There are different sign conventions. Here, the elementary work (differential form of work)  $dW$  is *the work exerted to the environment by the system*. In this case positive work means loss of energy by the system. In the paradigmatic *SVN* - system<sup>1</sup> the work related to the change of the volume is

$$dW = p dV. \quad (1.13)$$

The work related to the surface energy of a liquid may be written as

$$dW = -\sigma dA, \quad (1.14)$$

where  $\sigma$  = surface tension and  $A$  = free surface area. With positive surface energy  $\sigma > 0$  and the surface tension tends to decrease the area. An elastic deformation gives rise to the work form:

$$dW = -F dL, \quad (1.15)$$

where  $F$  = the force stretching the rod and  $L$  = the rod length. The tension is  $\sigma = F/A$  = force/cross-section area. According to *Hooke's law*  $\sigma = E(L - L_0)/L_0$ , where  $E$  is Young's modulus and  $L_0$  the rest length of the rod.

The general expression of the differential form of work is

$$\boxed{dW = \sum_i f_i dX_i = \mathbf{f} \cdot d\mathbf{X}}, \quad (1.16)$$

where  $f_i$  are the coordinates of the *generalized force* and  $X_i$  the coordinates of the *generalized displacement*.

■ **Work in electromagnetism.** Treatment of energetic quantities in a system in electromagnetic field requires considerable care in the definition of the system, because usually the introduction of polarizable or magnetizable body in an electromagnetic field changes the field everywhere, not only in the body itself. Unambiguous definition may be obtained, if the whole electromagnetic field is considered a part of the system. In this case the elementary work required for a change of fields in the form familiar from electrodynamics (with the sign corresponding to our convention)

$$dW = - \int d^3r (\mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B}) \quad (1.17)$$

may be interpreted as the work carried out by the system.

With the aid of a special experimental setup in some cases it is possible to arrive at a situation in which *the polarized body does not affect the fields*  $\mathbf{E}$  and  $\mathbf{H}$  and the field energy outside the body may be dropped from the energy balance of the system so that

$$\boxed{dW = -V_0 (\mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B})}, \quad (\text{I}) \quad (1.18)$$

<sup>1</sup>One-component isotropic homogeneous material with the state variables  $S, V, N$  (*natural variables* of the internal energy), often referred to as the *pVT* system as well.

when the volume  $V_0$  is small enough so that the fields may be regarded as uniform.

If this is not possible, the energy corresponding to fields with the same sources (free charges and conducting currents) but without the polarizable body is nevertheless often subtracted from the energy related to the system including this body. The point here is that thermodynamics is brought about in the problem by the presence of polarizable material. Without it, the problem would be that of "pure" electrodynamics.

For simplicity, consider still the case in which the fields  $\mathbf{E}$  and  $\mathbf{H}$  are the same both with and without the polarizable body. In uniform fields then the total energy might be written as

$$E_{\text{tot}} = U + V_0 \left( \frac{1}{2} \varepsilon_0 \mathbf{E}^2 + \frac{1}{2} \mu_0 \mathbf{H}^2 \right) \quad (1.19)$$

thus excluding the energy of the "empty space" from the internal energy of the system considered. In this case the differential form of electromagnetic work related to the change of the internal energy defined as (1.19) assumes, according to (1.18) the form

$$\boxed{dW = -V_0 (\mathbf{E} \cdot d\mathbf{P} + \mu_0 \mathbf{H} \cdot d\mathbf{M})} \quad (\text{II}) \quad (1.20)$$

This convention is often used in condensed matter and solid state physics.

## 1.7 First law

The first law of thermodynamics is the *law of conservation of energy*.

$$\boxed{dE = dQ - dW} \quad (1.21)$$

Here,  $dE$  is the differential of the energy of the system. With the usual convention of thermodynamics, it may be identified by the differential of the internal energy:  $dE = dU$ , *provided the momentum, angular momentum and the potential energy in external field of the system remain unaltered.*

If the particle number may change, *the chemical potential*  $\mu$  is introduced by the definition

$$dU = dQ - dW + \mu dN.$$

In a general form for several particle species the first law is

$$\boxed{dU = dQ - \mathbf{f} \cdot d\mathbf{X} + \sum_i \mu_i dN_i} \quad (1.22)$$

■ **Heat capacity.** The ability of a body to receive heat is described by the *heat capacity*

$$\boxed{C_A = \left. \frac{\Delta Q}{\Delta T} \right|_A}, \quad (1.23)$$

where the subscript  $A$  refers to fixed variables, e.g.:  $C_V, C_p$ . *Specific heat* is the heat capacity per unit mass. Heat capacities are usually easy to measure contrary to the internal energy.

■ **Cyclic process.** Cyclic processes (cycles) are especially important in the theory of heat engines. In a cycle the system return to its initial state again and again after certain periodic stages. In a simple  $SVN$  system, in which  $dU = dQ - p dV$ , the area enclosed by the curve describing the process in the  $(V, p)$  plane is

$$\oint p dV = W. \quad (1.24)$$

Since  $\oint dU = 0$ , the work during a cycle is equal to the difference of the amounts of heat received and delivered by the system. The *thermal efficiency* of a cycle is  $\eta = \Delta W / \Delta Q^+$ , where  $\Delta Q^+$  is the amount of heat received by the system during a cycle.

## 1.8 Second law

From the formal point of view the second law states two things:

- for the differential form of heat there is an integrating factor (the temperature) giving rise to the extensive state variable *entropy*  $S$ ; in a reversible process:

$$\boxed{dS = \frac{dQ}{T}}. \quad (1.25)$$

- In an irreversible process

$$\boxed{dS > \frac{dQ}{T}}. \quad (1.26)$$

There are several traditional equivalent formulations of the second law:

(1.8a) *Heat cannot be transferred from a colder heat reservoir to a warmer heat reservoir without any other changes.* (Clausius)

(1.8b) *There is no cyclic process with the sole result of transferring the heat received to work.* (Kelvin)

(1.8c) *Of all heat engines working between the temperatures  $T_1$  and  $T_2$  the Carnot engine has the highest efficiency.* (Carnot)

All these statements are equivalent in the sense that each of them yields the others. Here, we shall not dwell on demonstration of this equivalence, however.

The first law in a reversible process may now be cast in the form

$$\boxed{dU = T dS - \mathbf{f} \cdot d\mathbf{X} + \sum_i \mu_i dN_i}. \quad (1.27)$$

## 1.9 Carnot's cycle

The notion of entropy may be approached by analyzing Carnot's cycle consisting of four reversible stages (Fig. 1-2):

a) isothermal	$T_2$	$\Delta Q_2 > 0$
b) adiabatic	$T_2 \rightarrow T_1$	$\Delta Q = 0$
c) isothermal	$T_1$	$\Delta Q_1 > 0$
d) adiabatic	$T_1 \rightarrow T_2$	$\Delta Q = 0$

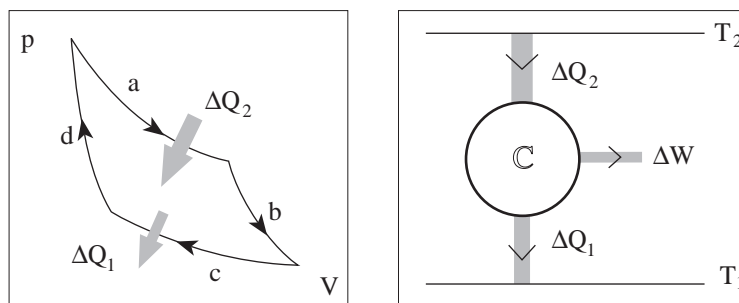


Figure 1-2: Carnot's cycle.

The thermal efficiency of the process is

$$\eta = \frac{\Delta W}{\Delta Q_2} = 1 - \frac{\Delta Q_1}{\Delta Q_2}. \quad (1.28)$$

Since the cycle is reversible, it may be also used as a *heat pump*. The efficiency of Carnot's cycle depends only on the temperatures  $T_1$  and  $T_2$  of the heat reservoirs but not on the details of realization.

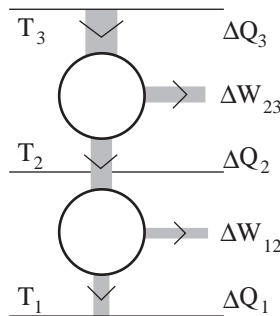


Figure 1-3: Determination of absolute temperature scale.

■ **Absolute temperature.** An absolute temperature scale may be determined with the aid of a serial connection of Carnot's cycles as in Fig. 1–3. The efficiency depends only on the reservoir temperatures, therefore

$$1 - \eta = \frac{\Delta Q_{\text{out}}}{\Delta Q_{\text{in}}} = f(T_{\text{max}}, T_{\text{min}}). \quad (1.29)$$

From relations  $f(T_3, T_2) = \Delta Q_2/\Delta Q_3$ ,  $f(T_2, T_1) = \Delta Q_1/\Delta Q_2$ ,  $f(T_3, T_1) = \Delta Q_1/\Delta Q_3$  the functional identity follows

$$f(T_3, T_2)f(T_2, T_1) = f(T_3, T_1),$$

which has to hold for all  $T_i$ . The simplest choice is

$$f(T_2, T_1) = \frac{T_1}{T_2} \quad (1.30)$$

which defines the thermodynamic (*absolute*) temperature scale up to the choice of the unit. For the efficiency of Carnot's cycle this yields

$$\eta = 1 - \frac{T_{\text{min}}}{T_{\text{max}}}. \quad (1.31)$$

Consider now a cyclic (quasistatic) process divided to a large number of subprocesses with temperatures  $T_i$  and the amount of heat received  $\Delta Q_i$ . Imagine that these portions of heat are transferred by Carnot engines working between the system a huge heat reservoir at the temperature  $T_0 > T_i$ , so that the  $i$ th engine receives the heat  $\Delta Q_{0i}$  from the reservoir. Calculate now the work done in one cycle by the system and all the Carnot engines. In one cycle the work done by the system equals the heat received:

$$W_{\text{system}} = \sum_i \Delta Q_i. \quad (1.32)$$

The work of  $i$ th Carnot engine is  $W_{Ci} = \Delta Q_{0i} - \Delta Q_i$ , so that the total work is equal to the heat received by our combined system from the heat reservoir:

$$W_{\text{total}} = \sum_i \Delta Q_i + \sum_i (\Delta Q_{0i} - \Delta Q_i) \sum_i \Delta Q_{0i} = Q_0 \leq 0, \quad (1.33)$$

which cannot be positive according to Kelvins statement of the second law, since the combined system consisting of the original cycle and the auxiliary Carnot machines did not give any heat to a heat reservoir at a temperature lower than  $T_0$ . Now  $\Delta Q_{0i}/T_0 = \Delta Q_i/T_i$ . Therefore, replacing the sum over subprocesses by a contour integral in the state variable space, we arrive at the *Clausius inequality*

$$\oint \frac{dQ}{T} \leq 0. \quad (1.34)$$

For any reversible process this is an equality, which means that the integrand is a differential of some state variable. This state variable is the entropy  $S$  and

$$\frac{dQ}{T} = dS.$$

If a finite portion of our process is reversible, say from state 1 to state 2, the corresponding part of the contour integral in Clausius's inequality (1.34) yields the difference between the values of entropy in these states:

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T}, \quad (1.35)$$

and Clausius's inequality takes the form

$$\boxed{S_2 - S_1 \geq \int_1^2 \frac{dQ}{T}.} \quad (1.36)$$

In particular, in a thermally isolated system the entropy cannot decrease.

■ The second law seems to be in contradiction with the time-reversal invariance of the basic microscopic laws of physics, since it establishes a preferred direction of processes. The origin of this time-reversal symmetry breaking in macroscopic physics remains unclear.

## 1.10 Third law

The third law thermodynamics, *Nernst's law*, states that the entropy of an equilibrium system vanishes, when the temperature approaches the absolute zero:

$$\boxed{\lim_{T \rightarrow 0} S = 0.} \quad (1.37)$$

In classical thermodynamics the conjecture is that this limit exists, the particular value 0 is explained in quantum statistical physics.

## 1.11 Problems

**Problem 1.1.** Show that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (1.38)$$

and that for any function  $F$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial F}{\partial y}\right)_z}{\left(\frac{\partial F}{\partial x}\right)_z}. \quad (1.39)$$

**Problem 1.2.** Which of the following differential forms are differentials? Find the integrating factor for those differential forms which are not differentials.

- (a)  $\delta u = \left(\frac{x^4}{y}\right) dx + y^2 dy$ .
- (b)  $\delta u = (10x + 6y)dx + 6x dy$ ,
- (c)  $\delta u = 12y^2 dx + 18xy dy$ .

**Problem 1.3.** Define the Legendre  $g(y)$  transform of the function  $f(x)$  as

$$g(y) = f(x) - xy, \quad y = \frac{df}{dx},$$

where on the right-hand side  $x$  is assumed to be expressed as a function of  $y$  from the condition  $y = f'$ .

(a) Show that

$$\left(\frac{d^2 f}{dx^2}\right) \left(\frac{d^2 g}{dy^2}\right) = -1.$$

- (b) Construct the Legendre transform of the function  $f = \frac{1}{2}x^2$ .
- (c) Construct the Legendre transform of the function  $f = -ax \ln x - b$ , where  $a$  and  $b$  are positive constants.

**Problem 1.4.** Thermal expansivity  $\alpha$  and isothermal compressibility  $\kappa$  of matter are defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p; \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T.$$

Show that

$$\left(\frac{\partial \alpha}{\partial p}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_p; \quad \frac{\alpha}{\kappa} = \left(\frac{\partial p}{\partial T}\right)_V.$$

**Problem 1.5.** Calculate the virial coefficients  $B_2$ ,  $B_3$  and  $B_4$  of **Clausius'** matter. Clausius' equation of state is

$$\left[p + \frac{aN^2}{T(V + cN)^2}\right] (V - bN) = NT,$$

where  $a$ ,  $b$  and  $c$  are positive experimental constants and  $N$  the total number of particles. Can you determine all the virial coefficients for this matter?

**Problem 1.6.** Consider a spherical capacitor with external radius  $b$  and internal radius  $a$  charged to an initial charge  $Q$ . The capacitor is half-filled by a dielectric substance of permittivity  $\varepsilon$  in such a way that the dielectric fills the space between the plates to one side of a cross-section plane dividing the spheres in two halves, while to the other side of the plane the capacitor is empty. Express the differential form of work in terms of electric induction  $D$  and electric field  $E$ . Calculate the work exerted on the capacitor, when the charge is increased by an infinitesimal amount  $\delta Q$ . Proceed by subtracting the differential form of work required to increase the charge by  $\delta Q$  from  $Q$  in an *empty* capacitor. Express the result in terms of the polarization vector  $P$ .

**Problem 1.7.** Consider the same capacitor but now with an initial potential difference  $\Delta\phi$  between the plates. Express the differential form of work in terms of electric induction  $D$  and electric field  $E$ . Calculate the work exerted on the capacitor, when the potential difference between the plates is increased by an infinitesimal amount  $\delta\phi$ . Proceed by subtracting the differential form of work required to increase the potential difference by  $\delta\phi$  from  $\Delta\phi$  in an empty capacitor. Express the result in terms of the polarization vector  $P$ .

**Problem 1.8.** Experimentally it has been found that a rubber band obeys:

$$\left(\frac{\partial F}{\partial L}\right)_T = a\frac{T}{L_0} \left[1 + 2\left(\frac{L_0}{L}\right)^3\right], \quad \left(\frac{\partial F}{\partial T}\right)_L = a\frac{L}{L_0} \left[1 - \left(\frac{L_0}{L}\right)^3\right],$$

where  $F$  is the tension and the constant  $a$  and the rest length of the band  $L_0$  are parameters.

- Calculate  $(\partial L/\partial T)_F$  and give a physical interpretation.
- Show that  $dF = \partial_L F dL + \partial_T F dT$  is a differential.
- Determine the equation of state  $F = F(L, T)$  of the band.

**Problem 1.9.** In a perfect gas the internal energy obeys the relation  $dU = C_V dT$ . Find the equation of state for such a gas in a process, in which the heat capacity  $C$  is a constant (polytropic process).

**Problem 1.10.** Stirling's cycle consists of two isotherms at  $T_1$  and  $T_2$  and two isochores (processes with constant volume) at  $V_1$  and  $V_2$ . Calculate the coefficient of thermal efficiency of Stirling's cycle working on the ideal gas. Compare with the thermal efficiency of Carnot's cycle.