THERMODYNAMICS

AN ADVANCED COURSE WITH PROBLEMS AND SOLUTIONS

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PREFACE TO ENGLISH EDITION

The original text of this volume is that of the first four chapters of the book "Problems and Solutions in Thermodynamics and Statistical Mechanics" itself one of the "University Series" published by the Shokabo Publishing Company. Although the last part of the original book was translated first and published as "Statistical Mechanics–An Advanced Course with Problems and Solutions" (North-Holland Publ. Co., 1965), the present volume should be regarded as the first volume of the whole work.

The English title is somewhat different from the original one and it seems to have caused some misunderstanding of the authors' intention of writing this book. This is not the usual type of textbook, but it is aimed primarily to help the student to study the subject by thinking for himself and by working problems by himself. The solutions of the problems, of course, can be used in various ways. The lectures, entitled the fundamental topics, are therefore meant to be as concise as possible to make it convenient for the reader to refer to them repeatedly. Much of the material usually treated in textbooks is included sometimes in disguised form, in the examples or problems. In this respect this book is selfcontained. However, it may be recommended students to use a standard textbook together with the present book.

Most of the translation was done by Dr. Hajime Seki, IBM Laboratory in Yorktown Heights, N. Y. and some parts were done by the original authors. As the editor of the original Japanese edition and of the English edition, I wish to express my deep appreciation to Dr. Seki, and also to Professor Bernard Springer of the University of Southern California and Professor Donald C. Worth of International Christian University, Tokyo, who kindly took the trouble of reading through the manuscript and helping us with linguistic difficulties. My thanks is also due to Mrs. N. Hashitsume and Mrs. M. Suzuki who helped us in preparation of the manuscript.

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PREFACE TO JAPANESE EDITION

Thermodynamics and statistical mechanics are indispensable tools in studying the physics of the properties of matter. Statistical mechanics, together with quantum mechanics, provides a foundation for modern physics which aims at the thorough understanding of physical phenomena from the microscopic viewpoint of atomic physics. Fundamental knowledge and training in statistical mechanics are therefore of vital importance not only for students studying the physical properties of matter but also for those who study nuclear physics or even astrophysics. Outside the realm of physics, its importance is rapidly penetrating into chemistry, biology and into those vast areas of technology which owe their growth to the advances in modern physics.

Thermodynamics belongs completely to classical physics and is sometimes regarded as unimportant by students of physics who are over-occupied in learning modern physics. Even for students in chemistry, the present is different from the time some decades ago when physical chemistry was almost nothing but chemical thermodynamics. However, it must be stressed here that the usefulness and unique significance of thermodynamics as a fundamental science remain as basic today as they were in the latter half of the last century. Thermodynamics teaches us the value of a phenomenological approach. It avoids explicit use of physical images or models such as atoms and molecules. Instead it deals with relations between somewhat abstract quantities such as energy, entropy, free energy and so forth. Admittedly it does not give intuitive pictures as atomic theories do, which is one of the reasons why students find it difficult to gain sufficient understanding and familiarity to use thermodynamics in real problems. But the simplicity of the logic of thermodynamics sometimes makes us see more clearly into the nature of the basic physics of a given problem from very general principles. This is the great advantage of a phenomenological approach.

Obviously, however, it is impossible to explore more deeply the underlying atomic processes in a given physical phenomenon if we confine our attention to thermodynamics. Such progress is made possible only by quantum mechanics and statistical mechanics. Statistical mechanics provides

us with a means to link the physical laws of the microscopic world to those of the macroscopic world. Without close cooperation with statistical mechanics, quantum mechanics itself would not be able to represent the physics of the real world. In these sense, statistical mechanics is indispensable as one of the keystones of modern physics.

Like any other science, statistical mechanics cannot be mastered easily just by learning its principles once. One has to think by oneself a great deal before one grasps the way in which to use the statistical approach in one's thinking, and to apply statistical mechanics to real physical problems. In statistical mechanics and in thermodynamics, there are certain aspects which are quite different from other fields of physics. We often meet students who find difficulty in mastering thermodynamics or statistical mechanics, lacking confidence in applying it to real problems, although they know the principles. Such difficulties are due to insufficient and inadequate training.

The purpose of the present book is to provide a guide for students studying and acquiring facility in thermodynamics and statistical mechanics. Thus it contains fundamental topics, examples and a fairly large number of problems with complete solutions. The fundamental topics are rather condensed, but still they cover all of the points which are basic. This book is meant to be readable without reference to other textbooks. By reading through these topics only, one would be able to obtain fundamental knowledge of thermodynamics and statistical mechanics. The examples are partly to supplement the fundamental topics, but they are primarily meant to show the reader how the principles are applied to physical problems.

The problems are classified into three groups, A, B and C, in order of increasing difficulty. If a reader has enough time he may go through all problems in each chapter. But, if not, it is recommended that he studies first the problems in group A throughout the whole book and then later comes back to try B and C. By just finishing group A problems, he will find himself to have obtained a much better understanding of physics. The number of group A problems is fairly large, so that he may even select about half of these and come back later to the other half. The subjects in the fundamental topics and examples which are marked by $^{+}$ are not needed in solving problems in group A.

In this book†, thermodynamics and statistical mechanical problems are

† The reader is reminded that this text is a translation of the Preface to the original Japanese edition, in which thermodynamics and statistical mechanics are contained in one volume.

mostly limited to those of equilibrium states. It might be desirable to include kinetic methods and extensions of thermodynamics and statistical mechanics which apply to non-equilibrium problems. We had, however, to content ourselves in treating such topics in a limited way only in the last chapter (Chapter 6 of "Statistical Mechanics"). This is because the whole volume had become much larger than the original plan and also because such non-equilibrium problems are certainly somewhat advanced.

As mentioned previously in this preface, quantum mechanics is the fundamental dynamics of the microscopic world. In this sense, statistical mechanics ought to be essentially quantum-statistics. However, since the present book devotes itself to clear understanding of the nature of statistical considerations, only an elementary knowledge of quantum mechanics is required in studying problems in groups A and B. Therefore, even those students who are not specializing in physics but have only an elementary background in quantum mechanics will not find any serious difficulty in starting to study this book.

What is most important in studying a physical problem is to grasp it as a problem in *physics*. Mathematical manipulations may sometimes be tedious and sometimes may require specialized techniques. Training in mathematical methods should not be ignored, but it would be a serious mistake if one was to be dazzled by the mathematics and to forget the physics. Teachers often meet students' papers in which the student seems to be in no doubt about the numerical answers although they are in error by two or three orders of magnitudes or are dimensionally incorrect. Professor H. Nagaoka (a pioneer physicist in Japan) was carrying out calculations on a blackboard in his class. He changed the sign of his answer saying "It is plus rather than minus. Isn't it?" Mathematical calculations may very often be in error. A physical mind is very important, for this can give you the right sign even when your calculation betrays you. An answer obtained by calculation is in many cases easily understood, at least qualitatively. It may not be guessed before making calculations, but one should not forget to think it over again in order to see if one can see some physical meaning contained in it. Such remarks are not given in each solution of the problems, so that we should like to emphasize here the importance of such reasoning.

Here and there between the pages some comments † are inserted under the title "Divertissement". While giving seminars to students we sometimes take a rest to drink a cup of tea and chat. We hope that the reader will spare a few

† These are revised in this English edition.

minutes at these spots to listen to a chat from the authors, drinking tea or coffee or just smoking.

The fundamental topics were mostly written by R. K. Examples and problems were selected after repeated discussion by all the authors. The final check of the solutions was made by R. K. and the whole design of the book was made by N. H. The authors would appreciate it if readers would kindly point out any mistakes which may have escaped our notice.

Five years have passed since this book was originally planned, and two years since we started actually to write it. The undertaking proved to be much more difficult than we anticipated. The authors are particularly grateful to Mr. K. Endo, editor of Shokabo Publishing Company, for his continual encouragement and help.

January, 1961 RYOGO KUBO

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CHAPTER 1

THERMODYNAMIC STATE AND THE FIRST LAW OF THERMODYNAMICS

This chapter deals with the concept of a thermodynamic state and with those concepts related to the first law of thermodynamics. Students of thermodynamics must have a clear understanding of the physical meaning of such concepts. It should be noted, in particular, that work and heat are not functions of state but are quantities which are determined by specifying the process of change.

Fundamental Topics

§ 1.1. THE OBJECTS OF THERMODYNAMICS

Some of the basic concepts and terms used in thermodynamics are listed with explanations. In order to avoid unnecessary confusion, not all the definitions given here have been made rigorous. When necessary, more rigorous definitions are given later.

System: Systems which are the objects of thermodynamics are *macroscopic* entities called systems with extensions in *space* and *time* which are accessible to normal processes of measurements. Such a system may consist of a great number of material particles (e.g. molecules, atoms, electrons, etc.) or of field quantities such as electromagnetic fields. In either case, they are dynamical systems containing an extremely large number of degrees of freedom. Systems composed of only a small number of degrees of freedom are not the object of thermodynamics.

Environment: If part of a whole system is chosen as the object of our observation, the remaining part is its surroundings. The surroundings may be abstracted as an environment which defines certain conditions imposed on the system of interest (such as constant temperature, pressure, chemical potential, etc.).

Isolated system: An independent system which has absolutely *no* interaction with its surroundings is an isolated system.

Closed system: A system which has no *material* exchange with its surroundings is a closed system.

Open system: A system which has interchange of material with its surroundings is an open system.

§ 1.2. THE CONCEPT OF THERMAL EQUILIBRIUM (THE ZEROTH LAW OF THERMODYNAMICS)

The thermal equilibrium state of an isolated system: Regardless of the complexity of its initial state, if an isolated system (e.g. a gas surrounded by a wall impervious to heat) is left standing, the system eventually comes to a final state which does not change. This final state is called the *thermal equilibrium state.* Microscopically the material particles still continue their complex motion, but macroscopically the thermal equilibrium state is a simple state defined by a few parameters such as temperature and pressure.

Thermal equilibrium of two systems: When two isolated systems A and B are brought into contact with one another the total system A+B eventually comes to thermal equilibrium. It is then said that A and B are in thermal equilibrium with each other. The two systems, A and B are themselves also separately in thermal equilibrium. *The equilibrium is not disturbed when the contact between the two is broken and is then restored after some time.* Therefore two systems, A and B, even when they are not in contact with each other, may be said to be in thermal equilibrium with each other ($A \sim B$) if there is no change when they are brought into contact.

The Zeroth law of thermodynamics (transitive law of thermal-equilibrium): If A and B are in thermal equilibrium in the above sense and B and C are also in thermal equilibrium, then A and C are in thermal equilibrium:

$$A \sim B,\ B \sim C \rightarrow A \sim C. \tag{1.1}$$

This empirical law is called the Zeroth law of thermodynamics.

Thermodynamic state or state: In a narrow sense this term is used in the same sense as thermal equilibrium state, but in general a whole system is considered to be in a thermodynamic state if the various parts are in thermal equilibrium, i.e. in *local equilibrium*, even when the system as a whole is not in a thermal equilibrium state. For example, if, in a system composed of two bodies A and B, each part is at a different temperature T_A and T_B, it may be said that the entire system is in a state which is specified by (T_A, T_B).

§ 1.3. THERMODYNAMIC CONTACT

Contacts which allow the following interactions between thermodynamic systems are called thermodynamic contacts.

1. *Mechanical interaction:* When one system does work on another system by means of mechanical or electromagnetic forces, the interaction is called mechanical.

2. *Thermal interaction:* An interaction which results in the exchange of

energy in the form of heat transfer by such means as thermal conduction and thermal radiation is called thermal interaction. A wall which cuts off thermal interaction is called an *adiabatic wall.*

3. *Mass interaction:* An interaction which involves the exchange of matter between two systems is called mass interaction. A semi-permeable membrane is an example.

Idealizations of 2 and 3 are interactions weak enough not to alter the properties of the systems yet strong enough to result in effective contacts during the process of observation.

If the environment is considered as a source which acts on the system under consideration in the way mentioned above, it is called respectively, a *work source*, a *heat reservoir* (heat bath) or a *particle source* (or reservoir). A source or reservoir is considered to be sufficiently larger than the system so that the source itself remains in a given equilibrium state regardless of the effect it exerts on the system through its contact with it.

§ 1.4. THERMODYNAMIC QUANTITIES

State quantities: Physical quantities which have a definite value for each thermal equilibrium state of the system are thermodynamic quantities, or state quantities. Examples: temperature, pressure, internal energy, enthalpy and entropy.

State variables or thermodynamic variables: In a narrow sense these are the thermodynamic quantities described above. In the broader sense of the thermodynamic state they denote the physical quantities which are defined by local equilibrium. If a set of independent variables is properly chosen so as to be necessary and sufficient to define a state, the other state quantities are their functions. The number of independent variables for a thermal equilibrium state of a system is determined empirically.

Intensive quantities and extensive quantities: If a system in a thermal equilibrium state is divided into parts by inserting walls, each part stays in equilibrium. Therefore an equilibrium state of a uniform system is an internal property and is determined by state quantities which are independent of the extension or size of the system. Such quantities are called intensive quantities. Examples: temperature, pressure, chemical potential. On the other hand, state quantities which vary in proportion to the extension or mass of the system, when it is divided without changing the equilibrium state, are called extensive quantities. Examples: mass of components, energy, entropy.

Internal variables and external variables: In some cases, thermodynamic variables are classified into the two categories: internal and external variables.

The external variables define the state of the surroundings. For example, the position of the piston in a cylinder containing a gas, and the strength of an electric field or a magnetic field acting on a system can be thought of as external variables. However, these may be considered as internal variables if the piston or the field sources are included in the system. Thus the distinction depends on where we draw the line between our system and the surroundings in contact with it. This should be made clear in order to avoid confusion, particularly in the case of mechanical contacts.

§ 1.5. PROCESSES OF CHANGE

In treating a change which a system undergoes, just by itself or in contact with other systems, thermodynamics confines itself to those changes for which the initial and the final states are thermodynamic states (not necessarily thermal equilibrium states). However, the intermediate states through which the system passes may or may not be thermodynamic states. In general, they are very complex states. Only when the process is extremely slow the intermediate states will be thermodynamic, and then the process can be described in terms of the change of a sufficient number of thermodynamic quantities.

Cycle: A cycle is a process in which the initial and final states of the system are identical.

Infinitesimal process: A change in which the difference between the initial and the final states is infinitesimally small is called an infinitesimal process.

Quasi-static process: This is an ideal process during which it may be assumed that both the system and its surroundings maintain thermal equilibrium. Such a process is approximately realized by making the change sufficiently slow. For example, to compress a gas the external pressure $p^{(e)}$ is maintained infinitesimally greater than the gas pressure p, while to expand the gas $p^{(e)}$ is maintained infinitesimally less than p (see Fig. 1.1). In the limit these two processes follow the same path in opposite directions. Thus a quasi-static process is *reversible* (cf. § 2.1). The following are the important quasi-static processes:

i) *Quasi-static isothermal process:* In this process the system is in contact with an environment of constant temperature (heat bath) and the process occurs quasi-statically at this temperature.

ii) *Quasi-static adiabatic process:* This is a quasi-static process in which the system has no thermal contact (and no mass contact) with its surroundings but work is done by or on the surroundings.

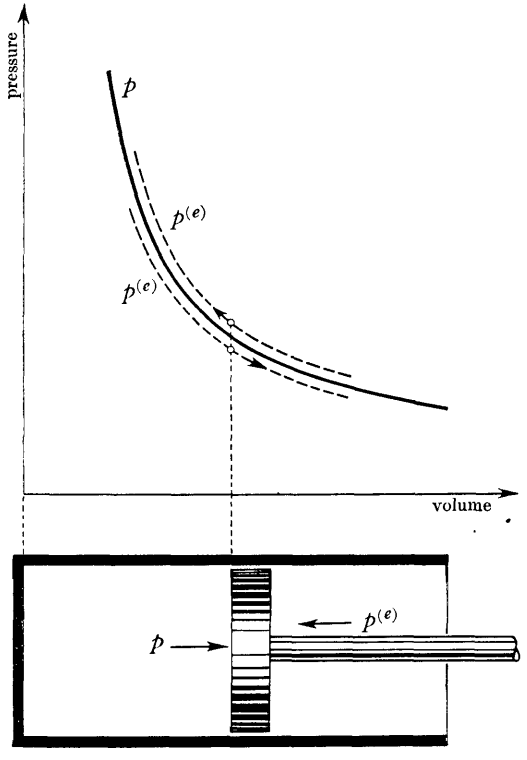

Fig. 1.1.

The quasi-static adiabatic process is sometimes called simply an adiabatic process but since there are irreversible adiabatic processes also it is better to distinguish the two clearly (see § 2.1 for the difference between reversible and irreversible processes).

§ 1.6. THE FIRST LAW OF THERMODYNAMICS

Although the first law of thermodynamics is a particular case of the general law of energy conservation, it implies the existence of the internal energy which is a thermodynamic quantity.

THE FIRST LAW OF THERMODYNAMICS. *When a system changes from an initial state 1 to a final state 2, the sum of the work A, the heat Q, and the mass action quantity Z, which it receives from its surroundings, is determined by the states 1 and 2: it does not depend on the intermediate process.*

This means that there exists an internal quantity U such that its difference

between the states 1 and 2 is given by

$$U_2 - U_1 = A + Q + Z. \tag{1.2}$$

The function U is the internal energy of the system. If the system is characterised by mechanical energies such as the kinetic energy and the potential energy, eq. (1.2) is replaced by

$$E_2 - E_1 = A + Q + Z, \tag{1.2'}$$

where E is the total energy of the system including mechanical energies.

The first law of thermodynamics is the law of conservation of energy. It can be expressed as

$$E_{\text{total}} = \text{constant}$$

if E_{total} is the energy of the entire system including every subsystem participating in the process of change in question. Eq. (1.2) or eq. (1.2′) is written for a subsystem the energy of which changes as the result of energy-transfer to it from other parts of the system (surroundings) through various mechanisms of contact. The work A, the heat Q, and the mass action Z are respectively the amounts of energy transferred through these contacts.

The reader must be familiar with the concepts of work and heat at least from elementary physics. He may be less familiar with that of mass action Z. This represents the amount of energy transferred to the system in a form other than work or heat when a certain mass of matter is transferred from the surroundings. This concept is usually introduced in textbooks of thermodynamics much later when heterogeneous systems are treated. But it is included here for the completeness in stating the first law of thermodynamics.

Perpetuum mobile of the first kind: If a system undergoes a cycle,

$$A + Q + Z = 0. \tag{1.3}$$

Thus the system does work, $-A$, on the surroundings at the expense of $Q+Z$ which it extracts from the surroundings. A perpetuum mobile of the first kind would operate in a cycle which does work on its surroundings without this expense. Therefore, the first law of thermodynamics is also called *the principle of the impossibility of a perpetuum mobile of the first kind.*

Internal energy: The internal energy is the energy within the system, usually excluding the kinetic energy of the system as a whole and the potential energy of the system in an external field (although in some cases the potential energy may be considered as a part of the internal energy). Microscopically, the internal energy is the sum of the molecular kinetic energy and the interaction

energy of the material particles, but thermodynamics usually does not ask its origin. The first law of thermodynamics stresses that the internal energy is a *state quantity*. The additive constant of the internal energy may be fixed by choosing a certain standard state for its zero. Figure 1.2 shows the internal energy of air as a function of temperature and pressure. The point C is the critical point (see example 8).

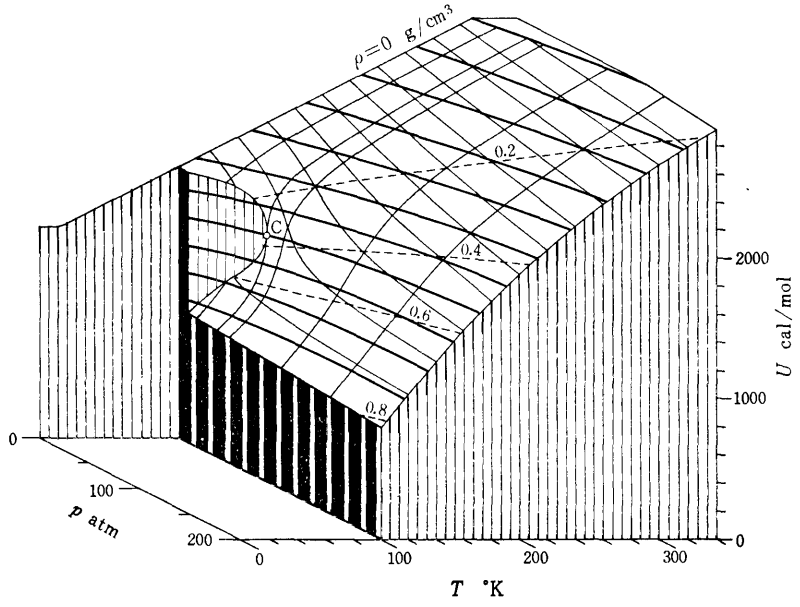

Fig. 1.2. The internal energy of air.

The dependence of work, heat and mass action on the process. Unlike U, each of the quantities A, Q and Z in eqs. (1.2) and (1.2′) depends on the process. For example, the same change $1 \to 2$ may be achieved through a mechanical action or a thermal action, or

$$\begin{aligned} U_2 - U_1 &= A \qquad \text{(Process I)} \\ &= Q \qquad \text{(Process II)}. \end{aligned} \tag{1.4}$$

Hence A, Q and Z are not state quantities nor can they be expressed in terms of the difference of state quantities. The positive statement of the first law is that, nevertheless, the sum $A+Q+Z$ is determined by the difference in state quantities.

DIVERTISSEMENT 1

Founders of the first law of thermodynamics. If a tomb of the Unknown Scientists had been built in the 1850's, the most appropriate inscription would have been "In memory of the grief and sacrifice of those who fought to realize a perpetuum mobile". But the law of conservation of energy, or the first law of thermodynamics, is associated primarily with three great names, Mayer, Helmholtz and Joule.

Julius Robert Mayer (1814–1878) was really a genius who was born in this world only with the errand to make this great declaration. Hermann Ludwig Ferdinand von Helmholtz (1821–1894) gave this law the name "Erhaltung der Kraft" or "the conservation of energy". Like Mayer, he started his career as a medical doctor but lived a glorious life as the greatest physiologist and physicist of the day. James Prescott Joule (1818–1889) worked over forty years to establish the experimental verification of the equivalence of work and heat.

Among the three, Mayer was the first who arrived at this law and the last whose work was recognized. His life was most dramatic. A lightening stroke of genius overtook him, a German doctor of the age of twenty six, one day on the sea near Java when he noticed that venous blood of a patient under surgical operation appeared an unusually fresh red. He considered that this might be connected with Lavoisier's theory of oxidation in animals, which process becomes slower in tropical zones because the rate of heat loss by animals will be slower there. A great generalization of this observation lead him to the idea of the equivalence of heat and mechanical work. For three years after his voyage, while he was working as a medical doctor at home, he devoted himself to complete the first work on the conservation of energy "Bemerkungen über die Kräfte der unbelebten Natur" which was sent to the Poggendorf Annalen and was never published by it. In 1842 Liebig published this paper in his journal (Annalen der Chemie und Pharmacie) but it was ignored for many years.

Mayer wrote four papers before 1851. During these years of unusual activity he cared for nothing other than his theory. In 1852 he became mentally deranged and was hospitalized. He recovered after two years but never returned to science.

§ 1.7. HEAT AND ENTHALPY

If a change $1 \rightarrow 2$ due to thermal action can also occur through a mechanical action (Process I of (1.4)), the heat Q which is introduced by the thermal action (Process II) can be measured in terms of the work A. This is the operational definition of heat, and heat in this sense is measured in units of work. The conventional unit is given by

$$1 \text{ cal} = 4.1840 \text{ joule} \qquad \text{(thermodynamic calorie*)}.$$

* Calorie as a practical unit has various definitions.

The equivalence of heat and work, as indicated by eq. (1.4), means essentially the first law. The experimental determination of the heat equivalent of work was achieved by Joule.

If the change takes place at *constant pressure* (isobaric process), the mechanical work associated with the change ΔV in volume is simply given by $-p\,\Delta V$. If there is no other work done, the first law states that

$$U_2 - U_1 = p(V_1 - V_2) + Q\,.$$

Therefore it is convenient to introduce the function

$$H = U + pV$$

and write

$$H_2 - H_1 = Q\,. \tag{1.4'}$$

The quantity H, introduced here, is called the enthalpy, or the heat function.

§ 1.8. THE FIRST LAW OF THERMODYNAMICS APPLIED TO INFINITESIMAL PROCESSES

For an infinitesimal process, eq. (1.2) can be written as

$$\mathrm{d}U = \mathrm{d}'Q + \mathrm{d}'A + \mathrm{d}'Z\,. \tag{1.5}$$

In particular, if the surroundings consist of a single simple system

$$\mathrm{d}'A = -\,p^{(e)}\,\mathrm{d}V + \sum_i X_i^{(e)}\,\mathrm{d}x_i\,, \tag{1.6a}$$

$$\mathrm{d}'Z = \sum_{j=1}^{c} \mu_j^{(e)}\,\mathrm{d}N_j \qquad \left(= \sum_{j=1}^{c} \bar{G}_j^{(e)}\,\mathrm{d}n_j\right), \tag{1.6b}$$

where $p^{(e)}$ = pressure of the surroundings, V = volume of the system, $X_i^{(e)}$ = i-th type force on the system due to the surroundings, x_i = the coordinate of the system corresponding to the force $X_i^{(e)}$, N_j = the number of molecules or the mole number* of the j-th component in the system, and $\mu_j^{(e)}$ = the chemical potential per molecule or mole of the j-th component in the surroundings. In a quasi-static infinitesimal process, the system is almost in equilibrium with its surroundings and

$$\mathrm{d}'A = -\,p\,\mathrm{d}V + \sum X_i\,\mathrm{d}x_i\,, \tag{1.7a}$$

$$\mathrm{d}'Z = \sum_j \mu_j\,\mathrm{d}N_j\,. \tag{1.7b}$$

* When N_j is the mole number, it is often written as n_j to indicate this and the corresponding chemical potential per mole is written as $\bar{G}_j$ (see § 3.3). Sometimes the mass of component j, M_j, is used instead of the number of molecules or mole number in which case the chemical potential is expressed per gram. In this book the chemical potential is either per molecule or per mole unless otherwise stated.

In the case of a *quasi-static process in general*

$$U_2 - U_1 = \int_1^2 \mathrm{d}'Q - \int_1^2 p\,\mathrm{d}V + \sum_i \int_1^2 X_i\,\mathrm{d}x_i + \sum_j \int_1^2 \mu_j\,\mathrm{d}N_j, \qquad (1.8)$$

where p and μ_j are the pressure and the chemical potential of the system itself, because they are equal to those of the surroundings, since the system is in equilibrium with the surroundings. Similarly the external forces are in equilibrium with the forces exerted by the system on the surroundings so that the superscript e of $X_i^{(e)}$ may be omitted. The integration in eq. (1.8) is along the path of the process.

Notation d′: Since the heat transferred, the mechanical work done and the mass action quantity depend on the process, their infinitesimal values are not exact differentials of state variables. The notation d′ is used to emphasize this point.

Work: In general, the force $X^{(e)}$ which the surroundings exert on the system is defined such that the infinitesimal work done due to a change in the general coordinate x is $X^{(e)}\,\mathrm{d}x$. The expression (1.6a) only indicates this definition. In the case of pressure $X \to -p$. In a quasi-static process, the system and its surroundings are in equilibrium and $p^{(e)} = p$; similarly $X^{(e)} = X$ (internal force).

Mass interaction: In the same way as above, (1.6b) may be considered as the definition of the chemical potential, $\mu_j^{(e)}$, of the j-th component in the surroundings. Although the meaning of the chemical potential may be no clearer here than that $\mu_j^{(e)}$ characterizes the state of the surroundings with respect to the j-th component, it will be used more extensively starting with Chapter 3. In a quasi-static process $\mu_j^{(e)} = \mu_j$.

§ 1.9. TEMPERATURE

The temperature is defined as a quantity which prescribes thermal equilibrium between two bodies in thermal contact. If θ_1 and θ_2 are the temperatures of the two bodies, $\theta_1 = \theta_2$ is the condition for thermal equilibrium, and if $\theta_1 > \theta_2$, θ_1 decreases while θ_2 increases when they are brought into thermal contact. Obviously, when $\theta_1 = \theta_2$ and $\theta_2 = \theta_3$, then $\theta_1 = \theta_3$, satisfying condition (1.1). Conversely, the concept of temperature is based on (1.1) (c.f. problem 23).

Although the choice of a temperature scale at this point is arbitrary, its absolute choice will be established with the introduction of the second law of thermodynamics. Anticipating this, the absolute temperature scale or the centigrade temperature scale will be used hereafter.

The absolute temperature will be denoted by T. As an *empirical* temperature scale it is possible to use the gas *thermometer*. An arbitrary temperature scale θ can be converted into T (°K, Kelvin) by

$$\frac{T}{T_0} = \lim_{p \to 0} \frac{(pV)_\theta}{(pV)_{\theta_0}}, \qquad T_{\text{triple point of water}} = 273.16\,^\circ\text{K} \tag{1.9}$$

(cf. Chapter 2, problem 37). The centigrade temperature scale is defined by

$$0\,^\circ\text{C} = 273.15\,^\circ\text{K}.$$

§ 1.10. HEAT CAPACITY, SPECIFIC HEAT

If a quantity of heat $\mathrm{d}'Q$ is introduced quasi-statically into a system by a process which, maintaining a quantity x constant, raises the temperature by $\mathrm{d}T$, the quantity C_x, defined by

$$C_x = \frac{\mathrm{d}'Q}{\mathrm{d}T}, \tag{1.10}$$

is the *heat capacity* of the system for this process. The heat capacity per unit mass of the material is its *specific heat*. The heat capacity for a mole is called the *molar heat* or *molecular heat*.

Since $\mathrm{d}'Q$ depends on the process it becomes a quantity of state only when the process (or when x) is specified. Examples: *heat capacity at constant pressure* (isobaric heat capacity), C_p, specific heat at constant pressure (isobaric specific heat), c_p, *heat capacity at constant volume* (isovolumic or *isochoric* heat capacity), C_V, specific heat at constant volume (isovolumic specific heat), c_V. It is possible to formally define C_{ad} $(=0)$ for an adiabatic process and $C_{\text{isoth.}}$ $(=\infty)$ for an isothermal processes.

Divertissement 2

Why do we have winter heating?

The layman will answer: "To make the room warmer." The student of thermodynamics will perhaps so express it: "To import the lacking (inner, thermal) energy." If so, then the layman's answer is right, the scientist's wrong.

We suppose, to correspond to the actual state of affairs, that the pressure of the air in a room always equals that of the external air. In the usual notation, the (inner, thermal) energy is, per unit mass,

$$u = c_v T.$$

(An additive constant may be neglected.) Then the energy content is, per unit of volume,

$$u^1 = c_v \rho T,$$

or, taking into account the equation of state,

$$p/\rho = RT,$$

we have

$$u^1 = c_v p/R.$$

For air at atmospheric pressure,

$$u^1 = 0.0604 \text{ cal/cm}^3.$$

The energy content of the room is thus independent of the temperature, solely determined by the state of the barometer. The whole of the energy imported by the heating escapes through the pores of the walls of the room to the outside air.

I fetch a bottle of claret from the cold cellar and put it to be tempered in the warm room. It becomes warmer, but the increased energy content is not borrowed from the air of the room but is brought in from outside.

Then why do we have heating? For the same reason that life on the earth needs the radiation of the sun. But this does not exist on the incident energy, for the latter apart from a negligible amount is re-radiated, just as a man, in spite of continual absorption of nourishment, maintains a constant body-weight. Our conditions of existence require a determinate degree of temperature, and for the maintenance of this there is needed not addition of energy but addition of entropy.

As a student, I read with advantage a small book by F. Wald entitled "The Mistress of the World and her Shadow". These meant energy and entropy. In the course of advancing knowledge the two seem to me to have exchanged places. In the huge manufactory of natural processes, the principle of entropy occupies the position of manager, for it dictates the manner and method of the whole business, whilst the principle of energy merely does the bookkeeping, balancing credits and debits.

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Zurich.

The above is a note published in Nature **141** (1938) 908. A. Sommerfeld found it so interesting that he cited it in his book *Thermodynamik und Statistik* (Vorlesungen über theoretische Physik, Bd. 5, Dietrich'sche Verlag, Wiesbaden; English translation by F. Kestin, Academic Press Inc., New York, 1956). R. Emden is known by his work in astrophysics and meteorology as represented by an article in der Enzyklopädie der mathematischen Wissenschaften *Thermodynamik der Himmelskörper* (Teubner, Leipzig-Berlin, 1926).

§ 1.11. EQUATION OF STATE

The existence of an equation of state: The thermal equilibrium state of a system is usually defined uniquely by specifying the values of a few state variables. For instance, the thermal equilibrium state of a fluid such as a

simple gas or liquid is determined by only two variables, the pressure p and the specific volume v (sometimes we may have more variables; for instance, if the fluid is put in an external electric field or in a magnetic field, the field quantities, E or H, are also variables on which the state of the fluid may depend). This fact, combined with the zeroth law of thermodynamics (1.1), shows that a functional relationship exists between the temperature θ (on an arbitrarily scale), and the state variables (see problem 23). If the latter are p and v, such a relation can be written as

$$\theta = f(p, v),$$

which is the equation of state. Similarly it may be shown, for a more general system, that there exists a functional relationship between temperature and a necessary and sufficient number of variables (other than temperature), i.e. that there exists an equation of state. However, thermodynamics does not say anything about its functional form except that it must satisfy certain stability conditions (see § 3.8). Equations of state are determined empirically or for a given system theoretically by statistical mechanics, so that in the framework of thermodynamics they are regarded as something given in order to specify the system.

The equation of state of an ideal gas: The general form is $pV = g(\theta)$, but, if the temperature scale of the gas thermometer is used (it can be shown by the second law of thermodynamics that this agrees with the absolute temperature scale, see § 2.5), it is written as

$$pV = nRT = NkT, \tag{1.11}$$

where n is the mole number, N is the number of molecules, R the gas constant and k is the Boltzmann constant:

$$R = 8.314 \times 10^7 \text{ erg mol}^{-1} \text{ deg}^{-1} = 1.9872 \text{ cal mol}^{-1} \text{ deg}^{-1},$$
$$k = 1.3803 \times 10^{-16} \text{ erg deg}^{-1} = 8.616 \times 10^{-5} \text{ eV deg}^{-1}.$$

Any real gas becomes ideal in the limit of high temperatures or low densities. It can be shown from the second law of thermodynamics that the internal energy of an ideal gas is independent of the volume, V (cf. Chapter 2, problem 2):

$$(\partial U/\partial V)_T = 0, \qquad U = U(T). \tag{1.12a}$$

The form of $U(T)$ is determined empirically or theoretically by statistical mechanics. In the normal range of temperature

$$U = nC_V^0 T \tag{1.12b}$$

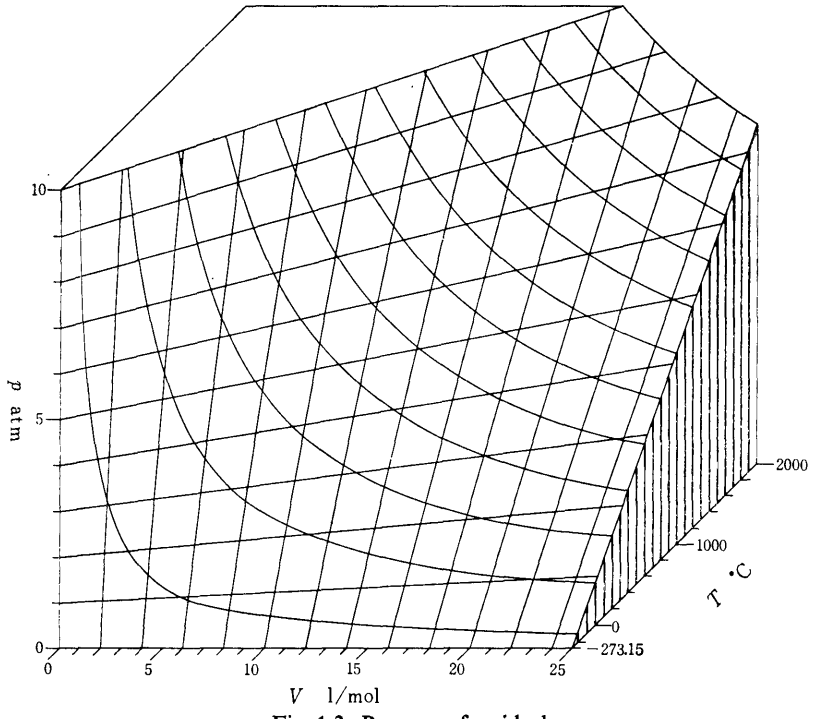


Fig. 1.3. Pressure of an ideal gas.

is a good approximation for most pure gases, so that the specific heat is constant. For those temperatures, the isovolumic molar specific heat, C_V^0 is

$$\left.\begin{aligned} C_V^0 &= \tfrac{3}{2}R && \text{(monatomic gas)} \\ &= \tfrac{5}{2}R && \text{(diatomic gas)} \\ &= 3R && \text{(polyatomic gas)}. \end{aligned}\right\} \tag{1.13}$$

Mixture of ideal gases: A mixture of r species of ideal gases, consisting of n_i moles of the i-th gas ($i = 1, 2, \ldots, r$), obeys the equation of state

$$pV = nRT, \qquad n = \sum_i n_i. \tag{1.14}$$

Corresponding to (1.12), the equation

$$U = \sum n_i C_{Vi}^0 T \tag{1.15}$$

usually holds for the normal range of temperatures.

The partial pressure p_i of the i-th component is defined by

$$p_i V = n_i RT \tag{1.16}$$

and therefore

$$p = \sum p_i .$$

The ideal gas law applies to real gases as a limiting law: it is a good approximation when the pressure is sufficiently low and the temperature sufficiently high. For higher pressures (higher densities) and lower temperatures, deviations from the ideal gas law become more noticeable. Figures 1.4 and 1.5 illustrate this for argon. In fact even liquefaction starts when a dense gas is cooled down. There are a number of equations of states to describe dense gases, of which we mention here only the following two.

The Van der Waals equation of state is given by

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT , \tag{1.17}$$

where $v = V/n$ is the molar volume of the gas. Because of its simple analytical form, it is often used as an approximation for real gases. The constants a and b for various gases are given in Table 1.1.

Table 1.1

Gas	a (atm cm^6/mol^2)	b (cm^3/mol)
He	0.03415×10^6	23.71
Ne	0.2120×10^6	17.10
H_2	0.2446×10^6	26.61
A	1.301×10^6	30.22
N_2	1.346×10^6	38.52
O_2	1.361×10^6	32.58
CO	1.486×10^6	39.87
CO_2	3.959×10^6	42.69
N_2O	3.788×10^6	44.18
H_2O	5.468×10^6	30.52
Cl_2	6.501×10^6	56.26
SO_2	6.707×10^6	56.39

(P. S. Epstein, Textbook of thermodynamics, John Wiley & Sons, New York 1937)

Virial expansion (Kamerlingh-Onnes' equation of state): A practical expansion for real gases has the form

$$pv = RT\left\{1 + \frac{A_2}{v} + \frac{A_3}{v^2} + \cdots\right\} \tag{1.18}$$

or

$$pv = RT\,\{1 + B_2 p + B_3 p^2 + \cdots\}, \tag{1.19}$$

where $A_2, A_3, \ldots$, or $B_2, B_3, \ldots$ are functions of temperature and are called *virial coefficients.*

Ideal paramagnet and the Curie law: The magnetization M of a magnetic body is a function of the external field H, and the temperature T. If the equation of state is simply

$$M = f(H/T), \qquad (f(0) = 0) \tag{1.20}$$

the material is said to be an ideal paramagnet. In particular, when H/T is

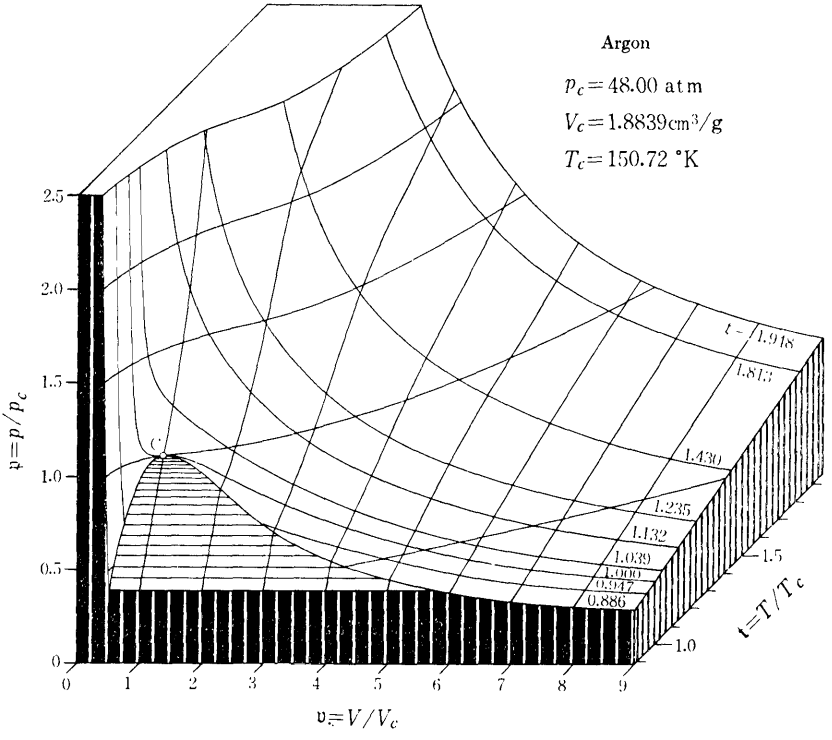


Fig. 1.4. A relief of the equation of state of argon.

small, eq. (1.20) is approximated by

$$M = CH/T \tag{1.21}$$

which is the Curie law, C being the Curie constant. Non-metallic crystals containing paramagnetic metal ions often obey this law. However, this ideal law is bound to break down as the temperature approaches the absolute zero (see Chapter 3, problem 26).

§ 1.12. CHANGE OF INDEPENDENT VARIABLES

Sometimes, in a thermodynamic treatment, p and V are considered to be the independent variables and at other times T and V are so considered. Hence, just writing $\partial U/\partial V$ does not indicate which variables are chosen as independent. To clarify this, the other variables which are kept constant in partial differentiation are indicated by subscripts, e.g.,

$$(\partial U/\partial V)_p, \qquad (\partial U/\partial V)_T.$$

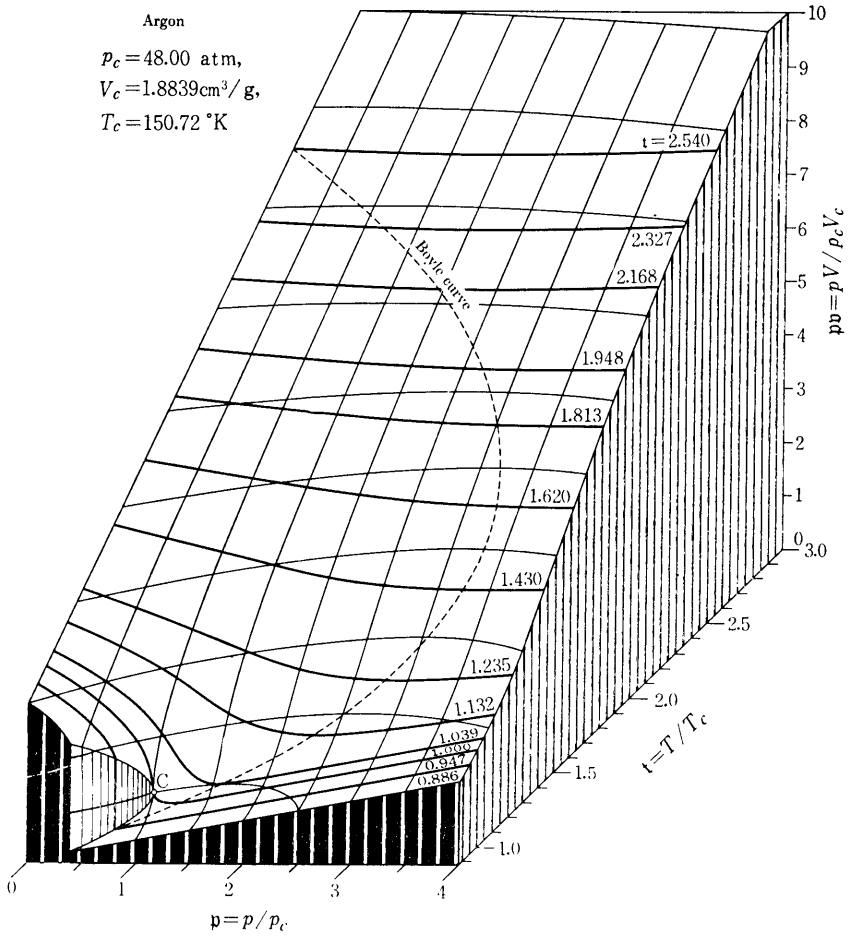


Fig. 1.5. A relief of the pV-surface of argon.

Some of the thermodynamic relations are simply relations between partial derivatives with different choices of independent variables, and are obtained by a change of independent variables.

The following identity is particularly useful: when three variables x, y and z have a functional dependence, it is possible to consider z as a function of x and y, or x as a function of y and z, or y as a function of z and x. Then we have

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1\,, \tag{1.22}$$

or

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \Big/ \left(\frac{\partial z}{\partial x}\right)_y . \tag{1.23}$$

This follows immediately from

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y . \tag{1.24}$$

If $z = \text{const.}$, $\mathrm{d}z = 0$ and the ratio $\mathrm{d}x : \mathrm{d}y = (\partial x/\partial y)_z$ must be (1.23).

Examples

1. A magnetic body is inserted in a coil and is magnetized by the magnetic field created by a current through the coil. For the sake of simplicity, assume that the field, $\boldsymbol{H}$, and the magnetization, $\boldsymbol{M}$, are uniform throughout the magnetic body. Show that the work done by the electric source in the process of magnetization is

$$A = \int_0^M \boldsymbol{H} \cdot \mathrm{d}\boldsymbol{M}$$

per unit volume of the magnetic body. Assume that the magnetic body has no deformation by magnetization.

SOLUTION

Let us consider the case where a coil is wound around a sufficiently long cylindrical magnetic body. The magnetic field in a coil with n turns per unit length is $H_J = 4\pi nJ/c$ when a current J is passed through the coil. The field H inside the magnetic material is the sum of H_J and the demagnetizing field H_M, which, however, is small if the specimen is a long needle. Therefore we may assume here $H = H_J$. If the coil is wound over the entire length of the cylinder, whose length is l and cross-sectional area is σ, the flux through the coil is $\Phi = \sigma nlB = VnB$, where $V = \sigma l$ is the volume of the magnetic body and $B = H + 4\pi M$ is the flux density in the magnetic body. When the current J is increased, then H and M, and accordingly B, also change so that a counter-electromotive force $-(1/c)\,\mathrm{d}\Phi/\mathrm{d}t = -V(n/c)\,\mathrm{d}B/\mathrm{d}t$ is induced, according to Faraday's induction law. The work which the electric source must do against this counter-electromotive force in a time interval $\mathrm{d}t$ as a charge

$$J\,\mathrm{d}t = \tfrac{1}{4}cH_J\,\mathrm{d}t/\pi n$$

passes through each section of the wire, is

$$(1/c)\,(\mathrm{d}\Phi/\mathrm{d}t)\,J\,\mathrm{d}t = \tfrac{1}{4}VH\,\mathrm{d}B/\pi = \tfrac{1}{4}V\,(H\,\mathrm{d}H + 4\pi H\,\mathrm{d}M)/\pi$$
$$= \mathrm{d}\left[\tfrac{1}{8}VH^2/\pi\right] + VH\,\mathrm{d}M\,.$$

Of this work, $\mathrm{d}[\frac{1}{8}VH^2/\pi]$ is the work which is needed to create a field H irrespective of the presence of the magnetic body. Thus, the work $H\,\mathrm{d}M$ can be identified with the work per unit volume required to increase the magnetization, M, by $\mathrm{d}M$. Hence, $A = \int_0^M H\mathrm{d}M$ is the work per unit volume required

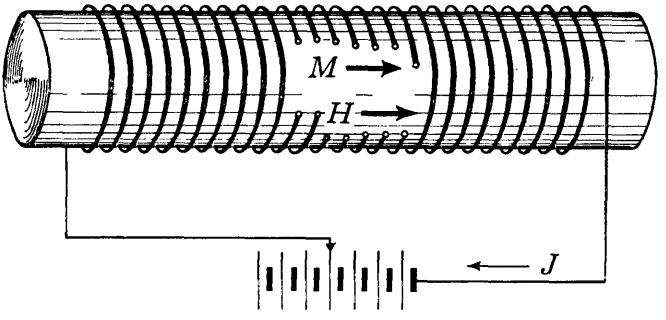


Fig. 1.6

to increase the magnetization from 0 to M. (If it were possible to fix the final value of magnetization at M, then the work $\frac{1}{8}VH^2/\pi$ would be fed back to the electric source in the process of decreasing H to zero, because then we would have $\mathrm{d}B = \mathrm{d}H$.)

2. Let $\mathrm{d}'q$ be the heat necessary to change the temperature of a gram of a material by $\mathrm{d}T$ keeping the state quantity x constant. For the sake of simplicity, assume that there are only two independent variables, e.g. the specific volume, v, and the temperature, T. Show that the specific heat c_x is given by the equation

$$c_x = \left(\frac{\mathrm{d}'q}{\mathrm{d}T}\right)_x = \left(\frac{\partial u}{\partial T}\right)_v + \left\{\left(\frac{\partial u}{\partial v}\right)_T + p\right\}\left(\frac{\partial v}{\partial T}\right)_x$$

where u is the internal energy per unit mass and p is the pressure.

SOLUTION

Since the mass of the system is constant, we need only consider the work done by the pressure. From eqs. (1.5) and (1.7a), the first law of thermodynamics applied to unit mass is $\mathrm{d}'q = \mathrm{d}u + p\,\mathrm{d}v$. The change $\mathrm{d}u$ in u due to changes

$\mathrm{d}T$ and $\mathrm{d}v$ in T and v is $\mathrm{d}u = (\partial u/\partial T)_v\,\mathrm{d}T + (\partial u/\partial v)_T\,\mathrm{d}v$. Substituting this into the equation for $\mathrm{d}'q$, we have

$$\mathrm{d}'q = \left(\frac{\partial u}{\partial T}\right)_v \mathrm{d}T + \left\{\left(\frac{\partial u}{\partial v}\right)_T + p\right\}\mathrm{d}v. \tag{1}$$

Although the parameter x is given as a function of T and v for equilibrium states, it is possible to consider v as a function of T and x taking T and x as the independent variables. Thus if x is kept constant and T is changed, $\mathrm{d}v = (\partial v/\partial T)_x\,\mathrm{d}T$. Substituting this into (1) and dividing by $\mathrm{d}T$ we obtain the answer.

3. Show that there is a relation

$$C_p = C_V + R \qquad \text{(Mayer's relation)}$$

between the isobaric and the isovolumic specific heats per mole of an ideal gas.

$$\left(\frac{d'q}{dT}\right)_p = \left(\frac{d'q}{dT}\right)_v + R.$$

SOLUTION

The first law of thermodynamics for an infinitesimal quasi-static process of a mole of gas is

$$\mathrm{d}'Q = \mathrm{d}U + p\,\mathrm{d}V$$

((1.5), (1.7a)). Since the internal energy U of an ideal gas does not depend on the volume, V, we have $\mathrm{d}U = C_V(T)\,\mathrm{d}T$ and

$$\mathrm{d}'Q = C_V(T)\,\mathrm{d}T + p\,\mathrm{d}V. \tag{1}$$

The isovolumic specific heat $(\mathrm{d}'Q/\mathrm{d}T)_V$ is in fact C_V. We rewrite eq. (1) as

$$\mathrm{d}'Q = C_V\,\mathrm{d}T + \mathrm{d}(pV) - V\,\mathrm{d}p \tag{2}$$

and substitute $pV = RT$ to obtain

$$\mathrm{d}'Q = (C_V + R)\,\mathrm{d}T - V\,\mathrm{d}p, \tag{3}$$

or

$$C_p = (\mathrm{d}'Q/\mathrm{d}T)_{\mathrm{d}p=0} = C_V + R.$$

4. Given the density of air at NTP (normal temperature and pressure, that is, 0 °C, 1 atm), $\rho = 0.00129$ g/cm^3, the specific heat at constant pressure, $c_p = 0.238$ cal/g deg, and its ratio to the isovolumic specific heat, $\gamma = c_p/c_V = 1.41$, calculate the work equivalent of heat J. Assume air to be an ideal gas with a volume of 22.4 l at NTP.

SOLUTION

The gas constant, R, may be obtained in units of joule/mol deg from the ideal gas equation of state $pV=RT$. It can also be obtained in units of cal/mol deg from Mayer's equation $C_p-C_V=R$ (example 3) and if we express that by R', then $J=R/R'$. The normal state (NTP) is an equilibrium state where the temperature, $T=0\ °C=273\ °K$, and the pressure, $p=1$ atm$=1.013\times10^6$ dyne/cm^2. The volume of a mole at NTP is $V=22.4\times10^3$ cm^3. Hence:

$$R = pV/T = 1.013 \times 10^6 \times 22.4 \times 10^3/273 = 8.32 \times 10^7 \text{ erg/mol deg}$$
$$= 8.32 \text{ joule/mol deg}.$$

Since the isobaric specific heat per unit mass is the isobaric heat capacity per mole divided by the mass of a mole of air (average molecular weight), m, which is

$$m = \rho V = 0.00129 \times 22.4 \times 10^3 = 28.9 \text{ g/mol},$$

we have

$$C_p = mc_p = 28.9 \times 0.238 = 6.88 \text{ cal/mol deg}.$$

The isovolumic specific heat per mole $C_V=mc_V=mc_p/\gamma=C_p/\gamma=6.88/1.41=4.88$ cal/mol deg. Therefore we have

$$R' = C_p - C_V = 2.00 \text{ cal/mol deg}$$

and

$$J = R/R' = 8.32/2.00 = 4.16 \text{ joule/cal}.$$

5. (i) Calculate the heat necessary to heat air which has a volume of 27m^3 at one atmosphere from 0 °C to 20 °C at constant volume.

(ii) How much heat is necessary if the initial volume at 0 °C is 27m^3 and the air is heated to 20 °C at constant pressure?

(iii) If the air is in an insulated room of 27m^3 with a small leaking hole connected to the outside at 1 atm, how much heat must be put into the room to raise the temperature slowly from 0 °C to 20 °C? Refer to example 4 for the characteristics of air. Consider the specific heat to be constant.

SOLUTION

(i) This is a case of isovolumic heating. The mass M of air which has a volume of 27m^3 at 0 °C and 1 atm is calculated from its density, $\rho=0.00129$ g/cm^3, as

$$M = 0.00129 \times 27 \times 10^6 = 3.48 \times 10^4 \text{ g}.$$

The isovolumic heat capacity C_V is calculated from the isovolumic specific heat

$$c_V = c_p/\gamma = 0.238/1.41 = 0.169 \text{ cal/g deg},$$
$$C_V = Mc_V = 0.169 \times 3.48 \times 10^4 = 5.88 \times 10^3 \text{ cal/deg}.$$

Considering the heat capacity as constant, the heat Q_V, necessary to raise the temperature from T_1 to T_2 is

$$Q_V = \int_{T_1}^{T_2} C_V \, dT = (T_2 - T_1) C_V = 20 \times 5.88 \times 10^3 = 1.176 \times 10^5 \text{ cal}.$$

(ii) In the case of isobaric heating we use the isobaric heat capacity C_p instead of C_V:

$$C_p = Mc_p = \gamma C_V = 1.41 \times 5.88 \times 10^3 = 8.29 \times 10^3 \text{ cal/deg}.$$

Then the desired heat Q_p is

$$Q_p = (T_2 - T_1) C_p = 20 \times 8.29 \times 10^3 = 1.658 \times 10^5 \text{ cal}.$$

(iii) We may assume that the pressure in the room is maintained at 1 atm since the heating is slow. When the air is heated at constant pressure, p, and constant volume, V, the mass of the air, $M(T)$, in the room at temperature T can be determined from the equation of state $pV = RTM/m$ (m is the average molecular weight of air), or $M(T)T = \text{const}$. If the mass of the air in the room is M_1 when the temperature is T_1, then $M(T) = M_1 T_1/T$. Since the air of mass $M(T)$ is being heated at constant pressure, its heat capacity is $M(T)c_p$, so that the heat required to raise the temperature to T_2 is

$$Q = \int_{T_1}^{T_2} M(T) \, c_p \, dT = c_p M_1 T_1 \int_{T_1}^{T_2} \frac{dT}{T} = c_p M_1 T_1 \log \frac{T_2}{T_1}.$$

Since $T_1 = 0$ °C $= 273$ °K, $T_2 = 20$ °C $= 293$ °K and $C_p = 8.29 \times 10^3$ cal/deg as calculated above, so

$$Q = 8.29 \times 10^3 \times 273 \times \log \frac{293}{273} = 2.26 \times 10^6 \times 0.0706 = 1.596 \times 10^5 \text{ cal}.$$

6. Show that the relation $pV^\gamma = \text{const.}$ (Poisson's equation) holds in a quasi-static adiabatic process of an ideal gas and derive the work W which the gas does to its surroundings in a quasi-static adiabatic process from (p_1, V_1, T_1) to (p_2, V_2, T_2). Assume the specific heat to be constant.

SOLUTION

The equation for the first law in the case of a quasi-static process of an ideal gas is $d'Q = C_V\, dT + p\, dV$ (eq. (1) of example 3). Substituting the equation of state, the adiabatic condition $d'Q = 0$ can be written as

$$C_V\, dT + nRT(dV/V) = 0. \tag{1}$$

Using Mayer's relation (example 3), $C_p = C_V + nR$ (for n moles) and integrating eq. (1) we have $C_V \log T + (C_p - C_V) \log V = \text{const.}$, which, as $C_p/C_V = \gamma$, becomes

$$TV^{\gamma-1} = \text{const}. \tag{2a}$$

and, if we use the equation of state,

$$pV^{\gamma} = \text{const}. \tag{2b}$$

(We can also get $dp/p + dV/V = dT/T$ from $pV = nRT$ and, eliminating dT/T with eq. (1), $dp/p + \gamma dV/V = 0$ which gives (2b).)

When the volume is changed from V_1 to V_2 along the adiabatic line, the work, W, done by the gas is

$$W = -A = \int_{V_1}^{V_2} p\, dV = \int_{V_1}^{V_2} p_1 V_1^{\gamma} \frac{dV}{V^{\gamma}} \qquad (\text{as } pV^{\gamma} = p_1 V_1^{\gamma})$$

$$= \frac{p_1 V_1^{\gamma}}{\gamma - 1}(V_1^{1-\gamma} - V_2^{1-\gamma}) = \frac{1}{\gamma - 1}(p_1 V_1 - p_2 V_2) \tag{3}$$

$$= \frac{nR}{\gamma - 1}(T_1 - T_2) = C_V(T_1 - T_2) \quad (\text{as } C_V(\gamma - 1) = C_p - C_V = nR). \tag{4}$$

In the case of an adiabatic expansion ($V_2 > V_1$), $T_1 > T_2$. The gas does work while the internal energy decreases, so that the temperature naturally decreases (cf. Chapter 3, example 5).

7. Show that the following relation exists between the adiabatic compressibility $\kappa_{\text{ad}} = -(1/v)(\partial v/\partial p)_{\text{ad}}$ and the isothermal compressibility $\kappa_T = -(1/v)(\partial v/\partial p)_T$:

$$\kappa_{\text{ad}} = \frac{c_v}{c_p}\kappa_T,$$

where c_v and c_p are the specific heats at constant volume and constant pressure respectively.

SOLUTION

When we say adiabatic or isothermal compressibility, we of course mean the compressibility for quasi-static adiabatic compression or quasi-static isothermal compression. If we consider the internal energy u to be a function of p and v (we are considering unit mass of material), the condition for adiabatic process, $\mathrm{d}u+p\,\mathrm{d}v=0$, becomes

$$\left(\frac{\partial u}{\partial p}\right)_v \mathrm{d}p + \left\{\left(\frac{\partial u}{\partial v}\right)_p + p\right\}\mathrm{d}v = 0.$$

Therefore

$$\left(\frac{\partial p}{\partial v}\right)_{\mathrm{ad}} = -\left\{p + \left(\frac{\partial u}{\partial v}\right)_p\right\}\Big/\left(\frac{\partial u}{\partial p}\right)_v. \tag{1}$$

If we write $u=u\{T(p, v), v\}$, we have

$$\left(\frac{\partial u}{\partial p}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v\left(\frac{\partial T}{\partial p}\right)_v = c_v\left(\frac{\partial T}{\partial p}\right)_v, \tag{2}$$

and if we write $u=u\{T(p, v), p\}$, we have

$$\left(\frac{\partial u}{\partial v}\right)_p = \left(\frac{\partial u}{\partial T}\right)_p\left(\frac{\partial T}{\partial v}\right)_p,$$

which gives

$$\left(\frac{\partial u}{\partial v}\right)_p + p = \left[\left(\frac{\partial u}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p\right]\left(\frac{\partial T}{\partial v}\right)_p = c_p\left(\frac{\partial T}{\partial v}\right)_p, \tag{3}$$

where we have used the relation, $c_p=(\partial u/\partial T)_p+p(\partial v/\partial T)_p$. Substituting eqs. (2) and (3) in eq. (1) gives

$$\left(\frac{\partial p}{\partial v}\right)_{\mathrm{ad}} = -\frac{c_p\,(\partial T/\partial v)_p}{c_v\,(\partial T/\partial p)_v}. \tag{4}$$

Now using the relation, $(\partial p/\partial v)_T=-(\partial T/\partial v)_p/(\partial T/\partial p)_v$, which is obtained from

$$\mathrm{d}T = \left(\frac{\partial T}{\partial v}\right)_p \mathrm{d}v + \left(\frac{\partial T}{\partial p}\right)_v \mathrm{d}p$$

(an application of (1.23)), we get

$$\left(\frac{\partial p}{\partial v}\right)_{\mathrm{ad}} = \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T, \tag{5}$$

from which the relation which was to be proved follows immediately. (Alternative solution: see Chapter 2, problem 14.)

NOTE: Since $c_p/c_v > 1$, eq. (5) means that $(\partial p/\partial v)_{ad} > (\partial p/\partial v)_T$, i.e. at any point (p, v) in the p-v plane the slope is greater for the adiabatic line than for the isothermal line.

8. Determine the pressure, p_c, the volume, V_c, and the temperature, T_c, at the critical point for a gas which obeys the van der Waals equation of state,

$$\left(p + \frac{an^2}{V^2}\right)(V - bn) = nRT,$$

where n is the mole number and $a > 0$, $b > 0$. Rewrite the equation in terms of the reduced variables, $\mathfrak{p} = p/p_c$, $\mathfrak{v} = V/V_c$, and $\mathfrak{t} = T/T_c$, expressed in units of p_c, V_c, and T_c, respectively. Using this "corresponding state" expression, plot the isothermal lines in the $\mathfrak{p}$-$\mathfrak{v}$ plane and also the curves for $(\partial\mathfrak{p}/\partial\mathfrak{v})_{\mathfrak{t}} = 0$ and $(\partial(\mathfrak{p}\mathfrak{v})/\partial\mathfrak{p})_{\mathfrak{t}} = 0$ (the latter is the Boyle curve).
NOTE: When the van der Waals equation is plotted in the p-V plane for constant T, at sufficiently low temperatures the curve has a maximum and a minimum while it becomes monotonic at high temperatures as can be seen in Fig. 1.7. The critical state (critical point) is the point where $(\partial p/\partial v)_T = 0$ on the $T = T_c$ curve.

SOLUTION

Write the equation of state in the form

$$p = \frac{nRT}{V - bn} - \frac{an^2}{V^2}. \tag{1}$$

Then $(\partial p/\partial V)_T = 0$ and $(\partial^2 p/\partial V^2)_T = 0$ gives

$$RT/(V - bn)^2 = 2an/V^3, \tag{2}$$

and

$$RT/(V - bn)^3 = 3an/V^4. \tag{3}$$

So we have $V - bn = 2V/3$ or $V = 3bn$, and $RT = 8a/27b$. Substituting this in (1) gives $p = a/27b^2$. These are the values of p, V and T at the critical point, i.e.

$$p_c = \frac{1}{27}\frac{a}{b^2}, \qquad V_c = 3nb, \qquad T_c = \frac{8}{27}\frac{a}{Rb}. \tag{4}$$

Now substitute $p = p_c\mathfrak{p}$, $V = V_c\mathfrak{v}$, and $T = T_c\mathfrak{t}$ in (1) and divide by p_c. Then

$$\mathfrak{p} = \frac{nRT_c\mathfrak{t}}{p_cV_c\mathfrak{v} - p_cbn} - \frac{an^2}{p_cV_c^2\mathfrak{v}^2}.$$

Substitute eq. (4) and we have the desired expression,

$$\mathfrak{p} = \frac{8\mathfrak{t}}{3\mathfrak{v} - 1} - \frac{3}{\mathfrak{v}^2},$$

or

$$\left(\mathfrak{p} + \frac{3}{\mathfrak{v}^2}\right)(3\mathfrak{v} - 1) = 8\mathfrak{t}. \tag{5}$$

Written in this form the material constants, a and b, do not appear explicitly. Thus all gases (which obey the van der Waals equation) may be considered to be in the same state when the values of $\mathfrak{p}$, $\mathfrak{v}$ and $\mathfrak{t}$ are the same (i.e. each gas is measured in units of its particular values of V_c, T_c, p_c). This is the law of corresponding states.

In plotting the $\mathfrak{t}=$const. curves in a $\mathfrak{p}$-$\mathfrak{v}$ plane, note the following points. Firstly, the regions of negative pressure, i.e. $\mathfrak{v}<\frac{1}{3}$ and $\mathfrak{p}<-3/\mathfrak{v}^2$, need not be considered. When $\mathfrak{v}\gg\frac{1}{3}$ and $\mathfrak{v}\gg 9/(8\mathfrak{t})$, then eq. (5) gives $\mathfrak{p}\mathfrak{v}\approx\frac{8}{3}\mathfrak{t}$: the gas behaves like an ideal gas when $\mathfrak{v}$ is large. As $\mathfrak{v}$ approaches $\frac{1}{3}$, $\mathfrak{p}$ becomes infinite. For a given $\mathfrak{v}$ there is one value of $\mathfrak{p}$, but, for a given $\mathfrak{p}$ there are either one or three real values of $\mathfrak{v}$. In the case where there are three values of $\mathfrak{v}$, let them be $\mathfrak{v}_D \leqq \mathfrak{v}_E \leqq \mathfrak{v}_F$. Looking at the derivative,

$$(\partial\mathfrak{p}/\partial\mathfrak{v})_\mathfrak{t} = -24\mathfrak{t}/(3\mathfrak{v} - 1)^2 + 6/\mathfrak{v}^3 \tag{5'}$$

obtained from eq. (5), we see that the first term on the right-hand side of (5′) is larger than the second one when $\mathfrak{v}\approx\frac{1}{3}$ and $\mathfrak{v}\to+\infty$ so that there we have $(\partial\mathfrak{p}/\partial\mathfrak{v})_\mathfrak{t}<0$. Therefore $(\partial\mathfrak{p}/\partial\mathfrak{v})_\mathfrak{t}<0$ when $\mathfrak{v}=\mathfrak{v}_D$ and $\mathfrak{v}=\mathfrak{v}_F$, and $(\partial\mathfrak{p}/\partial\mathfrak{v})_\mathfrak{t}>0$ when $\mathfrak{v}=\mathfrak{v}_E$. Since eq. (5) is the difference of two monotonic continuous functions, the isothermal curve has a minimum between $\mathfrak{v}_D$ and $\mathfrak{v}_E$ and a maximum between $\mathfrak{v}_E$ and $\mathfrak{v}_F$. Let the abscissae of these extrema be $\mathfrak{v}_G$ and $\mathfrak{v}_H$, which are determined by $(\partial\mathfrak{p}/\partial\mathfrak{v})_\mathfrak{t}=0$ or

$$4\mathfrak{t} = (3\mathfrak{v} - 1)^2/\mathfrak{v}^3. \tag{6}$$

The corresponding values of $\mathfrak{p}$, $\mathfrak{p}_G$ and $\mathfrak{p}_H$, can be obtained by substituting $\mathfrak{v}_G$ and $\mathfrak{v}_H$ in eq. (5). As $\mathfrak{t}$ is changed, the maximum point $(\mathfrak{v}_H, \mathfrak{p}_H)$ and the minimum point $(\mathfrak{v}_G, \mathfrak{p}_G)$ describe curves in the $\mathfrak{p}$-$\mathfrak{v}$ plane. The equations for these curves are obtained by eliminating the parameter $\mathfrak{t}$ from eqs. (5) and (6), or

$$\mathfrak{p} = (3\mathfrak{v} - 2)/\mathfrak{v}^3. \tag{7}$$

The curve is simple, $\mathfrak{p}=-27$ when $\mathfrak{v}=\frac{1}{3}$, $\mathfrak{p}=0$ when $\mathfrak{v}=\frac{2}{3}$, and $\mathfrak{p}\to 3/\mathfrak{v}^2$ when $\mathfrak{v}\to+\infty$. It has a maximum at $\mathfrak{v}=1$, $\mathfrak{p}=1$ (critical point) and an inflection point at $\mathfrak{v}=\frac{4}{3}$ and $\mathfrak{p}=\frac{27}{32}$. The curve JGCHK in Fig. 1.7 illustrates

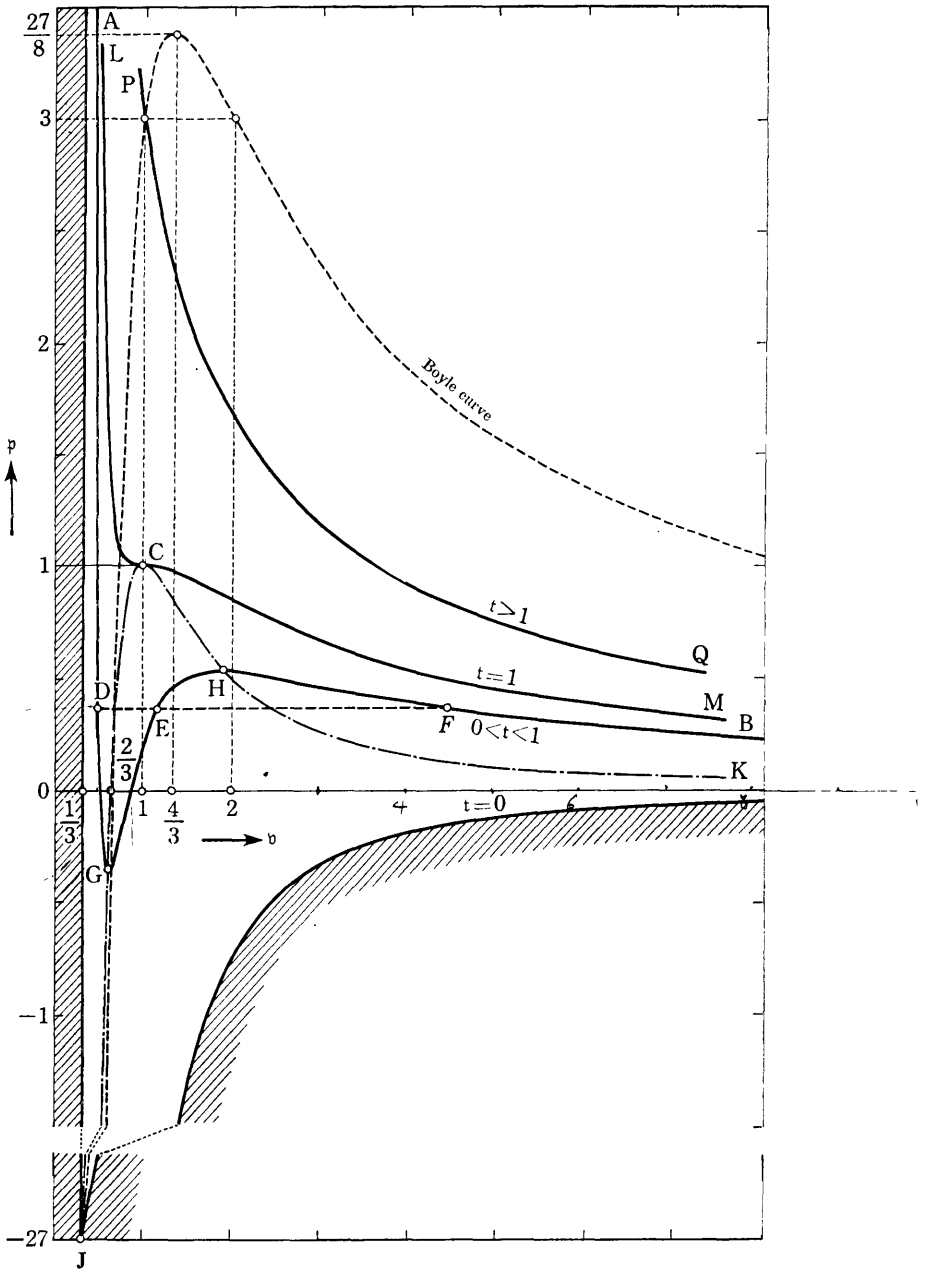

27/8
3
2
1
0
−1
−27
p
v
A
L
P
C
D
E
H
F
G
J
Q
M
B
K
Boyle curve
t>1
t=1
0<t<1
t=0
1/3
2/3
1
4/3
2
4
6
8

Fig. 1.7

this. The intercepts of eqs. (5) and (7) are the minima, G, and the maxima, H, of the curve, (5). The isothermal curve of eq. (5) for $\mathfrak{t}=1$ passes through the maximum, C ($\mathfrak{v}=1$, $\mathfrak{p}=1$) of eq. (7) and on this isothermal curve G and H coincide at C, becoming an inflection point, which is the critical point. If we consider that eq. (5) for a given $\mathfrak{v}$, $\mathfrak{p}$ is a monotonically increasing function of $\mathfrak{t}$, then for $\mathfrak{t}>1$, eqs. (5) and (7) do not intersect. The isothermal curves have maxima and minima when $0<\mathfrak{t}<1$. These considerations show that the isothermal curves have the form ADGEHFB for $0<\mathfrak{t}<1$, LCM for $\mathfrak{t}=1$, and PQ for $\mathfrak{t}>1$ as shown in Fig. 1.7.

Finally let us determine the Boyle curve. From eq. (5) we obtain

$$\left(\frac{\partial(\mathfrak{p}\mathfrak{v})}{\partial\mathfrak{v}}\right)_{\mathfrak{t}}=\frac{3}{\mathfrak{v}^2}-\frac{8\mathfrak{t}}{(3\mathfrak{v}-1)^2},$$

So, for $(\partial(\mathfrak{p}\mathfrak{v})/\partial\mathfrak{v})_{\mathfrak{t}}=0$ we have

$$8\mathfrak{t}=3(3\mathfrak{v}-1)^2/\mathfrak{v}^2.$$

Substituting this in eq. (5) and eliminating $\mathfrak{t}$, we have

$$\mathfrak{p}=3(3\mathfrak{v}-2)/\mathfrak{v}^2. \tag{8}$$

This curve passes through the points ($\mathfrak{v}=\frac{1}{3}$, $\mathfrak{p}=-27$), ($\mathfrak{v}=\frac{2}{3}$, $\mathfrak{p}=0$), and ($\mathfrak{v}=1$, $\mathfrak{p}=3$). It has a maximum at ($\mathfrak{v}=\frac{4}{3}$, $\mathfrak{p}=\frac{27}{8}$) and $\mathfrak{p}\to 9/\mathfrak{v}$ as $\mathfrak{v}\to\infty$. The point of inflection lies at ($\mathfrak{v}=2$, $\mathfrak{p}=3$). Fig. 1.8 shows the relief of the van der Waals diagram.

NOTE: The isothermal curve has parts where $\mathfrak{p}<0$ when $0<\mathfrak{t}<1$ and this part is either metastable ($(\partial\mathfrak{p}/\partial\mathfrak{v})_{\mathfrak{t}}<0$) or unstable ($(\partial\mathfrak{p}/\partial\mathfrak{v})_{\mathfrak{t}}>0$). The equilibrium of the gas phase ($\mathfrak{p}>0$) and the liquid phase is determined by Maxwell's rule (see Chapter 4), so that $\mathfrak{p}$ must be positive in a stable thermal equilibrium state.

9. In the Joule-Thomson porous plug experiment, gas at pressure p_1 is slowly forced through a porous (cotton) plug into a region of pressure p_2 (the plug prevents the gas from acquiring kinetic energy) as shown in Fig. 1.9. When a gas of volume V_1 is forced into a volume V_2, show that the enthalpy, $H=U+pV$, is conserved in this process and that the change of temperature T_1-T_2 is determined by this condition.

SOLUTION

Initially the piston P_2 is in contact with the plug S and the gas is introduced between the plug and the piston P_1 where the volume is V_1, the pressure p_1

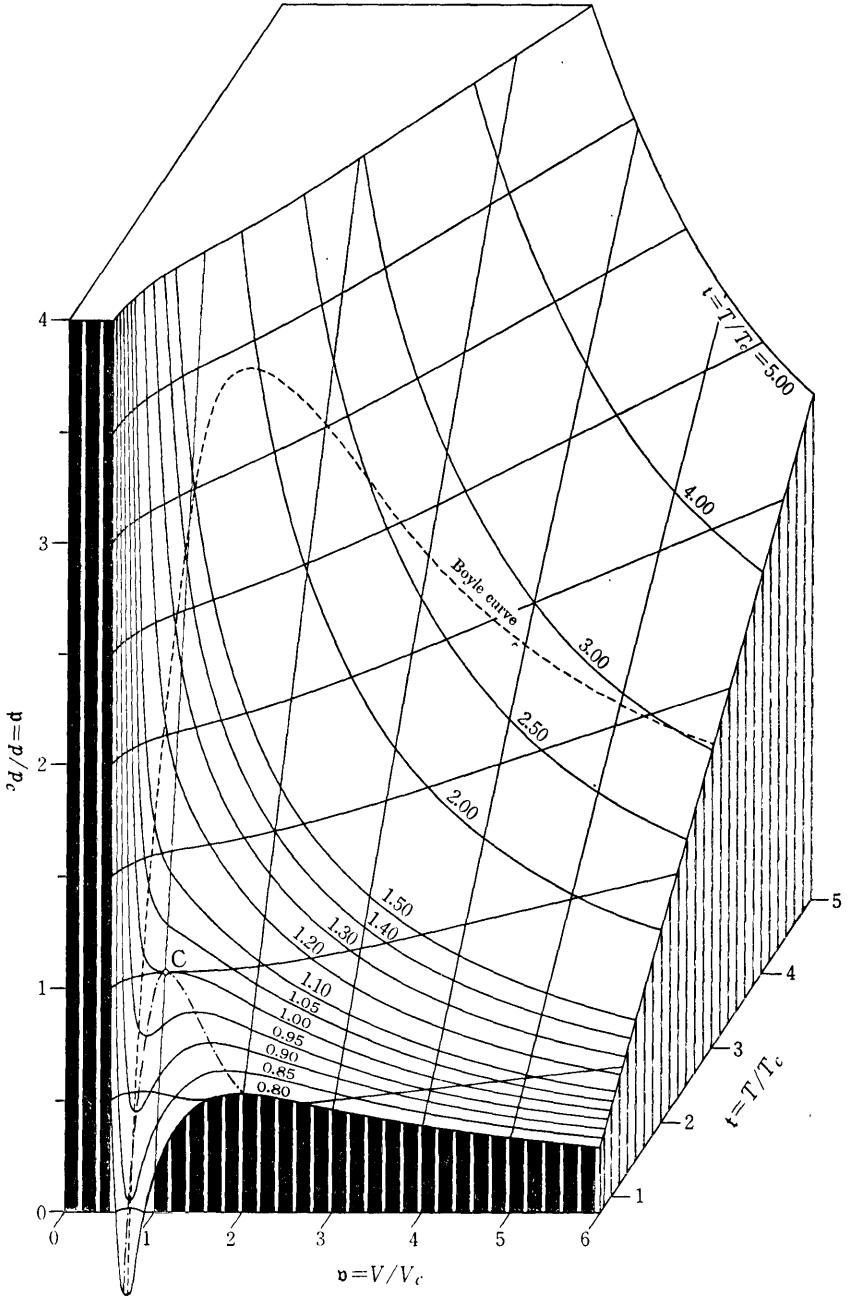

$t=T/T_c=5.00$
4.00
3.00
2.50
2.00
1.50
1.40
1.30
1.20
1.10
1.05
1.00
0.95
0.90
0.85
0.80
Boyle curve
C
p/p_c
$v=V/V_c$
$t=T/T_c$
0
1
2
3
4
5
6

Fig. 1.8

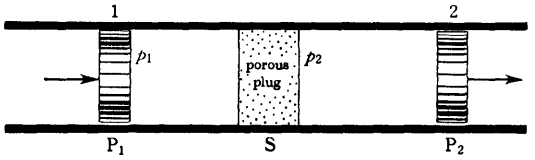


Fig. 1.9

and the temperature T_1. Then the piston P_1 is slowly pushed while maintaining its pressure at p_1 until P_1 comes into contact with S and P_2 is pushed down so that the volume between S and P_2 is V_2. The total work done by the pistons is

$$A = -\int_{V_1}^{0} p_1 \, dV - \int_{0}^{V_2} p_2 \, dV = p_1 V_1 - p_2 V_2 .$$

From the first law

$$U(p_2, V_2) - U(p_1, V_1) = p_1 V_1 - p_2 V_2 ,$$

$$U_1 + p_1 V_1 = U_2 + p_2 V_2 , \qquad \text{or} \qquad H(p_1, V_1) = H(p_2, V_2) . \tag{1}$$

Therefore, if the enthalpy H is considered as a function of p and T for a given mass of gas, eq. (1) can be written as

$$H(p_1, T_1) = H(p_2, T_2) . \tag{2}$$

This determines T_2 when p_1, T_1, and p_2 are given.

Problems

[A]

1. When the equation of state is given in the form $p = p(T, V)$, show that the following relation holds:

$$p\alpha_p = k\alpha_V ,$$

where $\alpha_p = (\partial p/\partial T)_V/p$ is the thermal coefficient of the pressure at constant volume, $\alpha_V = (\partial V/\partial T)_p/V$ the thermal expansion coefficient at constant pressure, and $k = -V(\partial p/\partial V)_T$ is the isothermal bulk modulus.

2. For small changes dp, dV and dT of the pressure, p, the volume, V, and temperature, T, in a quasistatic process show that

$$dp = k(-dV/V + \alpha_V \, dT) .$$

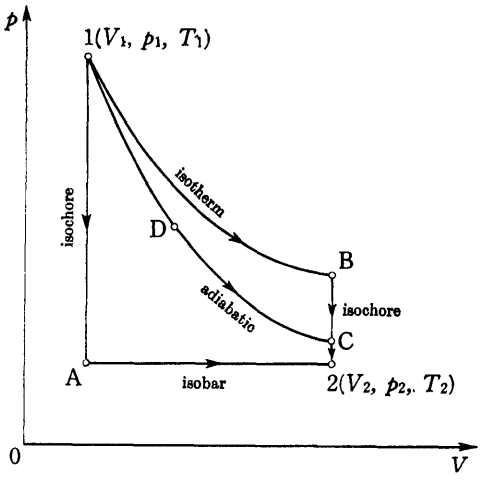
3. At NTP, oxygen has a specific heat at constant pressure, $c_p = 0.2203$ cal/deg g, and a specific heat at constant volume, $c_V = 0.1578$ cal/deg g. Considering oxygen as an ideal gas, calculate the work equivalent of heat.

4. A mole of an ideal gas is expanded quasi-statically at a constant temperature of 20 °C from an initial pressure of 20 atm to 1 atm. What is the work done by the gas in joule? How much heat in calories must be supplied to the gas?

5. Derive the compressibility (adiabatic compressibility), κ_{ad}, when an ideal gas is quasi-statically and adiabatically compressed. The velocity of sound is given by $c = \sqrt{dp/d\rho}$ (ρ is the density). Consider this as a derivative for an adiabatic change and calculate the sound velocity through air at 1 atm, 0 °C, and the change of velocity with temperature.

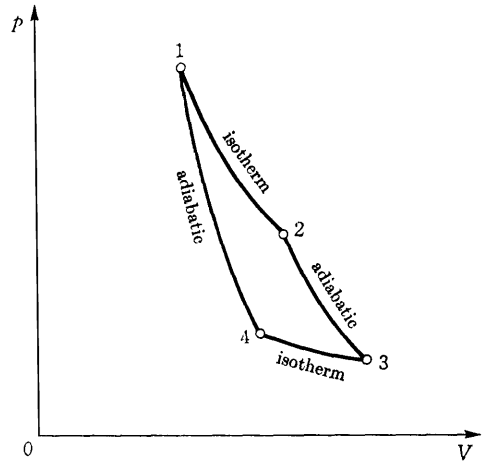
6. An ideal gas is changed from a state (p_1, V_1, T_1) to a state (p_2, V_2, T_2) by a quasi-static adiabatic process. Show that, if the heat equivalent of the work done by the gas in this process is added to the gas in the final state while maintaining the volume constant, the temperature will return to T_1.

7. An ideal gas is changed from an initial state (p_1, V_1, T_1) to a final state (p_2, V_2, T_2) by the following three quasi-static processes as seen in the figure: (i) 1A2, (ii) 1B2, and (iii) 1DC2. What is the increase in the internal energy for $1 \to 2$? Also obtain the work that must be done to the system and the heat that must be added in each process. Assume that the specific heat is constant.



8. Assuming that when air rises it undergoes an adiabatic quasi-static expansion as of an ideal gas, determine the change in temperature with height. What is the decrease in temperature at a height of 1 km?

9. Consider the quasi-static and cyclic process of an ideal gas (the Carnot cycle) shown in the figure. The change from 1 to 2 is an isothermal expansion in contact with a heat bath at temperature T_1, that from 2 to 3 an adiabatic expansion, that from 3 to 4 an isothermal compression in contact with



a heat bath at temperature T_2, and finally that from 4 to 1 an adiabatic compression. If the heat absorbed from the heat bath at T_1 is Q_1 and the heat absorbed from the heat bath at T_2 is Q_2, show that

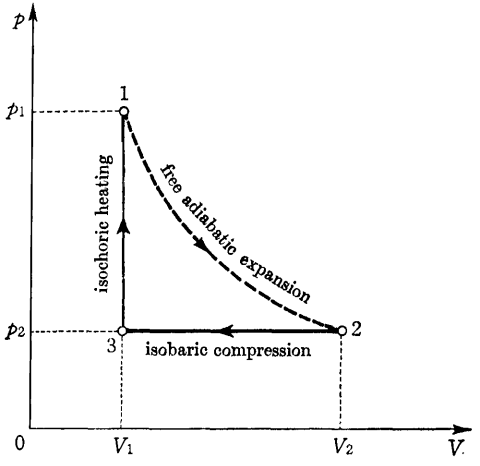
$$Q_1/T_1 + Q_2/T_2 = 0. \qquad \text{(Clausius equation)}$$

Assume the specific heat to be constant.

10. If the specific heat of an ideal gas for a process where x is kept constant is c_x, show that $pv^f = \text{const.}$ for this process, where f is equal to $(c_x - c_p)/(c_x - c_v)$, p is the pressure, v is the specific volume, and c_p and c_v are the (constant) specific heats at constant pressure and constant volume.

11. A mole of an ideal gas with pressure, p_1, and volume, V_1, is freely (and adiabatically) expanded to V_2. Then it is quasi-statically compressed to a

volume V_1 while maintaining the pressure at p_2. Finally the gas is heated quasi-statically until the pressure returns to p_1 while the volume remains V_1. This cycle is called Mayer's cycle. Prove Mayer's relation (see example 35) using this cycle. Assume that the molar specific heat is constant.



12. Consider a gas which obeys the Dieterici equation of state

$$p = \frac{nRT}{V - nb} \exp\left(-\frac{na}{RTV}\right),$$

where p is the pressure, V the volume, T the absolute temperature, n the mole number, R the gas constant, and a and b are material constants. Show that the pressure, volume, and temperature at the critical point are

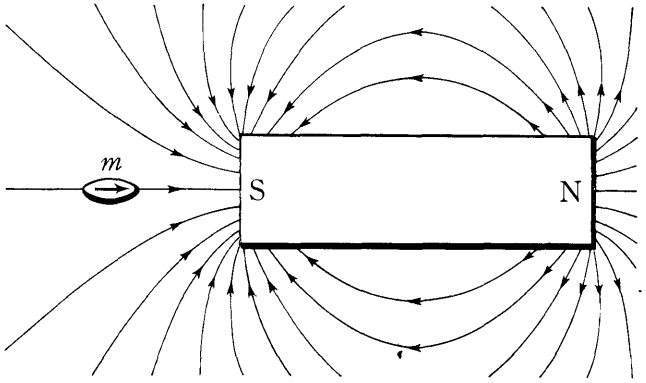
$$p_c = \frac{a}{4e^2b^2}, \quad V_c = 2nb, \quad T_c = \frac{a}{4Rb},$$

and rewrite the equation of state in a form which shows the law of corresponding states.

13. Calculate the specific heat at constant volume of air by assuming it to be a mixture of oxygen, O_2, and nitrogen, N_2, with a mass ratio of 23:77. The specific heat at constant volume of gaseous oxygen is 0.158 cal/g deg and that of gaseous nitrogen is 0.176 cal/g deg.

[B]

14. A small iron needle, which is initially unmagnetized, is magnetized by bringing it slowly from infinity into the magnetic field of a permanent bar magnet. As shown in the figure, the direction of the needle is kept parallel to the axis of the bar magnet. Assuming that the strength of the bar magnet is



unchanged by the presence of the needle, and that the volume of the needle is unchanged by this process, show that the work done in order to magnetize the needle to a magnetic moment m_1 is given by

$$A = \int_0^{m_1} H \, \mathrm{d}m,$$

where H is the field at the position where the needle has the magnetic moment m.

15. Consider a vertical column of air infinitely high with a constant cross-section. Calculate the heat capacity, assuming the air to be an ideal gas in a constant gravitational field.

16. Consider a closed system for which any two of the pressure, p, the volume, V, and the temperature, T, may be chosen as the independent variables to define a thermodynamic equilibrium state. Denoting the internal energy by U and the enthalpy by $H = U + pV$, prove the following:

(i) The specific heat at constant volume $C_V = (\partial U/\partial T)_V$ and the specific heat at constant pressure $C_p = (\partial H/\partial T)_p$;

(ii) $$C_p - C_V = \left(\frac{\partial V}{\partial T}\right)_p \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} = -\left(\frac{\partial p}{\partial T}\right)_V \left\{p\left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial U}{\partial p}\right)_T\right\};$$

(iii) $$\left(\frac{\partial H}{\partial p}\right)_T - V = \left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T;$$

(iv) $$(C_p - C_V)\frac{\partial^2 T}{\partial p \partial V} + \left(\frac{\partial C_p}{\partial p}\right)_V \left(\frac{\partial T}{\partial V}\right)_p - \left(\frac{\partial C_V}{\partial V}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = 1.$$

NOTE: Since the left side of (iv) consists of measurable quantities, the first law of thermodynamics may be confirmed by checking this relation experimentally.

17. If c is the speed of sound $c = \sqrt{(\partial p/\partial \rho)_{\text{ad}}}$ (where p is the pressure and ρ is the density and the partial derivative is for an adiabatic process) and γ the ratio of the specific heats at constant pressure and at constant volume, show that the internal energy, u, and the enthalpy, h, per unit mass of an ideal gas with a constant specific heat may be expressed by the following expressions:

$$u = \frac{c^2}{\gamma(\gamma - 1)} + \text{const.}, \qquad h = \frac{c^2}{\gamma - 1} + \text{const.}$$

18. If the internal energy is U and the magnetic moment is I, show that the specific heat of a uniform magnetic material in a process where the magnetic field H is constant can be expressed as follows

$$C_H = \left(\frac{\partial U}{\partial T}\right)_H - H\left(\frac{\partial I}{\partial T}\right)_H,$$

where T is the absolute temperature of the magnetic material. The change in volume due to magnetization may be considered negligible.

19. If the heat capacity for constant magnetization of a uniform material is denoted by C_M and the heat capacity by C_H for a constant magnetic field, show that the following relation exists between the isothermal magnetic susceptibility and the adiabatic magnetic susceptibility:

$$\chi_{\text{ad}} = \frac{C_M}{C_H}\chi_T.$$

The change in volume of the material may be neglected.

20. Discuss a Carnot cycle using thermal radiation as its working material. The internal energy density, u, of the radiation is given by the Stefan-Boltzmann law, $u=\sigma T^4$, where T is the absolute temperature [$\sigma(>0)$ is a constant], and the radiation pressure, p, is given by the equation of state $p=\frac{1}{3}u$.

DIVERTISSEMENT 3

Nicolas Leonard Sadi Carnot. In the first half of the last century, the steam engine, completed by introduction of the condenser (the low-temperature heat reservoir), due to James Watt (1765) had come to produce more and more revolutionary effects on developments in industry and transportation. Many eminent physicists like Laplace and Poisson set about to study the Motive Power of Fire. Sadi Carnot (1796–1832) was a son of Lazare Carnot, Organizer of Victory in the French Revolution, and was born and died in Paris. He probably learned the caloric theory of heat, in which heat was assumed to be a substance capable either of flowing from body to body (heat conduction) or of making chemical compound with atoms (latent heat). He wrote a short but very important book, *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* (Paris, 1824), which was reprinted by his brother (1878) together with some of Carnot's posthumous manuscripts.

Carnot directed his attention to the point that, in the heat engine, work was done *not* at the expense of heat but in connection with the transfer of heat from a hot body to a cold body, and thus heat could not be used without a cold body, in analogy of water falling from a high reservoir to a low reservoir. In his book he assumed the law of conversation of heat, namely that the quantity of heat was a state function, although he later abandoned this law and arrived at the law of equivalence of heat and work: he actually proposed many methods to estimate the mechanical equivalent of heat. He introduced what came to be known as Carnot's cycle, and established Carnot's principle.

Carnot's book had been overlooked until B. P. E. Clapeyron (1834) gave Carnot's theory an analytical and graphical expression by making use of the indicator diagram devised by Watt. The law of conservation of heat assumed by Carnot was corrected by R. Clausius (1850), based on the work of J. R. von Mayer (1841) and J. P. Joule (1843–49), into the form that not only a change in the distribution of heat but also a consumption of heat proportional to the work done is necessary to do work, and vice versa. Clausius named this modification the First Law of Thermodynamics. H. L. F. von Helmholtz (1847) and Clausius generalized this law to the principle of the conservation of energy. W. Thomson (Lord Kelvin), who introduced Kelvin's scale of temperature (1848) based on Carnot's work, also recognized the law of equivalence of heat and work. The Second Law of Thermodynamics was formulated by Thomson (1851) and Clausius (1867).

A sketch of the history of early thermodynamics is given by E. Mendoza,

Physics Today **14** (1961) No. 2, p. 32. See also E. Mach: *Principien der Wärmelehre* (vierte Aufl. 1923, Verlag von Johann Ambrosius Barth, Leipzig).

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21. Neglecting internal friction (viscosity) and thermal conductivity, show that the sum of the enthalpy density and the kinetic energy density is conserved in the steady flow of a fluid. Assume that there are no external forces such as a gravitational field.

22. Obtain the final temperature and the upper limit of the flow velocity in steady-state flow when steam superheated to 300 °C at 5 atm is flowing out through a suitable nozzle into the air at 1 atm. Assume that superheated steam is an ideal gas with a specific heat at constant pressure $c_p = 0.49$ cal/g deg, and a specific heat ratio $\gamma = 1.33$. Thermal conductivity and gravitation may be neglected.

23. Consider systems A, B, C, ... whose thermal equilibrium states are determined by the pressure, p, and the specific volume, v. Show that according to the zeroth law of thermodynamics there exists a function characteristic of each system such that $\theta_A = f_A(p, v), \ldots$, and that the condition for thermal equilibrium between two systems (e.g. A and B) is that the values of these functions are equal (i.e., $\theta_A = \theta_B$) (Theorem of existence of temperature). Use the empirical fact that there exists a functional relation between the independent parameters of the two systems in equilibrium.

24. Generalize the problem of example 1 considering the effect of the demagnetizing field in the case where the magnetic field, H, the magnetization, M, and the magnetic flux density, B, are not uniform. (Start from Maxwell's equations.)

Solutions

1. The relation between the differentials, $\mathrm{d}p$, $\mathrm{d}T$ and $\mathrm{d}V$, of p, T and V are obtained from the equation of state as

$$\mathrm{d}p = (\partial p/\partial T)_V \, \mathrm{d}T + (\partial p/\partial V)_T \, \mathrm{d}V .$$

By definition we have

$$\mathrm{d}p = p\alpha_p \, \mathrm{d}T - k(\mathrm{d}V/V) .$$

The ratio of dV and dT when $p=$ const. is obtained by letting $dp=0$, or

$$(\partial V/\partial T)_p = Vp\alpha_p/k\,, \qquad \text{and therefore } k\alpha_V = p\alpha_p\,.$$

2. From the results of the previous solution we have

$$dp = k\alpha_V\,dT - k(dV/V) = k\{\alpha_V\,dT - (dV/V)\}\,.$$

3. As in the case of example 4 the ratio of the gas constants calculated from the equation of state and by Mayer's relation will give the answer. The molecular weight of oxygen is 32 and $m=32$ g/mol. Under standard conditions the volume of 1 mole of gas is 22.4 l, so the volume of 1 gram of oxygen under standard conditions is

$$V = 22.4 \times 10^3/32 = 700\ \text{cm}^3\,.$$

Since 1 atm $=1.013\times 10^6$ dyne/cm^2, for $p=1$ atm and $T=273$ °K,

$$\begin{aligned} R/m = pV/T &= 1.013 \times 10^6 \times 700/273 \\ &= 2.60 \times 10^6\ \text{erg/g deg} = 0.260\ \text{joule/g deg}\,. \end{aligned}$$

From the difference in specific heats we get

$$R/m = c_p - c_V = 0.2203 - 0.1578 = 0.0625\ \text{cal/g deg}\,.$$

Therefore the work equivalent is given by

$$J = 0.260/0.0625 = 4.16\ \text{joule/cal}\,.$$

4. If the volume of 1 mole of an ideal gas is V, the work done by the gas is given by (1.7a) as $-d'A=p\,dV$. Since it is a quasi-static process, the pressure p is given by the equation of state $pV=RT$. The work done by the gas at an absolute temperature, T, when the volume expands from V_1 to V_2 is

$$-A = \int_{V_1}^{V_2} p\,dV = RT\int_{V_1}^{V_2} \frac{dV}{V} = RT\log\frac{V_2}{V_1} = RT\log\frac{p_1}{p_2}\,,$$

where we have used the relations $p_1V_1=RT$, and $p_2V_2=RT$. With $T=20$ °C$=$ 293 °K, $RT=8.31\times 293=2.43\times 10^3$ joule/mol. For $p_1=20$ atm, $p_2=1$ atm, $\log(p_1/p_2)=\log 20=2.30\times 1.301=2.99$. Therefore $RT\log(p_1/p_2)=2.43\times 10^3\times 2.99=7.26\times 10^3$ joule/mol is the work done by the gas.

The heat supplied is obtained from the first law of thermodynamics (1.2): $U_2-U_1=Q+A$. At thermal equilibrium the internal energy U of a mole of gas is a function of T only and the internal energy does not change in an

isothermal process: $U_2 - U_1 = 0$. Hence the heat supplied to the gas is $Q = -A = 7.26 \times 10^3$ joule/mol. This is converted into calories by dividing by the work equivalent J; $Q = 7.26 \times 10^3/4.18 = 1.937$ kcal/mol.

5. From Poisson's equation (example 6) $pV^\gamma = \text{const.}$, we have $(\mathrm{d}p/p) + \gamma(\mathrm{d}V/V) = 0$. Therefore

$$\kappa_{\text{ad}} = -V(\partial p/\partial V)_{\text{ad}} = \gamma p. \tag{1}$$

If the compression and expansion due to the sound wave may be considered as quasi-static adiabatic processes (this would apply to sound at low frequencies)

$$\left(\frac{\mathrm{d}p}{\mathrm{d}\rho}\right)_{\text{ad}} = -\frac{V}{\rho}\left(\frac{\partial p}{\partial V}\right)_{\text{ad}} \qquad \left(\text{as } \frac{\mathrm{d}\rho}{\rho} = -\frac{\mathrm{d}V}{V}\right) \tag{2}$$
$$= \kappa_{\text{ad}}/\rho = \gamma p/\rho.$$

If there are n moles of gas in a volume V, and M is the molecular weight, we have $\rho = nM/V$. Therefore the equation of state may be written as

$$\frac{p}{\rho} = \frac{RT}{M}. \tag{3}$$

Substitute this in eq. (2) and we have

$$c = (\gamma RT/M)^{\frac{1}{2}}.$$

For $\gamma = 1.41$, an average molecular weight of 28.9, $T = 273$ °K, and $R = 8.31 \times 10^7$ erg/mol deg^2, we have

$$c = 3.32 \times 10^4 \text{ cm/sec} = 332 \text{ m/sec}.$$

The change of velocity with temperature $\mathrm{d}c/\mathrm{d}T = \frac{1}{2}c/T$ at $T = 273$ °K is 0.607 m/sec deg.

6. In the adiabatic process $1 \to 2$, we have $U_2 - U_1 = A = -W$ (W is the work done by the gas). In the process $2 \to 3$, where the gas is heated by the heat Q at constant volume, consequently without work, we have $U_3 = U_2 + Q$. If $Q = W$, then $U_3 = U_2 + W = U_1$. Since the internal energy of an ideal gas does not depend on volume but only on temperature, we must have $T_3 = T_1$.

7. Since the internal energy, U, may be expressed as $U = C_V T + \text{const.}$ ($C_V = \text{const.} = nC_V^0$; n = mole number; C_V^0 = molar heat), it is obvious that $U_2 - U_1 = C_V(T_2 - T_1)$.

(i) $A_{1\to A}=0$, so that $A(\mathrm{i})=A_{A\to 2}=-\int_{V_1}^{V_2} p_2\,\mathrm{d}V=-p_2(V_2-V_1)$,

$$Q_{1\to A}=\int_{T_1}^{T_A} C_V\,\mathrm{d}T=C_V(T_A-T_1),\quad Q_{A\to 2}=\int_{T_A}^{T_2} C_p\,\mathrm{d}T=C_p(T_2-T_A). \tag{1}$$

On the other hand, since T_A is determined by $p_2V_1=nRT_A$ using Mayer's relation, $C_p=C_v+nR$ (example 3),

$$\begin{aligned} Q(\mathrm{i}) &= Q_{1\to A}+Q_{A\to 2}=C_pT_2-C_VT_1-(C_p-C_V)T_A \\ &= C_pT_2-C_VT_1-p_2V_1=C_V(T_2-T_1)+p_2(V_2-V_1). \end{aligned} \tag{2}$$

(ii) In the process B→2 no work is involved, so that

$$A(\mathrm{ii})=A_{1\to B}=-\int_{V_1}^{V_2} nRT_1\frac{\mathrm{d}V}{V}=nRT_1\log\frac{V_1}{V_2}. \tag{3}$$

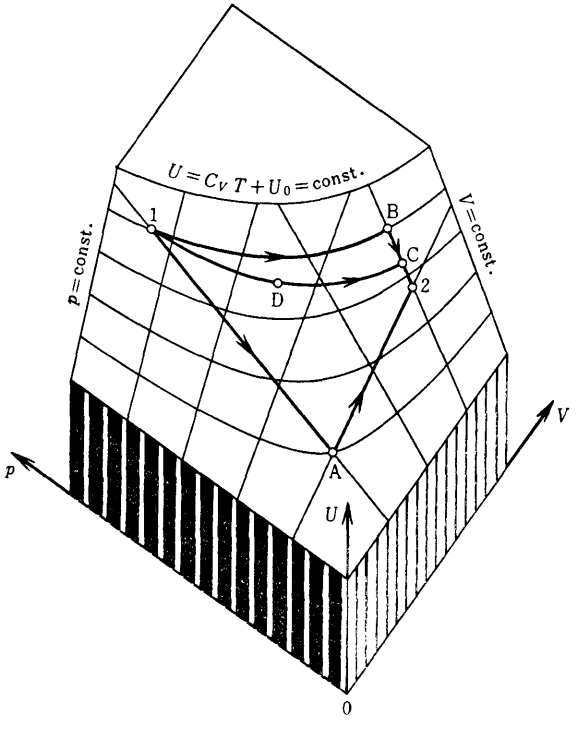


Fig. 1.10

The heat absorbed in $1 \to B$ is $d'Q = p dV$ (U=const. since T=const.). Therefore

$$Q_{1\to B} = \int_1^B p\, dV = -A_{1\to B} = -nRT_1 \log(V_1/V_2), \qquad \text{or}$$

$$Q_{B\to 2} = \int_{T_1}^{T_2} C_V\, dT = C_V(T_2 - T_1)$$

and thus

$$Q(\text{ii}) = C_V(T_2 - T_1) + nRT_1 \log(V_2/V_1). \tag{4}$$

(iii) There is no work involved in $C \to 2$. The work in the adiabatic process $1 \to C$ is calculated as in example 6;

$$A(\text{iii}) = A_{1\to C} = C_V(T_C - T_1) = -C_V T_1 \{1 - (V_1/V_2)^{\gamma-1}\}. \tag{5}$$

No heat is absorbed in $1 \to C$ and

$$Q(\text{iii}) = Q_{C\to 2} = \int_{T_C}^{T_2} C_V\, dT = C_V(T_2 - T_C) = C_V\left\{T_2 - T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}\right\}. \tag{6}$$

In all cases $A + Q[(1)+(2), (3)+(4), (5)+(6)]$ is equal to $C_V(T_2 - T_1)$.

8. First we examine how the pressure of the atmosphere in thermal equilibrium changes with the height, z. This is determined from the fact that thermal equilibrium involves the balance of forces. Consider a cylinder of air between heights z and $z + dz$ with a cross-section S. The force acting on the upper and lower planes are $-p(z+dz)\,S$ and $p(z)\,S$, respectively. The gravitational force acting on the air in the cylinder is $-\rho(z)\,S\,g dz$ where $\rho(z)$ is the density of the air and g is the gravitational acceleration. From the balance of these three forces,

$$-p(z + dz)\,S + p(z)\,S - \rho(z)\,S\,g dz = 0,$$

we get $dp(z)/dz = -\rho(z)\,g$. If the average molecular weight of air is m, $m/\rho(z)$ gives the volume of a mole of air. Hence the equation of state (1.11) can be expressed as $p(z)\,m/\rho(z) = RT(z)$. By expression $\rho(z)$ in terms of $p(z)$ we get $dp(z)/dz = -mgp(z)/RT(z)$.

The condition for adiabatic quasi-static expansion is (1) in example 6. From $pV = nRT$ we have

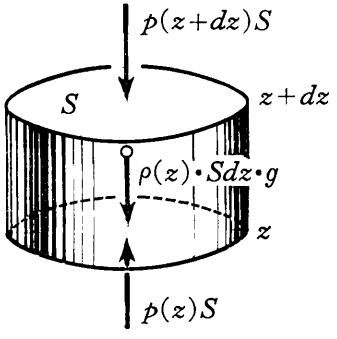
$$dp/p + dV/V = dT/T.$$

Elimination of dV/V gives

$$dT/T = (\gamma - 1)\, dp/\gamma p$$

or

$$(\partial T/\partial p)_{ad} = (\gamma - 1)\, T/\gamma p\,.$$



From this condition, the dependence of the temperature $T(z)$ on z can be derived from the relationship between the pressure and the height. We thus have

$$\frac{dT(z)}{dz} = \left(\frac{\partial T}{\partial p}\right)_{ad} \cdot \frac{dp(z)}{dz} = \frac{(\gamma - 1)\, T(z)}{\gamma p(z)} \cdot \frac{-mgp(z)}{RT(z)} = \frac{-(\gamma - 1)\, mg}{\gamma R}\,.$$

The constants for air have been given in the solution to example 4: $\gamma = 1.41$, $m = 29$ g/mol and $g = 980$ cm/sec^2. Therefore,

$$(\gamma - 1)\, mg/\gamma R = 0.41 \times 29 \times 980/(1.41 \times 8.3 \times 10^7) = 1.00 \times 10^{-4} \text{ deg/cm}$$
$$= 10.0 \text{ deg/km}\,,$$

i.e., there is a 10 °C drop in the temperature for every km increase in height. NOTE: The air in the troposphere (of the atmosphere) is rising or falling. Since the thermal conductivity of air is negligible, the air may be considered to undergo adiabatic changes in these movements. The actual decline in temperature is about 6 °C per kilometer. The discrepancy is due to other phenomena such as the condensation of water vapour.

9. Since there is no change in internal energy of an ideal gas in an isothermal process, the energy absorbed in such a process is equal to the work done by the gas, $\int p\,dV$. Therefore, in the process $1 \to 2$,

$$Q_1 = \int_{V_1}^{V_2} nRT \frac{dV}{V} = nRT_1 \log \frac{V_2}{V_1} \qquad (1)$$

for n moles of gas. Similarly, in the process $3 \to 4$,

$$Q_2 = \int_{V_3}^{V_4} nRT_2 \frac{\mathrm{d}V}{V} = nRT_2 \log \frac{V_4}{V_3}. \tag{2}$$

In the case described by the figure, we see that $Q_1 > 0$ and $Q_2 < 0$ since $V_2 > V_1$ and $V_3 > V_4$. In the adiabatic processes $2 \to 3$ and $4 \to 1$ we have

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}, \qquad T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}. \tag{3}$$

(From Poisson's equation $pV^\gamma = \text{const.}$ or $TV^{\gamma-1} = \text{const.}$ See example 6.) From (3) $(V_2/V_1)^{\gamma-1} = (V_3/V_4)^{\gamma-1}$ or $V_2/V_1 = V_3/V_4$. Therefore from (1) and (2) we have

$$Q_1/T_1 = -Q_2/T_2.$$

10. By definition, the heat $\mathrm{d}'Q$ absorbed in the process is equal to $C_x\,\mathrm{d}T$, so that we have

$$C_x\,\mathrm{d}T \equiv \mathrm{d}'Q = C_V\,\mathrm{d}T + p\,\mathrm{d}V = C_V\,\mathrm{d}T + (C_p - C_V)\,T\,\mathrm{d}V/V,$$

where we have used the relations, $p = nRT/V$ and $C_p - C_V = nR$. The above equation gives

$$(C_x - C_V)\frac{\mathrm{d}T}{T} = (C_p - C_V)\frac{\mathrm{d}V}{V},$$

which becomes

$$(C_x - C_V)\frac{\mathrm{d}p}{p} = (C_p - C_x)\frac{\mathrm{d}V}{V}$$

when $\mathrm{d}T/T$ is eliminated by the relation

$$\frac{\mathrm{d}T}{T} = \frac{\mathrm{d}p}{p} + \frac{\mathrm{d}V}{V}.$$

By putting $f = (C_x - C_p)/(C_x - C_V)$, we get

$$\log p + f \log V = \text{const.}$$

or

$$pV^f = \text{const.}$$

11. Although the initial state 1 and the final state 2 are thermal equilibrium states, a free expansion is not a quasi-static process, so that, in the expression for the work $\mathrm{d}'A = -p^{(e)}\,\mathrm{d}V$, $p^{(e)}$ is not the pressure as determined by the equation of state of the gas, but it is the external pressure, which is zero in the

case of free expansion. Thus the gas does no work in a free expansion: $A_{1\to 2}=0$. Since no heat is absorbed, $Q_{1\to 2}=0$ so that the internal energy, U, is unchanged and therefore the temperature remains constant, i.e., $T_1=T_2$, because of the assumption of an ideal gas.

If state 3 is the state after quasi-static compression at constant pressure from state 2, the work received by the gas in this process $2\to 3$ is

$$A_{2\to 3} = -\int_{V_2}^{V_1} p_2\,\mathrm{d}V = p_2(V_2 - V_1).$$

The temperature changes from T_2 to T_3 in this process and the gas must be cooled. The heat absorbed by the gas is

$$Q_{2\to 3} = \int_{T_2}^{T_3} C_p\,\mathrm{d}T = C_p(T_3 - T_2) \qquad \text{(this is negative)},$$

where C_p is the molar heat at constant pressure. In the quasi-static isovolumic heating process $3\to 1$ there is no work involved: $A_{3\to 1}=0$. If the molar heat at constant volume is C_V, the absorbed heat is

$$Q_{3\to 1} = \int_{T_3}^{T_1} C_V\,\mathrm{d}T = C_V(T_1 - T_3).$$

From the first law of thermodynamics the sum of the total heat absorbed and the work done on the system must be zero in a cyclic process. Therefore

$$Q_{1\to 2} + Q_{2\to 3} + Q_{3\to 1} + A_{1\to 2} + A_{2\to 3} + A_{3\to 1} = 0.$$

Substituting the above results, we have

$$(C_p - C_V)(T_3 - T_1) + p_2(V_2 - V_1) = 0. \tag{1}$$

From the equation of state of a mole of ideal gas, $pV=RT$, we have

$$p_2V_2 = RT_1 \qquad \text{and} \qquad p_2V_1 = RT_3$$

and

$$p_2(V_2 - V_1) = R(T_1 - T_3).$$

Substitute this into (1) and we have the desired result

$$(C_p - C_V)(T_3 - T_1) + R(T_1 - T_3) = 0$$

or

$$C_p - C_V = R.$$

12. The critical state is a state where p, T and V simultaneously satisfy the three equations: the equation of state, $(\partial p/\partial V)_T=0$, and $(\partial^2 p/\partial V^2)_T=0$. Since

$$(\partial p/\partial V)_T = p\left[-(V-nb)^{-1} + na/RTV^2\right],$$
$$(\partial^2 p/\partial V^2)_T = p\left[-(V-nb)^{-1} + na/RTV^2\right]^2 + \\ + p\left[(V-nb)^{-2} - 2na/RTV^3\right],$$

we have, from $(\partial p/\partial V)_T=0$,

$$V^2/(V-nb) = na/RT, \tag{1}$$

and, from $(\partial^2 p/\partial V^2)_T=0$,

$$V^3/(V-nb)^2 = 2na/RT. \tag{2}$$

Dividing both sides of (2) by the corresponding expressions in (1) we get the equation for V_c

$$V_c/(V_c - nb) = 2$$
$$V_c = 2nb.$$

T_c is determined by substituting this into eq. (1):

$$T_c = na(V_c - nb)/RV_c^2.$$

We then substitute V_c and T_c into the equation of state to obtain p_c, or

$$p_c = [nRT_c/(V_c - nb)]\exp[-na/RT_cV_c)] = a/4b^2\,\mathrm{e}^2.$$

We then use the reduced variables, $\mathfrak{p}=p/p_c$, $\mathfrak{v}=V/V_c$, $\mathfrak{t}=T/T_c$ to obtain the expression for the law of "corresponding states". Substituting $nRT_c/p_cV_c=\frac{1}{2}\mathrm{e}^2$, $nb/V_c=\frac{1}{2}$, and $na/RT_cV_c=2$ into

$$\mathfrak{p} = [nRT_c\mathfrak{t}/\{p_cV_c(\mathfrak{v} - nb/V_c)\}]\exp[-na/RT_cV_c\mathfrak{t}\mathfrak{v}]$$

we obtain

$$\mathfrak{p} = \frac{\frac{1}{2}\mathfrak{t}\mathrm{e}^2}{\mathfrak{v}-\frac{1}{2}}\exp\left(-\frac{2}{\mathfrak{t}\mathfrak{v}}\right).$$

13. According to eq. (1.15), the internal energy of a mixture of chemically non-reacting ideal gases is the sum of the internal energies of the component gases. If the mass of the i-th component gas is M_i and its specific heat at constant volume is c_{Vi}, then we have

$$M\,\mathrm{d}u = \sum_i M_i c_{Vi}\,\mathrm{d}T,$$

where $M=\sum_i M_i$ is the total mass and u the internal energy per unit mass of

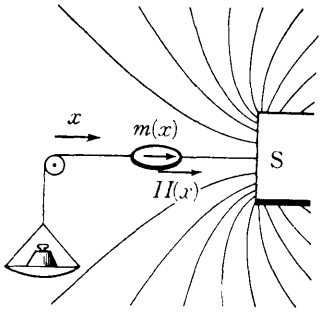
the mixture. The specific heat at constant volume of the mixture is given by

$$c_V = \mathrm{d}u/\mathrm{d}T = \sum_i M_i c_{Vi}/M .$$

For air, this becomes

$$c_V = 0.23 \times 0.158 + 0.77 \times 0.176 = 0.036 + 0.136 = 0.172 \text{ cal/g deg} .$$

14. Let us take the x-axis along the permanent bar magnet and the needle, so that the magnetic field H_S is also in the x-direction as shown in the figure. The field, $H_S(x)$, is zero for $x = -\infty$ and monotonically increases with x. The needle is brought slowly along the x-axis from $-\infty$ to x, where it acquires



a magnetic moment m, which is of course along the axis of the needle. The demagnetizing field is considered negligible for a needle, so that the magnetizing field H is equal to H_S. Since the needle is small, it may be treated as a magnetic dipole with magnetic moment $m(x)$, which is a function of the position x. The force on the needle by the permanent magnet is given by

$$K(x) = m(x)\,\mathrm{d}H(x)/\mathrm{d}x .$$

In order to bring the needle from $x = -\infty$ to $x = x_1$ infinitely slowly, the needle must be restrained by a force infinitesimally smaller than $-K(x)$. The work done by this force (supplied by a mechanical source, say a weight) on the system, the needle and the permanent magnet, is

$$A_1 = -\int_{-\infty}^{x_1} K(x)\,\mathrm{d}x = -\int_{-\infty}^{x_1} m(x)\frac{\mathrm{d}H(x)}{\mathrm{d}x}\,\mathrm{d}x \left[= -\int_0^{H(x_1)} m\,\mathrm{d}H\right]. \qquad (2)$$

However, only a part of this has been used in magnetizing the iron needle, the other part being only a sort of potential energy. If a magnetic dipole of magnetic moment $m(x)=m_1$ is placed in a field $H(x_1)$, it has a potential energy $-m_1H(x_1)$ (interaction energy between the magnetic dipole and the permanent magnet). To subtract this we consider the following process: suppose we could by some means, fix the magnetization of the needle to a given $m_1=m(x_1)$ and then bring the needle from x_1 to $-\infty$. In this process, the permanent magnet is pulling the needle with the force

$$K(x) = m_1 \frac{\mathrm{d}H(x)}{\mathrm{d}x}, \tag{3}$$

so that the outside mechanical source must do the following amount of work

$$A_2 = -\int_{x_1}^{-\infty} K'(x)\,\mathrm{d}x = m_1 \int_{-\infty}^{x_1} \frac{\mathrm{d}H(x)}{\mathrm{d}x}\,\mathrm{d}x$$

$$= m_1H(x_1) = \int_{-\infty}^{x_1} \frac{\mathrm{d}\{m(x)\,H(x)\}}{\mathrm{d}x}\,\mathrm{d}x. \tag{4}$$

Therefore, the total work which is required to magnetize the iron needle is

$$A_1 + A_2 = \int_{-\infty}^{x_1} H(x)\,\frac{\mathrm{d}m(x)}{\mathrm{d}x}\,\mathrm{d}x = \int_0^{m_1} H\,\mathrm{d}m. \tag{5}$$

NOTE: If we consider the needle and the permanent magnet as our thermodynamic system, then their interaction energy is included in the internal energy U' of the system. If U is the internal energy of the needle, U' is given by

$$U' = U - Hm + \text{const.},$$

so that

$$\mathrm{d}U' = \mathrm{d}U - H\,\mathrm{d}m - m\,\mathrm{d}H = -\,m\,\mathrm{d}H.$$

Note this difference between the definitions of the thermodynamic system for U and U'. Although this is straightforward, it often leads to confusion.

15. Since the density of air ρ changes with the height z, the air in the cylinder is not a uniform system. However, in thermal equilibrium the temperature T must be uniform. If a non-uniform system can be divided into parts in such a way that each part may be considered uniform and the interaction between

the parts is negligibly small, the energy of the system is just the sum of the energies of the partial system. A cylinder between z and $z+\mathrm{d}z$ may be considered such a uniform partial system with an internal energy $\rho(z)\,Su(T)\,\mathrm{d}z$ and a potential energy $\rho(z)\,Sgz\,\mathrm{d}z$, where S is the cross-sectional area of the cylinder, $u(T)$ the internal energy of a unit mass of air assuming it to be an ideal gas, and g the gravitational acceleration. Since the total energy of the part between z and $z+\mathrm{d}z$ is $S\{u(T)+gz\}\,\rho(z)\,\mathrm{d}z$, the energy of the entire cylinder from $z=0$ to $z=\infty$ is given by

$$E(T) = S\int_0^\infty \{u(T) + gz\}\,\rho(z)\,\mathrm{d}z\,.$$

The dependence of ρ on height is given by the equation $\mathrm{d}p(z)/\mathrm{d}z = -\rho(z)g$ (see the solution of problem 8). Using the equation of state, $p(z) = RT\rho(z)/m$, to eliminate $p(z)$, we have

$$\mathrm{d}\rho(z)/\mathrm{d}z = -\rho(z)\,mg/RT$$

and

$$\log\rho(z) = -mgz/RT + \text{const.}$$

or

$$\rho(z) = \rho(0)\exp\{-mgz/RT\}\,.$$

It is more convenient to use the total mass of the air cylinder after integration rather than the density of air $\rho(0)$ at the ground where $z=0$, or,

$$M = \int_0^\infty \rho(z)\,S\mathrm{d}z = \rho(0)\,S\int_0^\infty \exp[-mgz/RT]\,\mathrm{d}z = \rho(0)\,SRT/mg\,,$$

which gives

$$S\rho(z) = [Mmg/RT]\exp[-mgz/RT]\,.$$

Using this relation, we find that the energy of the cylinder is

$$\begin{aligned} E(T) &= \int_0^\infty \{u(T) + gz\}\,\{Mmg/RT\}\exp[-mgz/RT]\,\mathrm{d}z \\ &= M\int_0^\infty \{u(T) + RT\xi/m\}\exp(-\xi)\,\mathrm{d}\xi \\ &= M[u(T) + (RT/m)\int_0^\infty \xi\mathrm{e}^{-\xi}\,\mathrm{d}\xi] = M[u(T) + RT/m]\,. \end{aligned}$$

This is a function of the temperature only, and the heat capacity is given by

$$C = \mathrm{d}E(T)/\mathrm{d}T = M[\mathrm{d}u/\mathrm{d}T + R/m] = M(c_v + R/m).$$

If we use Mayer's relation $c_p = c_v + R/m$,

$$C = Mc_p.$$

16. The heat received by a system in a quasi-static process is given by the first law of thermodynamics, $\mathrm{d}'Q = \mathrm{d}U + p\,\mathrm{d}V$. If we consider the internal energy U as a function of T and V, we have

$$\mathrm{d}U = (\partial U/\partial T)_V\,\mathrm{d}T + (\partial U/\partial V)_T\,\mathrm{d}V.$$

Then the first law becomes

$$\mathrm{d}'Q = (\partial U/\partial T)_V\,\mathrm{d}T + \{(\partial U/\partial V)_T + p\}\,\mathrm{d}V. \tag{1}$$

For the enthalpy, $H = U + pV$, we have

$$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p$$

and

$$\mathrm{d}U + p\,\mathrm{d}V = \mathrm{d}H - V\,\mathrm{d}p.$$

Therefore we can write

$$\mathrm{d}'Q = \mathrm{d}H - V\,\mathrm{d}p.$$

It is convenient to consider H as a function of T and p: $\mathrm{d}H = (\partial H/\partial T)_p\,\mathrm{d}T + (\partial H/\partial p)_T\,\mathrm{d}p$. Therefore the heat equation may be rewritten as

$$\mathrm{d}'Q = (\partial H/\partial T)_p\,\mathrm{d}T + \{(\partial H/\partial p)_T - V\}\,\mathrm{d}p. \tag{2}$$

(i) The heat capacity in an isovolumic process is $\mathrm{d}'Q/\mathrm{d}T$ for $\mathrm{d}V = 0$, and from eq. (1) we have $C_V = (\partial U/\partial T)_V$. In a process at constant pressure, $\mathrm{d}p = 0$, and from eq. (2) we have $C_p = (\partial H/\partial T)_p$.

(ii) As was shown in the solution of example 2, the heat capacity at constant pressure is obtained from eq. (1) by considering V as a function of p and T from the equation of state and substituting $\mathrm{d}V = (\partial V/\partial T)_p\,\mathrm{d}T + (\partial V/\partial p)_T\,\mathrm{d}p$ into (1), which gives

$$\mathrm{d}'Q = C_V\,\mathrm{d}T + \{(\partial U/\partial V)_T + p\}\,\{(\partial V/\partial T)_p\,\mathrm{d}T + (\partial V/\partial p)_T\,\mathrm{d}p\}.$$

Setting $\mathrm{d}p = 0$ for $\mathrm{d}'Q/\mathrm{d}T$ we have

$$C_p = C_V + \{(\partial U/\partial V)_T + p\}(\partial V/\partial T)_p.$$

This is the first part of (ii). To obtain the second part, we derive C_V from

eq. (2). Since $\mathrm{d}p=(\partial p/\partial T)_V\,\mathrm{d}T+(\partial p/\partial V)_T\,\mathrm{d}V$, we have

$$\mathrm{d}'Q = C_p\,\mathrm{d}T + \{(\partial H/\partial p)_T - V\}\,\{(\partial p/\partial T)_V\,\mathrm{d}T + (\partial p/\partial V)_T\,\mathrm{d}V\}\,.$$

$\mathrm{d}'Q/\mathrm{d}T$ for $\mathrm{d}V=0$ gives

$$C_V = C_p + \{(\partial H/\partial p)_T - V\}\,(\partial p/\partial T)_V\,.$$

Combining this with (iii), we get the second part of (ii).

(iii) Since $H=U+pV$,

$$(\partial H/\partial p)_T = (\partial U/\partial p)_T + (\partial(pV)/\partial p)_T = (\partial U/\partial p)_T + p(\partial V/\partial p)_T + V\,.$$

(iv) Since $(\partial V/\partial T)_p=1/(\partial T/\partial V)_p$, the first part of (ii) gives

$$(C_p - C_V)\,(\partial T/\partial V)_p = (\partial U/\partial V)_T + p\,.$$

Considering both sides of the equation to be functions of p and V, we get, by differentiating with respect to p,

$$(C_p - C_V)\,\frac{\partial^2 T}{\partial p\partial V} + \left(\frac{\partial C_p}{\partial p}\right)_V\cdot\left(\frac{\partial T}{\partial V}\right)_p - \left(\frac{\partial C_V}{\partial p}\right)_V\cdot\left(\frac{\partial T}{\partial V}\right)_p = \left(\frac{\partial(\partial U/\partial V)_T}{\partial p}\right)_V + 1\,. \tag{3}$$

We now rewrite the third term on the left-hand side and the first term on the right-hand side. Although these are partial derivatives of p at constant V, it is convenient to choose T and V as the natural state variables for C_p and $(\partial U/\partial T)_V$. If we consider T in $C_V(T, V)$ to be a function of p and V through the equation of state, we can write

$$\left(\frac{\partial C_V}{\partial p}\right)_V = \frac{\partial C_V(T(p, V), V)}{\partial p} = \left(\frac{\partial C_V}{\partial T}\right)_V\cdot\left(\frac{\partial T}{\partial p}\right)_V\,.$$

Similarly, considering T in $(\partial U/\partial V)_T=\partial U(T, V)/\partial V$ to be a function of p and V, we should first differentiate with respect to T and then multiply it with the partial derivative of T with respect to p to get the partial derivative with respect to p:

$$\left(\frac{\partial(\partial U/\partial V)_T}{\partial p}\right)_V = \frac{\partial^2 U(T, V)}{\partial T\partial V}\cdot\left(\frac{\partial T}{\partial p}\right)_V = \left(\frac{\partial C_V}{\partial V}\right)_T\left(\frac{\partial T}{\partial p}\right)_V\,.$$

Hence

$$\left(\frac{\partial C_V}{\partial p}\right)_V\cdot\left(\frac{\partial T}{\partial V}\right)_p - \frac{\partial(\partial U/\partial V)_T}{\partial p} = \left\{\left(\frac{\partial C_V}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p + \left(\frac{\partial C_V}{\partial V}\right)_T\right\}\left(\frac{\partial T}{\partial p}\right)_V\,. \tag{4}$$

On the other hand, by considering T in $C_V(T, V)$ to be a function of p and

V, we have

$$\left(\frac{\partial C_V}{\partial V}\right)_p = \frac{\partial C_V(T(p, V), V)}{\partial V} = \left(\frac{\partial C_V}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p + \left(\frac{\partial C_V}{\partial V}\right)_T,$$

by means of which eq. (4) gives

$$\left(\frac{\partial C_V}{\partial p}\right)_V \left(\frac{\partial T}{\partial V}\right)_p - \frac{\partial(\partial U/\partial V)_T}{\partial p} = \left(\frac{\partial C_V}{\partial V}\right)_p \left(\frac{\partial T}{\partial p}\right)_V.$$

On substituting this into eq. (3) derived previously, we have the desired results.

17. Using the result of problem 5, $c^2 = \gamma p/\rho$, and the relation

$$\frac{p}{\rho} = \frac{RT}{M} = \frac{(C_p - C_V)\,T}{M} = (c_p - c_V)\,T = (\gamma - 1)\,c_V T,$$

we have $c^2 = \gamma(\gamma - 1)\,c_V T$ or $c_V T = c^2/\{\gamma(\gamma - 1)\}$. Furthermore we know that $u = c_v T + \text{const.}$ and

$$h = u + pv = u + (c_p - c_v)\,T = u + (\gamma - 1)\,c_v T = \gamma c_v T + \text{const.}$$

Thus we obtain the desired result.

18. The work equation, at constant magnetic field H, is $\mathrm{d}'A = H\,\mathrm{d}I$, so that, from the first law of thermodynamics, the heat absorbed is

$$\mathrm{d}'Q = \mathrm{d}U - \mathrm{d}'A = \mathrm{d}U - H\,\mathrm{d}I.$$

If we consider U and I to be functions of temperature, T, and field, H, we have

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_H \mathrm{d}T + \left(\frac{\partial U}{\partial H}\right)_T \mathrm{d}H,$$

$$\mathrm{d}I = \left(\frac{\partial I}{\partial T}\right)_H \mathrm{d}T + \left(\frac{\partial I}{\partial H}\right)_T \mathrm{d}H,$$

and

$$\mathrm{d}'Q = \left\{\left(\frac{\partial U}{\partial T}\right)_H - H\left(\frac{\partial I}{\partial T}\right)_H\right\}\mathrm{d}T + \left\{\left(\frac{\partial U}{\partial H}\right)_T - H\left(\frac{\partial I}{\partial H}\right)_T\right\}\mathrm{d}H.$$

The desired heat capacity C_H is $\mathrm{d}Q/\mathrm{d}T$ for $\mathrm{d}H = 0$. Thus we obtain the answer.

19. For a unit volume of magnetic material in a quasi-static process, the first law may be written as follows:

$$\mathrm{d}'Q = \mathrm{d}U - H\,\mathrm{d}M$$

(from eq. (1.5) and example 1). Comparing this with the case of a gas where $\mathrm{d}'Q = \mathrm{d}U + p\,\mathrm{d}V$, we see the correspondence $p \to -H$ and $V \to M$. Since

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \qquad \text{and} \qquad \chi_{\mathrm{ad}} = \left(\frac{\partial M}{\partial H}\right)_{\mathrm{ad}}$$

correspond to $1/(\partial p/\partial V)_T$ and $1/(\partial p/\partial V)_{\mathrm{ad}}$, the solution to example 7 gives the answer to this problem. Therefore, we may obtain the solution to this problem by following the argument of example 7, using this parallelism.

20. The internal energy of the heat radiation inside an enclosure of volume, V, is given by $U = Vu = \sigma V T^4$. Since the pressure $p = \frac{1}{3}u = \frac{1}{3}\sigma T^4$ is independent of V, p and T are not independent. Thus the natural state variables are (V, T) or (V, p). The first law of thermodynamics for a quasi-static process is

$$\mathrm{d}U = \mathrm{d}'Q - p\,\mathrm{d}V\,.$$

Substituting for U and p, we have

$$\mathrm{d}'Q = \mathrm{d}(\sigma V T^4) + \tfrac{1}{3}\sigma T^4\,\mathrm{d}V = \tfrac{4}{3}\sigma T^4\,\mathrm{d}V + 4\sigma T^3 V\,\mathrm{d}T\,.$$

Thus the condition for an adiabatic process is

$$\tfrac{4}{3}\sigma T^4 V\left(\frac{\mathrm{d}V}{V} + 3\,\frac{\mathrm{d}T}{T}\right) = 0$$

which, when integrated, becomes

$$\log V + 3 \log T = \text{const.}\,,$$

or

$$VT^3 = \text{const.}\,,$$

and, using the equation of state,

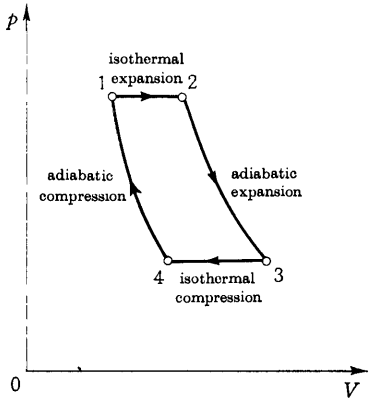
$$pV^{\frac{4}{3}} = \text{const.}$$

The heat capacity at constant volume is

$$C_V = (\partial U/\partial T)_V = 4\sigma T^3 V\,,$$

while the heat capacity at constant pressure may be considered infinite, since the temperature cannot be changed if the pressure is fixed.

As shown in the figure, the Carnot cycle is a quasi-static process in which the system goes from state 1 to state 2 by an isothermal expansion, from state 2 to state 3 by an adiabatic expansion, from state 3 to state 4 by an isothermal compression and returns to state 1 by an adiabatic compression.



In the process $1 \to 2$, let the volume increase from V_1 to V_2 at a constant temperature, T_1. The work received by the heat radiation is

$$A_{1\to 2} = -\int_{V_1}^{V_2} p\,\mathrm{d}V = -\tfrac{1}{3}\sigma T_1^4 (V_2 - V_1),$$

while the heat received is

$$Q_{1\to 2} = \tfrac{4}{3}\sigma T_1^4 \int_{V_1}^{V_2} \mathrm{d}V$$
$$= \tfrac{4}{3}\sigma T_1^4 (V_2 - V_1).$$

Therefore,

$$A_{1\to 2} + Q_{1\to 2} = \sigma T_1^4 (V_2 - V_1)$$

is certainly the increase in the internal energy. It is obvious that $Q_{2\to 3} = 0$ in the process $2 \to 3$, but in order to calculate $A_{2\to 3} = -\int_{V_2}^{V_3} p\,\mathrm{d}V$ we make use of the fact that

$$pV^{\frac{4}{3}} = p_1 V_2^{\frac{4}{3}} = \tfrac{1}{3}\sigma T_1^4 V_2^{\frac{4}{3}}.$$

Therefore,

$$A_{2\to 3} = -\tfrac{1}{3}\sigma T_1^4 V_2^{\frac{4}{3}} \int_{V_2}^{V_3} V^{-\frac{4}{3}}\,\mathrm{d}V = \sigma T_1^4 V_2^{\frac{4}{3}} (V_3^{-\frac{1}{3}} - V_2^{-\frac{1}{3}})$$
$$= \sigma T_1^4 V_2^{\frac{4}{3}} V_3^{-\frac{1}{3}} - \sigma T_1^4 V_2.$$

From $V_2T_1^3 = V_3T_3^3$ we get for the temperature at state 3: $T_3 = T_1(V_2/V_3)^{\frac{1}{3}}$ and

$$A_{2\to 3} = \sigma T_3^4 V_3 - \sigma T_1^4 V_2 .$$

This is also the increase in the internal energy. (We know that $Q_{2\to 3}=0$ and we immediately get this result from the first law.) In the process $3\to 4$ the temperature is constant, and

$$Q_{3\to 4} = \tfrac{4}{3}\sigma T_3^4 (V_4 - V_3),$$

and

$$A_{3\to 4} = -\tfrac{1}{3}\sigma T_3^4 (V_4 - V_3).$$

In the process $4\to 1$, $Q_{4\to 1}=0$ and $A_{4\to 1}=\sigma T_3^4 V_4 - \sigma T_1^4 V_1$.

Since $V_2 > V_1$, $Q_{1\to 2}>0$. This indicates that heat is absorbed from the heat reservoir (temperature T_1). From $V_2T_1^3 = V_3T_3^3$ and $V_4T_3^3 = V_1T_1^3$ we see that $V_3/V_4 = V_2/V_1 > 1$. Therefore $Q_{3\to 4}<0$. This indicates that, since $V_3 > V_2$, $T_3 = T_1(V_2/V_3)^{\frac{1}{3}} < T_1$, heat is given off to the low temperature heat reservoir (temperature T_3). The total energy received from the heat reservoir $Q_{1\to 2} - |Q_{3\to 4}| = Q_{1\to 2} + Q_{3\to 4}$ is equal to the total work done $-(A_{1\to 2} + A_{2\to 3} + A_{3\to 4} + A_{2\to 1})$. Furthermore,

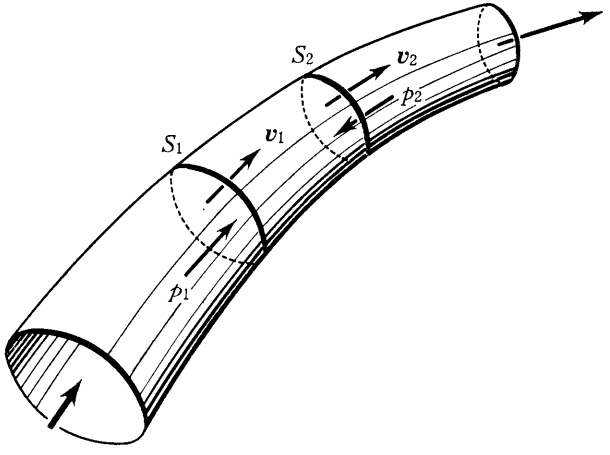
$$Q_{3\to 4}/T_3 = \tfrac{4}{3}\sigma T_3^3 (V_4 - V_3) = \tfrac{4}{3}\sigma T_1^3 (V_1 - V_2) = -Q_{1\to 2}/T_1 ,$$

which gives the Clausius equation $Q_{1\to 2}/T_1 + Q_{3\to 4}/T_3 = 0$.

21. (See example 9.) The streamlines do not change with time in a steady-state flow. Since the velocity, $\boldsymbol{v}$, the density, ρ, and the pressure, p, have differing values from point to point due to the motion of the fluid, the fluid as a whole is not in thermal equilibrium. However, if a sufficiently small volume element is taken, it may be considered to be in thermal equilibrium (local equilibrium), i.e. a small volume element may be considered to undergo a quasistatic change. In such a case, the pressure, p, may be considered to be determined by the density, ρ, and the temperature, T, of the volume element through the equation of state.

The equation of continuity for a fluid states that the mass of fluid which passes through a cross-section of a stream tube of area, S_1, perpendicular to the flow direction per unit time is equal to the amount of fluid passing through another cross-section on the same stream tube; i.e. $\rho_1 S_1 v_1 = \rho_2 S_2 v_2$. Writing l for the length along the stream tube, we thus have $\partial(\rho S v)/\partial l = 0$. Next we consider the first law of thermodynamics for the fluid between two cross-sections S_1 and S_2 separated by $\mathrm{d}l$. Since we neglect thermal conductivity, there is no heat flow from the surroundings. Ignoring the viscosity and the

gravitational force, the work done is only due to the external pressures, p_1 on the surface S_1 and p_2 on S_2. The work done on this fluid per unit time is $p_1S_1v_1 - p_2S_2v_2$. For an infinitesimal $\mathrm{d}l$, this is equal to $-\mathrm{d}l\cdot\partial(pSv)\partial l$. The internal energy density, u, of the fluid may be considered to be determined by the density, ρ, and the temperature, T, through the equation of state.



The fluid that was between S_1 and S_2 at a given moment t is displaced after a time interval, $\mathrm{d}t$, into the volume between the planes which are $v_1\,\mathrm{d}t$ and $v_2\,\mathrm{d}t$ removed from S_1 and S_2, respectively. Hence the energy of that portion of the fluid is increased by

$$-\rho_1(u_1 + \tfrac{1}{2}v_1^2)\,S_1v_1\,\mathrm{d}t + \rho_2(u_2 + \tfrac{1}{2}v_2^2)\,S_2v_2\,\mathrm{d}t\,.$$

To the first order in $\mathrm{d}l$, this increase per unit time is

$$\mathrm{d}l\cdot\frac{\partial[\rho Sv(u + \tfrac{1}{2}v^2)]}{\partial l}\,.$$

By the first law of thermodynamics this must be equal to the expression for the work derived previously; i.e.,

$$\frac{\partial[\rho Sv(u + \tfrac{1}{2}v^2)]}{\partial l} = -\frac{\partial(pSv)}{\partial l}\,.$$

This may be rewritten as

$$\frac{\partial[\rho Sv(u + \tfrac{1}{2}v^2 + p/\rho)]}{\partial l} = 0\,.$$

Using the continuity equation $\partial(\rho S v)/\partial l = 0$, this gives

$$\frac{\partial(u + \frac{1}{2}v^2 + p/\rho)}{\partial l} = 0,$$

which means that $u + p/\rho + \frac{1}{2}v^2$ is constant along the streamlines. Since $1/\rho$ is the specific volume, $h = u + \rho/p$ is the enthalpy density, and $\frac{1}{2}v^2$ is the kinetic energy of a unit mass.

22. We have seen in the previous problem, that the sum of the enthalpy density, h, and the kinetic energy, $\frac{1}{2}v^2$, is constant along a streamline. For an ideal gas with a constant specific heat, it can be seen from the equation of the internal energy $u = c_v T + \text{const.}$, that $h = u + p/\rho = c_p T + \text{const.}$ Therefore $c_p T + \frac{1}{2}v^2$ is a constant along the streamlines. In an adiabatic change of an ideal gas $p^{(1-\gamma)/\gamma} T$ is a constant, so that this quantity must be constant along the streamlines. If we assume that the velocity is zero in the container of the superheated steam where

$$T = 300\,^\circ\text{C} = 573\,^\circ\text{K} \qquad \text{and} \qquad p = 5\,\text{atm},$$

we have the equations

$$c_p T + \tfrac{1}{2}v^2 = 0.49 \times 573 = 281\ \text{cal/g} = 1.174 \times 10^{10}\ \text{cm}^2/\text{sec}^2$$

and

$$T = 573 \times (\tfrac{1}{5}p)^{0.33/1.33}\,^\circ\text{K}.$$

When the pressure $p = 1$ atm, then $T = 573 \times 5^{-0.248}\,^\circ$K. In order to calculate $x = 5^{-0.248}$ we take the logarithm of both sides

$$\log_{10} x = -0.248 \times \log_{10} 5 = -0.248 \times 0.699 = -0.1734 = \bar{1}.8266$$

and $x = 0.671$. The temperature is thus

$$T = 573 \times 0.671 = 384\,^\circ\text{K} = 111\,^\circ\text{C}.$$

The upper limit of the velocity is obtained from

$$v^2 = 2 \times (1.174 \times 10^{10} - 0.49 \times 384 \times 4.18 \times 10^7) = 0.774 \times 10^{10}\ \text{cm}^2/\text{sec}^2$$

as $v = 880$ m/sec.

23. Let the state variables of the system A be p_A and v_A, and the variables of systems B and C be p_B, v_B and p_C, v_C, respectively. When A and B are in equilibrium, there exists a single relation between the four variables p_A, v_A, p_B and v_B: let it be

$$F_3(p_A, v_A, p_B, v_B) = 0. \tag{1}$$

Similarly when B and C are in equilibrium, we have an equation

$$F_1(p_B, v_B, p_C, v_C) = 0. \tag{2}$$

According to the zeroth law, when eqs. (1) and (2) hold, A and C are in equilibrium and therefore a relation

$$F_2(p_A, v_A, p_C, v_C) = 0 \tag{3}$$

should result from eqs. (1) and (2). If eqs. (1) and (2) are solved for p_B so that

$$p_B = \phi_1(p_A, v_A, v_B), \qquad p_B = \phi_3(p_C, v_C, v_B),$$

then

$$\phi_1(p_A, v_A, v_B) = \phi_3(p_C, v_C, v_B) \tag{4}$$

must be equivalent to eq. (3). Then eq. (4) would have to hold independent of v_B and must be equivalent to an equation of the form

$$f_1(p_A, v_A) = f_3(p_C, v_C). \tag{5}$$

(This implies, for instance, that $\phi_1(p_A, v_A, v_B) = f_1(p_A, v_A)\,\eta(v_B) + \zeta(v_B)$, $\phi_3(p_C, v_C, v_B) = f_3(p_C, v_C)\,\eta(v_B) + \zeta(v_B)$.) Therefore eqs. (3) and (5) must be equivalent. By similar argument, eqs. (1) and (2) are equivalent to

$$f_1(p_A, v_A) = f_2(p_B, v_B), \tag{6}$$

$$f_2(p_B, v_B) = f_3(p_C, v_C). \tag{7}$$

(The fact that f_1 is the same in (5) and (6), f_2 is the same in (6) and (7) and f_3 is the same in (5) and (7), derives from the zeroth law.) If we now put

$$\theta = f_1(p_A, v_A),$$

θ will be a quantity which characterizes thermal equilibrium, that is, it is the temperature on a certain scale. The condition for equilibrium between systems A and B is that their values of θ, θ_A and θ_B, are equal.

24. In discussing the general case where the magnetic body has an arbitrary shape we have to start from Maxwell's equations, since the effect of the demagnetizing field cannot be ignored and the field, $\boldsymbol{H}$, the magnetization, $\boldsymbol{M}$, and the flux density, $\boldsymbol{B}$, are not uniform. The equivalent of Ampère's law is Maxwell's first equation where the magnetization is assumed to take place sufficiently slowly so that the displacement current can be ignored, i.e.

$$\operatorname{curl} \boldsymbol{H} = \frac{4\pi}{c}\boldsymbol{j} \qquad \text{(Maxwell's first equation)}. \tag{1}$$

Here $\boldsymbol{j}$ is the current density through the wire of the coil. If the magnetic body is at rest, Faraday's induction law takes the form

$$\operatorname{curl} \boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} \qquad \text{(Maxwell's second equation)}, \tag{2}$$

where $\boldsymbol{E}$ is the electric field. The magnetic flux density satisfies the equation

$$\operatorname{div} \boldsymbol{B} = 0 \qquad \text{(Maxwell's fourth equation)}. \tag{3}$$

The magnetic field, $\boldsymbol{H}$, is a sum of the part $\boldsymbol{H}_J$ due to the current in the wire of the coil and the part $\boldsymbol{H}_M$ due to the magnetization:

$$\boldsymbol{H} = \boldsymbol{H}_J + \boldsymbol{H}_M .$$

These partial fields are well known to satisfy the following equations, resulting from eqs. (1) and (3),

$$\operatorname{curl} \boldsymbol{H}_J = \frac{4\pi}{c}\boldsymbol{j}, \qquad \operatorname{div} \boldsymbol{H}_J = 0 ;$$

$$\operatorname{curl} \boldsymbol{H}_M = 0, \qquad \operatorname{div} \boldsymbol{H}_M = -4\pi \operatorname{div} \boldsymbol{M} .$$

$\boldsymbol{H}_J$ forms closed magnetic field lines around the current, and $\boldsymbol{H}_M$ is irrotational and forms force lines connecting the positive and negative magnetic charges in the magnetic body. $\boldsymbol{H}_M$ is determined by Coulomb's law and has a (pseudo) scalar potential. Therefore, integration over all space gives the relation

$$\int \boldsymbol{H}_J \cdot \boldsymbol{H}_M \, \mathrm{d}V = -\int \boldsymbol{H}_J \cdot \operatorname{grad} \varphi \, \mathrm{d}V = \int \varphi \operatorname{div} \boldsymbol{H}_J \, \mathrm{d}V = 0 . \tag{4}$$

We have assumed that the field vanishes at infinity. Now we take the scalar product of eq. (1) and $c\boldsymbol{E}/4\pi$, add to it the scalar product of eq. (2) and $-c\boldsymbol{H}/4\pi$, and integrate over space. The right-hand side becomes

$$\int (\boldsymbol{E} \cdot \operatorname{curl} \boldsymbol{H} - \boldsymbol{H} \cdot \operatorname{curl} \boldsymbol{E}) \, \mathrm{d}V = \int \operatorname{div} [\boldsymbol{H} \times \boldsymbol{E}] \, \mathrm{d}V = 0 .$$

Therefore, for the left-hand side, we have

$$\int \boldsymbol{E} \cdot \boldsymbol{j} \, \mathrm{d}V + \frac{1}{4\pi}\int \boldsymbol{H} \cdot (\partial \boldsymbol{B}/\partial t) \, \mathrm{d}V = 0 . \tag{5}$$

The first integral only needs to be carried out over the region where $\boldsymbol{j} \neq 0$, such as in the wires of the coil and the battery. If the specific resistance in the

wires or in the battery is ρ, from Ohm's law $\boldsymbol{E}+\boldsymbol{F}=\rho\boldsymbol{j}$, we get

$$\int \boldsymbol{E}\cdot\boldsymbol{j}\,\mathrm{d}V = \int \rho j^2\,\mathrm{d}V - \int \boldsymbol{F}\cdot\boldsymbol{j}\,\mathrm{d}V.$$

Here $\boldsymbol{F}$ is the electromotive force in the battery and $\int \boldsymbol{F}\cdot\boldsymbol{j}\,\mathrm{d}V$ is the work done per unit time by the battery to pass the current. If the temperature of the entire system is kept constant, $\int \rho j^2\,\mathrm{d}V$ is that part of the work which is dissipated as Joule heat. The second integral of eq. (5) may be rewritten as follows:

$$\begin{aligned}\frac{1}{4\pi}\int \boldsymbol{H}\cdot(\partial\boldsymbol{B}/\partial t)\,\mathrm{d}V &= \frac{1}{4\pi}\int \boldsymbol{H}\cdot\frac{\partial\boldsymbol{H}}{\partial t}\,\mathrm{d}V + \int \boldsymbol{H}\cdot\frac{\partial\boldsymbol{M}}{\partial t}\,\mathrm{d}V \\ &= \frac{1}{8\pi}\frac{\partial}{\partial t}\cdot\int \boldsymbol{H}^2\,\mathrm{d}V + \int \boldsymbol{H}\cdot\frac{\partial\boldsymbol{M}}{\partial t}\,\mathrm{d}V. \qquad (6)\end{aligned}$$

The first term of the last expression is the work done to create the field. Since $\int \boldsymbol{H}_j\cdot\boldsymbol{H}_M\,\mathrm{d}V=0$, it is seen from (5) that

$$\frac{1}{8\pi}\int \boldsymbol{H}^2\,\mathrm{d}V = \frac{1}{8\pi}\int \boldsymbol{H}_J^2\,\mathrm{d}V + \frac{1}{8\pi}\int \boldsymbol{H}_M^2\,\mathrm{d}V.$$

Here it should be noted that this includes the work done to create both the field due to the coil and the demagnetizing field due to the magnetization of the magnetic body. This work may be excluded from the definition of the work required to magnetize a magnetic body. The work done in magnetization is $\int \boldsymbol{H}\cdot(\partial\boldsymbol{M}/\partial t)\,\mathrm{d}V$. Multiplying by $\mathrm{d}t$, we get the work done to increase the magnetization by $\mathrm{d}\boldsymbol{M}$ from $\boldsymbol{M}$:

$$\mathrm{d}'A = \int (\boldsymbol{H}\cdot\mathrm{d}\boldsymbol{M})\,\mathrm{d}V = \int (\boldsymbol{H}_J + \boldsymbol{H}_M)\cdot\mathrm{d}\boldsymbol{M}\,\mathrm{d}V,$$

where the integration is over the volume of the magnetic body. The total work of magnetization is therefore

$$A = \int \mathrm{d}V \int_0^{\boldsymbol{M}} (\boldsymbol{H}_J + \boldsymbol{H}_M)\cdot\mathrm{d}\boldsymbol{M}.$$

It is important to notice that the demagnetizing field, $\boldsymbol{H}_M$, due to the magnetization must generally be included in the magnetic field. If the magnetic field, $\boldsymbol{H}$, and the magnetization, $\boldsymbol{M}$, are uniform, the volume integral simply gives a multiplication by the volume, V.

NOTE: It is only in the case where the magnetic body is an ellipsoid that the magnetic field in the body and the magnetization are uniform. If such is the case, the demagnetizing fields along the principal axes, x, y and z of the ellipsoid are given by

$$(\boldsymbol{H}_M)_\alpha = -N_\alpha M_\alpha \qquad (\alpha = x, y, z),$$

where the demagnetization coefficients N_x, N_y and N_z satisfy the rule

$$N_x + N_y + N_z = 4\pi .$$

The three coefficients can be calculated as functions of the axial ratios of the ellipsoid.

CHAPTER 2

THE SECOND LAW OF THERMODYNAMICS AND ENTROPY

In this chapter, we introduce the second law of thermodynamics and treat problems directly related to it. The object here is to understand the significance of this fundamental law and furthermore to obtain a concrete grasp of the concept of entropy, which is the most important thermodynamic quantity and still seems often somewhat too abstract to students.

Fundamental topics

§ 2.1. REVERSIBLE AND IRREVERSIBLE PROCESS

Reversible process: Suppose that when a system under consideration changes from a state, α, to another state, α', the environment changes from β to β'. If in some way it is possible to return the system from α' to α and at the same time to return the environment from β' to β, the process $(\alpha, \beta) \rightarrow (\alpha', \beta')$ is said to be reversible.

The above definition for reversibility is made in the broadest sense of the word. A narrower definition is often given as follows: a given process is reversible if it can be reversed in each step by infinitesimal changes of the conditions of the environment. A reversible process in this sense is none other than the quasi-static process explained in § 1.5. A quasi-static process can be reversed in this sense. A reversible process in the broader sense is not necessarily reversible in this strict sense. Although purely mechanical or electromagnetic phenomena are reversible in the broader sense, they may not be reversible in every respect*. Reversible processes which we normally consider are combinations of purely mechanical or electromagnetic processes and quasi-static thermal processes.

Therefore we may adopt the narrow definition of reversibility for thermal phenomena; a reversible process may be considered as a quasi-static process. Real physical processes proceed at finite speeds and are necessarily irre-

* Such an example is the motion of charged particles in a given magnetic field. In order to reverse the direction of motion, the magnetic field must be reversed because of the presence of the Lorentz forces. Thus without the reversal of magnetic field, such a motion is not reversible in the narrow sense.

versible, since they always involve some kind of friction. A reversible process is an idealization.

A process which is not reversible is said to be irreversible.

Reversible cycle and irreversible cycle: When the system under consideration changes from α to α while the environment changes from β to β' and the process $(\alpha, \beta) \rightarrow (\alpha, \beta')$ is reversible, the process is said to be a reversible cycle. When the process is irreversible, it is an irreversible cycle. In particular if the process is a quasi-static process, it is reversible in each step.

Reversible engine and irreversible engine: An arrangement which makes it possible to do work by making a system (working substance) pass through a cycle exchanging heat with the environment is called a *heat engine*. The engine is either reversible or irreversible depending on whether the cycle is reversible or irreversible.

§ 2.2. A LEMMA (CARNOT CYCLE)

A "Gedankenexperiment" using a Carnot cycle is one of the most powerful methods to treat problems concerning the second law of thermodynamics. Here we define the Carnot cycle in the narrow sense as one which uses an

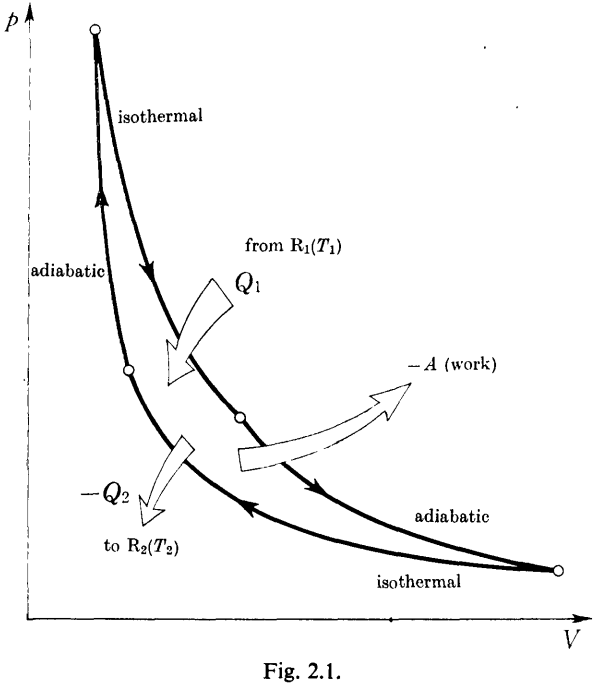


Fig. 2.1.

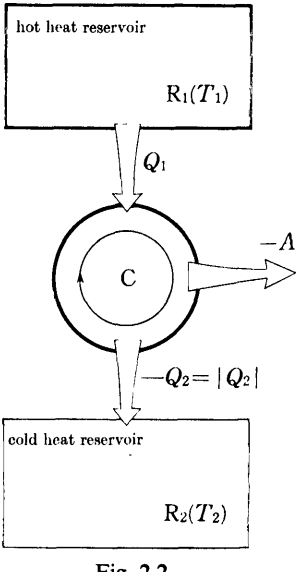


Fig. 2.2.

ideal gas as the working substance, as shown in Figure 2.1. If the amounts of heat absorbed during the isothermal processes in contact with heat reservoirs $R_1(T_1)$ and $R_2(T_2)$ are Q_1 and Q_2, then we must have

$$Q_1/T_1 + Q_2/T_2 = 0. \tag{2.1}$$

Since this can be proved using only the equation of state of an ideal gas and the first law of thermodynamics (see Chapter 1, problem 9), it may be regarded as a known lemma when discussing the second law of thermodynamics.

§ 2.3. THE SECOND LAW OF THERMODYNAMICS

Because it is an emperical law, there are many ways to state the second law of thermodynamics, and these are of course all equivalent. Here are the statements:

a) *Clausius' principle:* A process which involves no change other than the transfer of heat from a hotter to a cooler body is irreversible; or, it is impossible for heat to transfer spontaneously from a colder to a hotter body without causing other changes.

b) *Thomson's (or Kelvin's) principle:* A process in which work is transformed into heat without any other changes, is irreversible; or, it is impossible to convert all the heat taken from a body of uniform temperature into work without causing other changes.

c) *Principle of the impossibility of a perpetuum mobile of the second kind:* It is impossible to devise an engine operating in a *cycle* which does work by taking heat from a single heat reservoir without producing any other change (perpetuum mobile of the second kind).

d) *Carathéodory's principle:* For a given thermal equilibrium state of a thermally uniform system, there exists another state which is arbitrarily close to it but can never be reached from it by an adiabatic change.

NOTE: The statement "other changes" means changes that remain after the process is completed. The condition "operating in a cycle" in c) is important. It is possible to convert all the heat taken from a heat reservoir by isothermally expanding an ideal gas. However, this does not operate periodically. It is obvious that b) and c) are equivalent. Refer to problem 1 for the equivalence of a) and b). The proof showing the equivalence of d) to a) and b) is a little more difficult (see problem 30).

§ 2.4. THE EFFICIENCY OF A GENERAL CARNOT CYCLE

General Carnot cycle: Though there are various extensions of the Carnot

cycle, we refer to an engine which absorbs heat Q_1 and Q_2 from two heat reservoirs R_1 and R_2 and does work $A = Q_1 + Q_2$ on the environment. Therefore a Carnot cycle consists of two isothermal processes and two adiabatic processes. If these are reversible we have a *reversible Carnot cycle.*

Efficiency: If R_1 is the hot reservoir and R_2 the cold reservoir, then $Q_1 > 0$, $Q_2 < 0$, $A = Q_1 + Q_2 = Q_1 - |Q_2|$ and the efficiency η is

$$\eta = \frac{A}{Q_1} = 1 - \frac{|Q_2|}{Q_1}. \tag{2.2}$$

Therefore we have

$$1 - \eta = \frac{|Q_2|}{Q_1}. \tag{2.3}$$

Carnot's principle: The efficiency η of a reversible Carnot cycle operating between heat reservoirs R_1 and R_2 is uniquely determined by the temperatures θ_1 and θ_2 of the heat reservoirs and independent of the working substance. Furthermore, the efficiency, η', of any irreversible Carnot cycle operating between the same heat reservoirs is less than η: i.e.

$$\eta = \eta(\theta_1, \theta_2), \qquad \eta > \eta'. \tag{2.4}$$

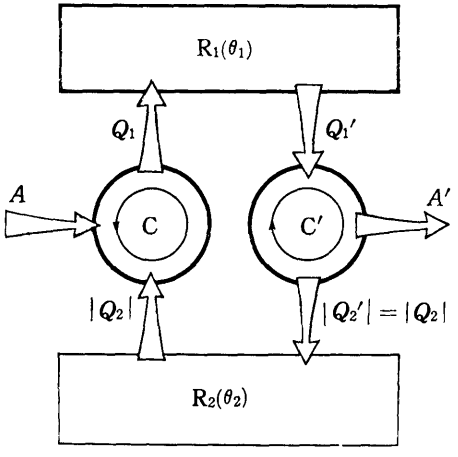


Fig. 2.3.

PROOF: Consider two Carnot cycles C and C′. C is a reversible cycle. It takes the heat Q_1 from the heat reservoir R_1 and gives $|Q_2|$ to R_2 doing the work $A = Q_1 - |Q_2|$. C′ is reversible or irreversible. It takes the heat Q_1' from R_1, giving $|Q_2'| = |Q_2|$ to R_2 and does the work $A' = Q_1' - |Q_2'|$. If C is operated in the reverse way (Fig. 2.3), the net result is that $Q_1' - Q_1$ is taken from R_1

and the work

$$A' - A = Q_1' - |Q_2'| - (Q_1 - |Q_2|) = Q_1' - Q_1$$

is done. According to Thomson's principle, we must have: $A' - A \leqq 0$, or

$$Q_1' \leqq Q_1 .$$

Therefore, we conclude that

$$\eta' = 1 - \frac{|Q_2|}{Q_1'} \leqq 1 - \frac{|Q_2|}{Q_1} = \eta .$$

If C′ is reversible, then C and C′ may be operated in reverse*, so that we have $\eta' \geqq \eta$, and hence $\eta = \eta'$.

§ 2.5. ABSOLUTE TEMPERATURE

The ratio of the absolute temperatures T_1 and T_2 of the heat reservoirs $R_1(\theta_1)$ and $R_2(\theta_2)$ is defined by

$$\frac{T_2}{T_1} = \frac{|Q_2|}{Q_1} = 1 - \eta(\theta_1, \theta_2), \tag{2.5}$$

where $\eta(\theta_1, \theta_2)$ is the efficiency of a reversible Carnot cycle operating between the two heat reservoirs. According to eq. (2.1), *the temperature given by an ideal gas thermometer agrees with the absolute temperature.* In order to fix the absolute temperature scale, it is necessary to give a numerical value to a reference point. When the reference point is set as

$$T_{\text{triple point of water}} = 273.16\,^\circ\text{K},$$

it is called *the Kelvin temperature scale.* In the following treatments, we will always use the absolute temperature unless we say otherwise.

Divertissement 4

Absolute temperature

The absolute temperature scale means that temperature scale which is determined by a thermodynamic method so that it does not depend on the choice of thermometric substance, the zero of the scale being defined as the lowest temperature which is possible thermodynamically. Absolute temperature, which is now used in thermal physics, was introduced by Lord Kelvin (William Thomson) in 1848 and is also called the Kelvin temperature.

* If C and C′ are reversible in each step, they can be operated in reverse. If they are reversible in the broad sense, they may not be operated in reverse. However, there exist processes $\bar{C}$ and $\bar{C}'$ which produce exactly the opposite effects in each cycle. Therefore we have the same result.

For the complete definition of the scale, we have two choices; one is to use two fixed points above zero and assign their temperature difference and the other is to use one fixed point and assign its numerical value. Until recently the calibration of the Kelvin temperature scale was performed using two fixed points: the ice point T_0 °K and the boiling point T_0+100 °K of pure water under 1 standard atm (= 101325 Newton/m²). We can measure T_0 by a gas thermometric method. At low pressures, the equation of state of a real gas can be written in the form

$$pV = \alpha + \kappa p.$$

We measure the values of pV, α and κ at the above two fixed points. Considering that α is equal to nRT, we have

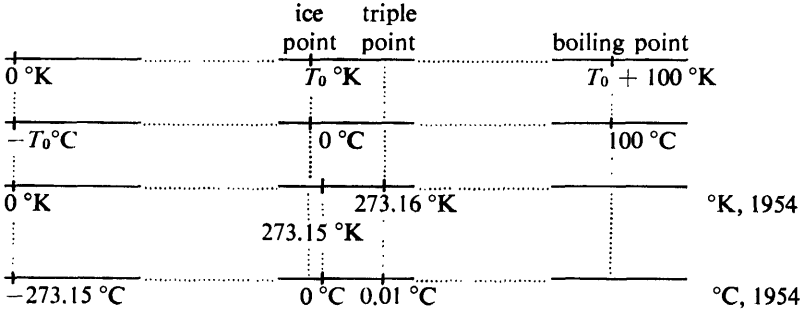
$$T_0 = \frac{100\alpha_0}{\alpha_{100} - \alpha_0}.$$

If we put $T_0=0$, we get the thermodynamic Celsius temperature scale. Hence $-T_0$ °C means absolute zero as measured by this scale.

The precise gas thermometric investigations of the Frenchman P. Chappuis from 1887 to 1917 gave the value of T_0 between 273.048 and 273.123. Inspired by this work, more than one hundred determinations of T_0 were performed until 1942. Among them, the results of W. Heuse and J. Otto of Germany, W. H. Keesom et al. of the Netherlands, J. A. Beattie et al. of the U.S.A. and M. Kinoshita and J. Oishi of Japan are noted for their high precision. Their values are found to lie between 273.149 and 273.174.

Considering these results and the fact that the triple point of pure water is very near to 0.0100 °C, the 10th General Conference on Weights and Measures in 1954 decided to use the triple point of the water as the fixed point and to assign the value 273.16 as its temperature. It also redefined the thermodynamic Celsius temperature t °C as $t = T - 273.15$, where T is the value of the absolute temperature determined from the above decision. The zero of the new thermodynamic Celsius temperature differs by about 0.0001° from the ice point.

For ordinary purposes, the differences in these new and old scales are quite negligible. However, for cases where a precision of 10^{-4} degree in the absolute value is required, we must take the differences into consideration.



NOTE: By eq. (2.5), the relation

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{2.6}$$

holds for a general reversible Carnot cycle, as in eq. (2.1). In order that the definition in eq. (2.5) is possible, it must be shown that

$$1 - \eta(\theta_1, \theta_2) = f(\theta_1, \theta_2) \tag{2.7}$$

where

$$f(\theta_1, \theta_2) = g(\theta_1)/g(\theta_2). \tag{2.8}$$

Once relation (2.8) is established, the arbitrary temperature scale, θ, is related to the absolute temperature scale, T, by $T(\theta) = Cg(\theta)$ where C is a constant. PROOF of eq. (2.8): Consider three Carnot cycles C_{12}, C_{23} and C_{13} as shown in Fig. 2.4 each of which operates between two of the three heat reservoirs R_1, R_2 and R_3. Let the amounts of heat received from each heat reservoir and the work done to the environment be denoted as indicated in the figure. From the first law, we have

$$A_{12} = Q_1 - Q_2, \qquad A_{23} = Q_2 - Q_3, \qquad A_{13} = Q_1' - Q_3.$$

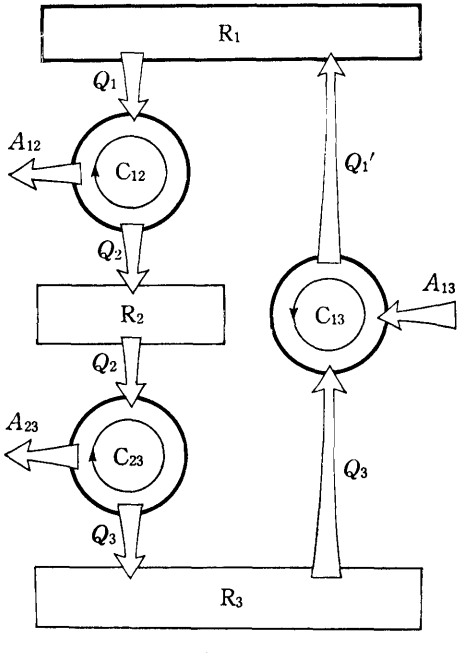


Fig. 2.4.

C_{13} is operated as a refrigerator in the figure. It is obvious that

$$Q_1 - Q_1' = A_{12} + A_{23} - A_{13} = 0,$$

for if $Q_1 - Q_1' > 0$ then net work is done by cooling R_1 alone in contradiction to Thomson's principle. If $Q_1 - Q_1' < 0$, we get the same contradiction to Thomson's principle when operating the system in reverse. Therefore we must have $Q_1 = Q_1'$. Therefore,

$$f(\theta_1, \theta_3) = \frac{Q_3}{Q_1} = \frac{Q_2}{Q_1}\frac{Q_3}{Q_2} = f(\theta_1, \theta_2) f(\theta_2, \theta_3).$$

The solution of this equation has the form given in eq. (2.8).

DIVERTISSEMENT 5

International practical temperature scale. Theoretically, the definition of the triple point of pure water as 273.16 °K is sufficient for the calibration of the entire Kelvin temperature scale. From a practical standpoint, however, the thermodynamic processes which are needed for the accurate measurement of the temperature are too cumbersome and some practical standard is required with which one can easily determine the temperature with fair accuracy. Such a standard was set up as the International Practical Temperature scale at the 7th General Conference on Weights and Measures in 1927, and was amended in 1948 and 1960. The temperatures measured using this scale are expressed on the Celsius scale and are designated as °C (Int. 1948). We sometimes write this as t_{int}. The international practical Kelvin temperature $T_{\text{int.}}$ is defined as $T_{\text{int.}} = t_{\text{int.}} + 273.16$, and is designated as T °K (Int. 1948).

The basis of the 1948 International Practical Temperature scale consists of the introduction of six fixed points of definition and the definition of the method of interpolation in four ranges. The fixed points of definition are shown in the table:

Boiling point of oxygen (Oxygen point)	−182.97 °C (Int. 1948)
Triple point of water	0.01
Boiling point of water	100
Boiling point of sulphur (Sulphur point)	444.6
Freezing point of silver (Silver point)	960.8
Freezing point of gold (Gold point)	1063

The freezing point of zinc, 419.505 °C, can replace the sulphur point. These values are at 1 standard atm except for the triple point of water.

The method of interpolation are as follows:

(a) 0° − 630.5° (freezing point of Sb)

t °C (Int. 1948) is defined by

$$R_t = R_0 (1 + At + Bt^2)$$

where R_t is the electrical resistance of the Pt wire used in the standard resistance thermometer at the temperature t. The quantities R_0, A and B should be determined from the values of R_t at the triple point of water, the boiling point of water and the sulphur point.

(b) $-182.97°$ (boiling point of oxygen) $-0°$

t is determined from

$$R_t = R_0 (1 + At + Bt^2 + C(t - 100)\, t^3)$$

where R_0, A and B are the same as in (a), and C is determined from R_t at the oxygen point.

(c) $630.5° - 1063°$ (freezing point of gold)

t is defined by

$$E = a + bt + ct^2$$

where E is the electromotive force of a Pt - Pt·Rh thermocouple when one junction is kept at 0 °C and the other is at t. The constants a, b and c should be determined from the values of E at 630.5 °C, the silver point and the gold point.

(d) above 1063° (gold point)

t is defined by

$$\frac{J_t}{J_{\mathrm{Au}}} = \frac{\exp(C_2/\lambda\,(t_{\mathrm{Au}} + T_0)) - 1}{\exp(C_2/\lambda\,(t + T_0)) - 1}$$

where J_t and J_{Au} are the spectral intensity at a wave-length λ of black body radiation at the temperature t and at the gold point t_{Au}, respectively. Also, $T_0 = 273.16$, $C_2 = 0.01438$ m deg and λ is measured in meters.

Detailed description of the other experimental conditions will be found in "Échelle Internationalle Pratique de Température de 1948, Edition amendée de 1960", the 11th General Conference on Weights and Measures.

In addition to the above six points of definition, nearly twenty fixed points are recommended as substandards: e.g., the solidifying point of CO_2, -78.5 °C.; the freezing point of Hg, -38.87 °C; the melting point of W, 3380 °C.; etc., under a pressure of 1 atm.

Below the oxygen point, we have no International Standard yet. However, workers in the field of physics at extremely low temperatures use a temperature scale defined by the vapor pressure equations of ^{4}He or ^{3}He.

The practical scale was determined with all possible care so that it can approximate the absolute temperature scale of 1954 with high precision. They can, however, in principle differ at each point. Their comparison in the U.S.A. gave 99.994 °C (thermodynamical, 1954) for the boiling point of water which is 100 °C (Int. 1948).

§ 2.6. CLAUSIUS' INEQUALITY FOR AN ARBITRARY CYCLE

When a system performs a cycle while in contact with the environment and absorbs heat $Q_i (i = 1, 2, \ldots, n)$ from the heat reservoir R_i at temperature

$T_i^{(e)}$ during the cycle, then the following holds

$$\sum_{i=1}^{n} Q_i/T_i^{(e)} \leqq 0. \tag{2.9}$$

If the change is continuous, the summation may be replaced by an integral, so that (2.9) becomes

$$\oint \mathrm{d}'Q/T^{(e)} \leqq 0. \tag{2.10}$$

PROOF: Consider an auxiliary heat source R_0 (at temperature T_0) and Carnot cycles $C_1, C_2, \ldots, C_n$. The cycle C_i operates between R_0 and the i-th heat reservoir R_i. Let Q_i' be the heat absorbed by C_i from R_0, and A_i' the work done on C_i by its surroundings when the cycle operates in such a way that it gives the heat Q_i to R_i. By (2.5) we have

$$Q_i' = Q_i \frac{T_0}{T_i^{(e)}}, \quad \text{and} \quad A_i' = Q_i - Q_i' = Q_i \left(1 - \frac{T_0}{T_i^{(e)}}\right).$$

If now the original cycle and auxiliary cycles $C_1, \ldots, C_n$ are operated together, the reservoirs $R_1, \ldots, R_n$ neither lose nor gain heat and the net result is that the heat $(Q_1' + \cdots + Q_n')$ is taken from the heat reservoir R_0 and work

$$\sum Q_i - \sum A_i' = T_0 \sum \frac{Q_i}{T_i^{(e)}}$$

is done on the environment. According to Thomson's principle, this must be equal to zero or negative. Thus, eq. (2.9) is proved. The equality holds when the cycle under consideration is reversible, because the operation can then be reversed.

§ 2.7. ENTROPY

Definition: A given thermal equilibrium state α_0 is chosen as the standard state of a system under consideration. The entropy $S(\alpha)$ of the system in another equilibrium state, α, is defined by

$$S(\alpha) = \int_{\substack{\alpha_0 \\ \text{quasi-static}}}^{\alpha} \mathrm{d}'Q/T, \tag{2.11}$$

where the integration is done along any quasi-static process which connects α to α_0, $\mathrm{d}'Q$ being the heat absorbed by the system at temperature T in an infinitesimal element of the whole process. In differential form this reads as

$$\mathrm{d}S = \mathrm{d}'Q/T. \tag{2.12}$$

According to the first law, eq. (1.5), this can be written as

$$\mathrm{d}S = (\mathrm{d}U - \mathrm{d}'A - \mathrm{d}'Z)/T\,. \tag{2.13}$$

If we use eqs. (1.7a) and (1.7b), this becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_i X_i\,\mathrm{d}x_i + \sum_j \mu_j\,\mathrm{d}N_j \qquad \text{(Gibbs' relation).} \tag{2.14}$$

This is a fundamental equation which combines the first and the second laws. Eq. (2.14) is a Pfaffian form

$$\mathrm{d}U = \sum_i y_i\,\mathrm{d}Y_i \tag{2.15}$$

(where $y_1 = T, y_2 = -p, y_3 = X_1, \ldots.\ Y_1 = S,\ Y_2 = V,\ Y_3 = x_1, \ldots$). For a closed system where we are only concerned with volume changes, eq. (2.14) becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V\,. \tag{2.16}$$

Entropy. A state quantity: Let L and L′ be two quasi-static processes connecting the states α_0 and α. If we apply eq. (2.10) to the reversible cycle, $\alpha_0(\mathrm{L})\alpha(\mathrm{L}')\alpha_0$, we have

$$\int_{\alpha_0(\mathrm{L})}^{\alpha} \frac{\mathrm{d}'Q}{T} + \int_{\alpha(\mathrm{L}')}^{\alpha_0} \frac{\mathrm{d}'Q}{T} = 0\,.$$

We know thus that the integral

$$\int_{\alpha_0(\mathrm{L})}^{\alpha} \frac{\mathrm{d}'Q}{T} = \int_{\alpha_0(\mathrm{L}')}^{\alpha} \frac{\mathrm{d}'Q}{T}$$

is determined by α_0 and α and is independent of L and L′. Therefore if α_0 is fixed, the integral, or $S(\alpha)$, is a state quantity uniquely defined for a given α.

NOTE: As mentioned in § 1.6, $\mathrm{d}'Q$, $\mathrm{d}'A$ and $\mathrm{d}'Z$ are not total differentials and depend on the process which connects the two states. In contrast to this, $\mathrm{d}'Q/T$ is a total differential for a quasi-static process and is equal to an infinitesimal change of the state quantity S; in other words, T is the *integrating denominator* of $\mathrm{d}'Q$.

Figure 2.5 illustrates the entropy of hydrogen gas as a function of temperature and pressure. Figure 2.6 shows the enthalpy of hydrogen gas as a function of pressure and entropy. Note that for the latter function, entropy can be conveniently used as an independent variable (see § 3.1).

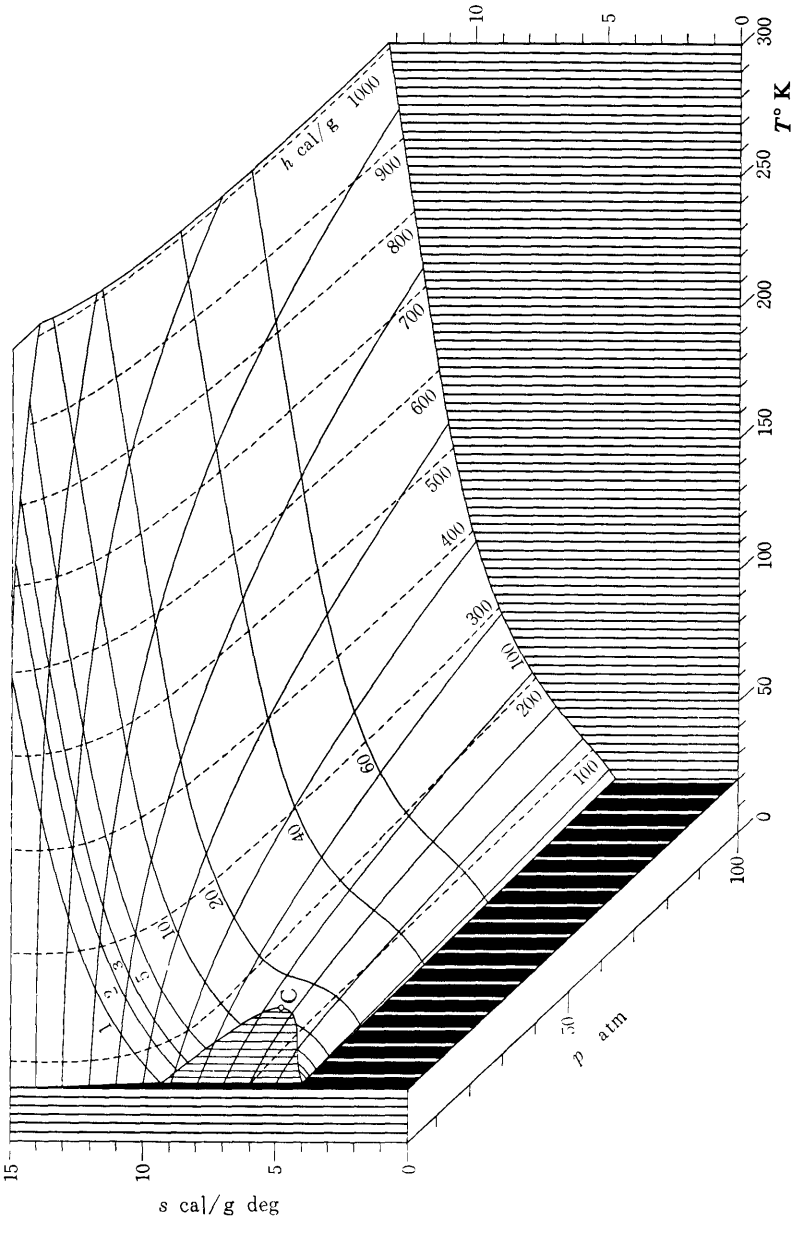


Fig. 2.5. Entropy of hydrogen.

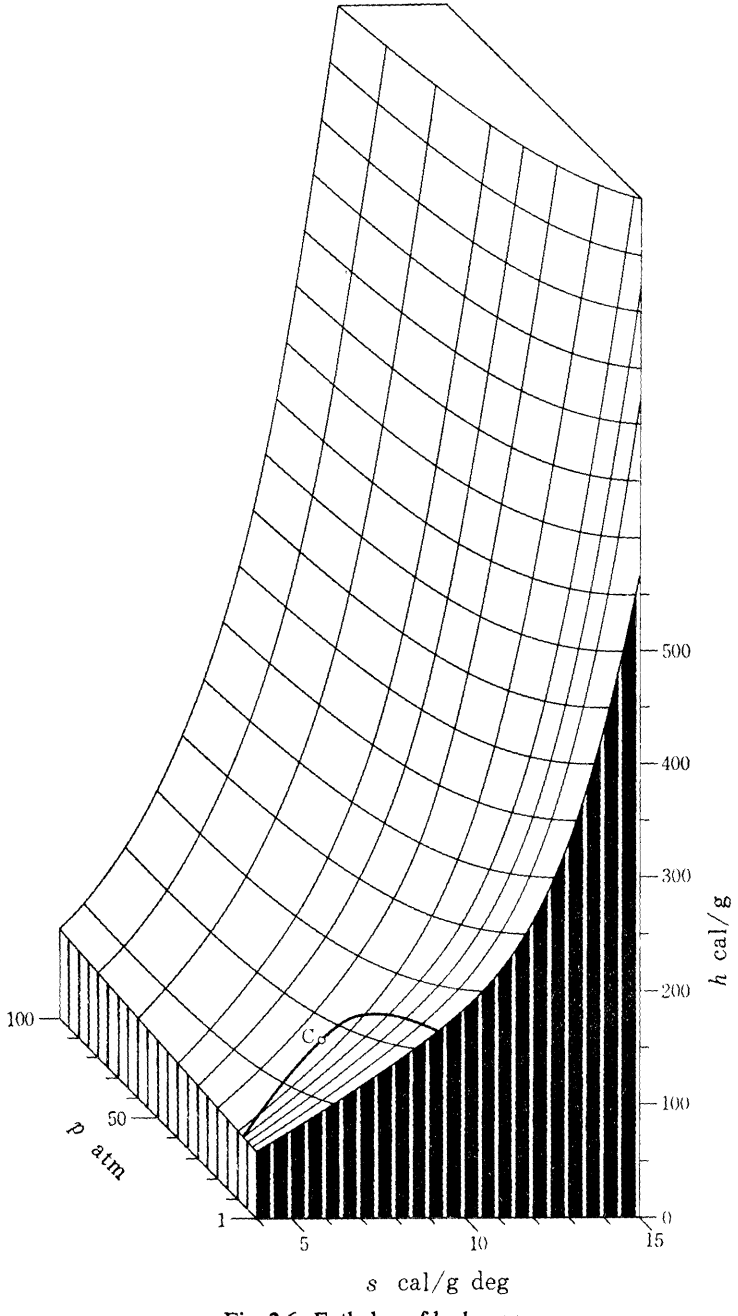


Fig. 2.6. Enthalpy of hydrogen

§ 2.8. ADDITIVITY OF ENTROPY

It would be almost obvious that the entropy is an extensive variable. If a homogeneous system is in thermal equilibrium, the entropy is proportional to the mass or volume, because the heat absorbed in each step of the process to bring the system in a thermodynamic state from a standard state is proportional to the mass.

A thermodynamic state in the general sense is a state in which local equilibrium exists. If the system is composed of subsystems, each of which is in thermal equilibrium, it is natural extension of the definition of the entropy to define it for the whole system as the sum of the entropies of subsystems. This means that, if the total entropy is S, then

$$S = S_{\mathrm{A}}(\alpha) + S_{\mathrm{B}}(\beta) + \cdots, \tag{2.17}$$

where the parts, A, B,... are in states α, β,... with entropies $S_{\mathrm{A}}(\alpha)$, $S_{\mathrm{B}}(\beta)$,... respectively. This is the generalization of the concept of entropy to general thermodynamic states.

§ 2.9. GENERAL EXPRESSION OF THE SECOND LAW

When a system under consideration, starting from a thermodynamic state α', reaches another state α'' through a certain process L, the following relations hold:
the second law:

$$\int_{\alpha'(\mathrm{L})}^{\alpha''} \sum \frac{\mathrm{d}'Q}{T^{(\mathrm{e})}} \leqq \Delta S, \qquad \text{where} \qquad \Delta S = S(\alpha'') - S(\alpha'); \tag{2.18}$$

the first law:

$$\int_{\alpha'(\mathrm{L})}^{\alpha''} \sum \mathrm{d}'Q = \Delta U - A - Z, \qquad \text{where} \qquad \Delta U = U(\alpha'') - U(\alpha'). \tag{2.19}$$

Here $\mathrm{d}'Q$ is the infinitesimal heat received by the various parts of the system from the environment (at temperature $T^{(\mathrm{e})}$), $\sum$ indicates the summation over the various parts of the system and the integration is carried along the process L. The equality holds only when L is a reversible process. For an infinitesimal process, eq. (2.18) becomes

$$\mathrm{d}'Q/T^{(\mathrm{e})} \leqq \mathrm{d}S. \tag{2.20}$$

If the temperature is uniform throughout the system, the environment may

be considered to be about at the same temperature. Then $T^{(e)}$ is replaced by the temperature T of the system, so that the relation, eq. (2.20), becomes

$$\mathrm{d}'Q \leqq T\,\mathrm{d}S, \tag{2.21}$$

or

$$\mathrm{d}U - T\,\mathrm{d}S \leqq \mathrm{d}'A + \mathrm{d}'Z. \tag{2.21a}$$

PROOF: Consider a quasi-static process, R, from α' to α'' and apply the inequality, eq. (2.9), to the cycle, $\alpha'(\mathrm{L})\alpha''(\mathrm{R})\alpha'$. Then we have

$$\int_{\alpha'(\mathrm{L})}^{\alpha''} \frac{\mathrm{d}'Q}{T^{(e)}} + \int_{\alpha''(\mathrm{R})}^{\alpha'} \frac{\mathrm{d}'Q}{T} \leqq 0,$$

hence

$$\int_{\alpha'(\mathrm{L})}^{\alpha''} \frac{\mathrm{d}'Q}{T^{(e)}} \leqq S(\alpha'') - S(\alpha').$$

The result, eq. (2.20), is the differential form of eq. (2.18). If the temperature of the system is uniform, the heat transfer takes place at that temperature so that we can assume $T^{(e)} = T$ and the relation eq. (2.21) holds. The inequality eq. (2.21a) is obtained by using the first law (1.5). Note that the inequalities (2.21) and (2.21a) are written only in terms of variables concerning the system under consideration.

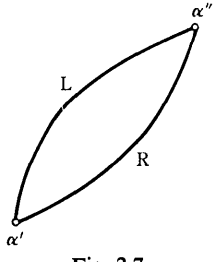


Fig. 2.7.

§ 2.10. THE DIRECTION OF AN ACTUAL CHANGE

A process L cannot be realized between two states α' and α'' of a given system if it violates inequality (2.18). This means that, for a system under a certain constraint, only those changes are possible which satisfy (2.18) with that constraint. If no conceivable change satisfies (2.18), the system cannot change and so it stays in equilibrium. Thus, inequality (2.18) gives conditions for possible changes or conditions for an equilibrium under various con-

ditions of constraint. These are summarized in the following:

Constraints	Direction of change	Equilibrium condition
a) General adiabatic system: $Q=0$	$\Delta S \geqq 0$	$S=\text{max.}$
a_1) Isolated system: $Q=0,\ A=0,\ Z=0,\ \Delta M=0$*	$(\Delta S)_{U,V,M} \geqq 0$	$S=\text{max.}$
b) Constant entropy: $\Delta S=0$	$\Delta U \leqq A+Z$	
b_1) Same as above, no work, closed system: $\Delta S=\Delta M=A=0$	$\Delta U \leqq 0$	$U=\text{min.}$
c) Closed system, constant temperature: $\Delta M=0,\ \Delta T=0$	$\Delta F \leqq A$	
c_1) Closed system, isothermal cycle: $\Delta M=0,\ \Delta T=0$	$0 \leqq A$	
c_2) Closed system, constant temperature and volume: $\Delta M=\Delta T=\Delta V=0$	$\Delta F \leqq 0$	$F=\text{min.}$
c_3) Closed system, constant temperature and pressure: $\Delta M=\Delta T=\Delta p=0$	$\Delta G \leqq 0$	$G=\text{min.}$

Here A is the externally applied work and

$$F = U - TS, \tag{2.22}$$

$$G = F + pV = H - TS. \tag{2.23}$$

F is called the Helmholtz free energy, and G, the Gibbs free energy (see Chapter 3).

NOTE: The left-hand side of (2.18) vanishes in case a) and therefore $\Delta S \geqq 0$ expresses the condition for a possible change. This can, of course, be applied also to a closed system *(Principle of the increase of entropy)*. The condition for a process of constant entropy b) is clear from (2.21a). Note, however, that we refer only to the system under consideration when we say constant entropy, for, in a general irreversible process, an increase in entropy may also take place in the environment. In isothermal processes c), the change ΔS_r of the entropy of the heat reservoir is

$$\Delta S_r = -Q/T^{(e)} = -Q/T$$

* By $\Delta M = 0$ we indicate that there is no exchange of matter.

($T^{(e)}=T$). Since the principle of the increase of entropy applies to the total entropy change, $\Delta S_t=\Delta S+\Delta S_r$, of the system and the heat reservoir, we must have

$$\Delta S_t = \Delta S - Q/T \geqq 0 .$$

Substituting $Q=\Delta U-A$, this becomes

$$\Delta U - T\Delta S \leqq A .$$

This is the condition for c) according to the definition of F. For a constant pressure $A=-p\Delta V$ is substituted to obtain the condition for c_3).

§ 2.11. MAXIMUM WORK AND MINIMUM WORK

Principle of maximum work: Consider the possible processes that may occur in an assembly of bodies which are not in thermal equilibrium with each other. The work that can be done on the surroundings in such a process is maximum when the process is reversible.

In particular, when the temperature, $T^{(e)}$, the pressure, $p^{(e)}$, and the chemical potential, $\mu_j^{(e)}$, of the j-th component are prescribed for the environment and the system undergoes a change that can be expressed by ΔS, ΔU, ΔV and ΔM_j, the first law (1.5) can be written as

$$Q = \Delta U + p^{(e)}\,\Delta V - \sum_j \mu_j^{(e)}\,\Delta M_j - W ,$$

where W is the work done by the environment on the system other than $-p^{(e)}\,\Delta V$ due to the change in volume. The second law (2.18), $Q \leqq T^{(e)}\,\Delta S$, gives the following theorems:

$$\text{i)}\quad W_{\min} \equiv \Delta U - T^{(e)}\,\Delta S + p^{(e)}\,\Delta V - \sum \mu_j^{(e)}\,\Delta N_j \leqq W . \tag{2.24}$$

Consider the case where $W_{\min}>0$. Then the work, W, that must be done by the environment in order to make this change is always greater than $W_{\min}$, which is the minimum work. W equals $W_{\min}$ only when the change is reversible.

$$\text{ii)}\quad W_{\max} \equiv -\left(\Delta U - T^{(e)}\,\Delta S + p^{(e)}\,\Delta V - \sum \mu_j^{(e)}\,\Delta N_j\right) \geqq -W . \tag{2.25}$$

Consider the case where $W_{\max}>0$. Then the work that can be extracted by this change, $-W=|W|>0$ is always less than $W_{\max}$ which is the maximum work. $|W|$ equals $W_{\max}$ only if the process is reversible.

Divertissement 6

Axiomatic foundation of thermodynamics. The axiomatic systematization of physics may not seem so important to the physicists of today. Now,

physics is more concerned, to be sure, with physical facts rather than man-made formal logic. At the same time, one should not forget that a systematic formulation of a theory is certainly very valuable, exhibiting clearly and helping us to understand what are the basic facts and what is the logic which weaves the fabric of physical theory. Towards the last decades of the nineteenth century, when physics became the queen of the exact sciences, the perfect axiomatization of physical theories was thought, at least by some physicists, to be the final goal of theoretical physics. This was most strongly influenced by the axiomatism which dominated mathematics at that time led by the great mathematician, David Hilbert.

Thermodynamics was probably the best suited among all physical theories for such axiomatization, the ideal model of which was Euclidean geometry. In fact, thermodynamics is unique even in the realm of classical physics in its highly logical construction upon a few basic laws – the abstraction of our experience being assumed as axioms. In its simple structure, it certainly resembles geometry.

Among a number of attempts at the axiomatization of thermodynamics, the best known and the most successful is probably that due to C. Carathéodory (Untersuchungen über die Grundlagen der Thermodynamik, Math. Ann. **61** (1909) 355). He replaced the traditional expressions of the second law by a very simple assertion as given by d) in § 2.3 in the text. This is based on a mathematical theorem which states that a Pfaffian form such as

$$\mathrm{d}'Q = X\,\mathrm{d}x + Y\,\mathrm{d}y + Z\,\mathrm{d}z$$

possesses an integrating factor if, and only if there exists in every neighborhood of a point P at least one point P′ which cannot be reached from P along any curve on the surface determined by the condition that $\mathrm{d}'Q=0$. A critical review of Carathéodory's theory, which is most easily accessible for physics students, is an old article by Max Born which appeared in Physikalische Zeitschrift XXII (1921) 218, 249 and 282. See also A. H. Wilson, *Thermodynamics and Statistical Mechanics* (Cambridge Univ. Press, 1957) p. 64.

Examples

1. Derive Clausius' principle from Thomson's principle. Also derive Thomson's principle from Clausius' principle.

SOLUTION

In order to show that Clausius' principle can be derived from Thomson's principle, it is sufficient to show that Thomson's principle is violated if Clausius' principle is violated. Clausius' principle would be violated if a positive amount of heat Q_1 could be removed from a low temperature heat reservoir, R_1, and be transferred to a hotter reservoir, R_2, without leaving

any other changes. If this process is possible, combine it with a Carnot cycle C between the two heat reservoirs in which the heat Q_1+Q_2 (Q_2 is also positive) is taken from R_2 and the work equivalent to Q_2 is done to the environment while Q_1 is given to R_1. Then the net result would be that the heat Q_2 was taken from R_2 and was completely converted to work. This would violate Thomson's principle.

Next we show that Clausius' principle is violated if Thomson's principle is violated. By violating Thomson's principle, it is possible, as mentioned above, to extract a positive heat Q_2 from the heat reservoir, R_2, and convert it completely into work (without any other changes). Apply this work to a Carnot cycle extracting heat, Q_1 ($Q_1>0$) from reservoir R_1 (cold) and giving the heat Q_1+Q_2 to R_2. By these two processes there is no change other than the transfer of heat Q_1 from a cold reservoir R_1 to a hot reservoir R_2. This is a contradiction of Clausius' principle.

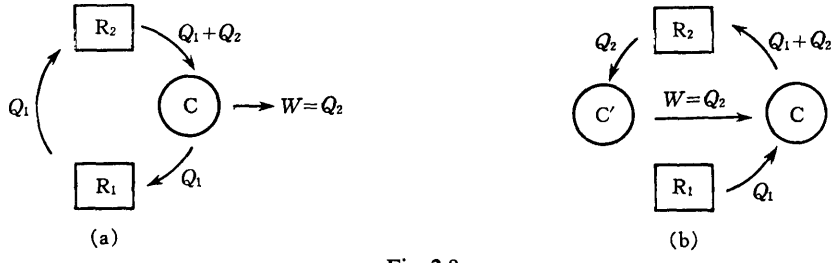


Fig. 2.8.

2. Show that the internal energy of a material whose equation of state has the form $p=f(V)T$ is independent of the volume. Here p is the pressure, T the absolute temperature, and $f(V)$ is a function of V only.

SOLUTION

If we let the internal energy be U and the entropy be S, from eq. (2.16) we have

$$\mathrm{d}S=\frac{1}{T}(\mathrm{d}U+p\,\mathrm{d}V), \tag{1}$$

$$\left(\frac{\partial S}{\partial V}\right)_T=\frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T+\frac{p}{T}, \tag{2}$$

$$\left(\frac{\partial S}{\partial T}\right)_V=\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V. \tag{3}$$

The equation, $\partial^2 S/\partial T\,\partial V=\partial^2 S/\partial V\,\partial T$ (the condition for $\mathrm{d}S$ to be an exact

differential), gives

$$\frac{\partial}{\partial T}\left(\frac{1}{T}\frac{\partial U}{\partial V}\right)+\frac{\partial}{\partial T}\left(\frac{p}{T}\right)=\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right).$$

Since $\partial^2 U/\partial T\,\partial V=\partial^2 U/\partial V\,\partial T$, we have

$$\left(\frac{\partial U}{\partial V}\right)_T=T^2\frac{\partial}{\partial T}\left(\frac{p}{T}\right)_V \tag{4}$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p. \tag{5}$$

Now, since $p=f(V)\,T$, the right side of eq. (4) vanishes and

$$(\partial U/\partial V)_T=0,$$

showing that U does not depend on V.

3. The internal energy, u, of a unit volume of a gas is a function of T only and the equation of state for the gas is given by $p=\frac{1}{3}u(T)$. Determine the functional form of $u(T)$.

SOLUTION

Consider this gas with volume V and at temperature T. The internal energy, U, can be written as

$$U=Vu(T). \tag{1}$$

Substitute eq. (1) and $p=\frac{1}{3}u(T)$ into eq. (5) of example 2, then we have

$$u(T)=\tfrac{1}{3}T\frac{\mathrm{d}u(T)}{\mathrm{d}T}-\tfrac{1}{3}u(T), \tag{2}$$

$$T\frac{\mathrm{d}u(T)}{\mathrm{d}T}-4u(T)=0.$$

By integration, we have

$$\log u(T)-4\log T=\text{const.},$$

$$u(T)=(\text{const.})\times T^4, \tag{3}$$

i.e., u is proportional to the fourth power of T. (A gas of light quanta (photons), i.e. the thermal radiation field is such a gas.)

4. Prove the following equation by operating a Carnot cycle using gas between

two heat reservoirs of temperature T_1 and $T_2 = T_1 - \mathrm{d}T$:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_T + p\right\},$$

where p, V and U are the pressure, the volume and the internal energy, respectively.

SOLUTION

Let the volume of the gas in state i ($i = 1, 2, 3, 4$) be V_i and the amounts of heat absorbed during the isothermal processes $1 \to 2$ and $3 \to 4$ be Q_1 and Q_2. By the first law (2.19) we have

$$Q_1 = \int_1^2 \left\{\left(\frac{\partial U}{\partial V}\right)_T + p\right\} \mathrm{d}V \tag{1}$$

and

$$Q_1 + Q_2 = \int_1^2 p\,\mathrm{d}V + \int_2^3 p\,\mathrm{d}V + \int_3^4 p\,\mathrm{d}V + \int_4^1 p\,\mathrm{d}V. \tag{2}$$

Because of the assumption of an ideal Carnot cycle, eq. (2.6) holds:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \tag{3}$$

Since $T_1 - T_2 = \mathrm{d}T$ is an infinitesimal, we may put $V_2 \fallingdotseq V_3$ and $V_4 \fallingdotseq V_1$ and

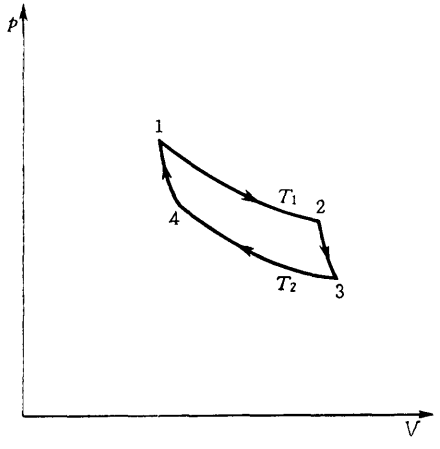


Fig. 2.9.

omit the second and the fourth terms in eq. (2). Further, the infinitesimal difference of p at the corresponding points (for the same value of V) on $1 \to 2$ and $3 \to 4$ can be put $(\partial p/\partial T)_V (T_2 - T_1) = -(\partial p/\partial T)_V \, \mathrm{d}T$, so that eq. (2) becomes

$$Q_1 + Q_2 = \int_1^2 p \, \mathrm{d}V + \int_3^4 p \, \mathrm{d}V = \int_1^2 p \, \mathrm{d}V - \int_4^3 p \, \mathrm{d}V = + \mathrm{d}T \int_1^2 \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V . \tag{4}$$

Now, eq. (3) can be written as

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \frac{1}{T_2}(Q_1 + Q_2) - \frac{\mathrm{d}T}{T_2^2} Q_1 = 0 , \tag{5}$$

or

$$Q_1 + Q_2 = + \frac{\mathrm{d}T}{T_2} Q_1 . \tag{6}$$

From eqs. (4), (6) and (1) we have

$$\int_1^2 \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V = \frac{1}{T_2} \int_1^2 \left\{ \left(\frac{\partial U}{\partial V}\right)_T + p \right\} \mathrm{d}V . \tag{7}$$

Since the state 2 can be any point on the isothermal line passing through the state 1, eq. (7) implies

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{T} \left\{ \left(\frac{\partial U}{\partial V}\right)_T + p \right\} . \tag{8}$$

5. Two kinds of ideal gases at equal pressure and temperature, initially separated in two containers, are mixed by diffusion. Show that the entropy is increased in this process by an amount

$$\Delta S = - R \left\{ n_1 \log \frac{n_1}{n_1 + n_2} + n_2 \log \frac{n_2}{n_1 + n_2} \right\} , \tag{1}$$

where n_1 and n_2 are the moles of component gases. Assume that no change in pressure and temperature occurs due to the diffusion and that the partial pressure of each gas in the mixture is proportional to the molar concentration.

SOLUTION

Initially the gases 1 and 2 had the volumes $V_1 = n_1 RT/p$ and $V_2 = n_2 RT/p$ and were separated by a wall. When the wall is removed, they mix by

diffusion. Instead of considering the diffusion process itself, we consider first a process which *reversibly* separates the mixed gas in the state $(V=V_1+V_2, T, p)$ into the pure gases, one in the state (V, T, p_1) and the other in (V, T, p_2). Such a process is realized by the arrangement shown in Fig. 2.10. Two containers of volume V, are superimposed where the wall b is semipermeable allowing only the gas 2 to pass while the wall a is semipermeable to the gas 1. The pressure of the impermeable gas on the semipermeable wall is equal to the partial pressure of that gas. Hence, as the two containers are drawn apart, the walls of the container with the gas 1 experience the partial pressure p_1, but this gives rise to no resultant force on the container, and so no work is done adiabatically, the internal energy and the temperature remains unchanged. There is no change in the entropy.

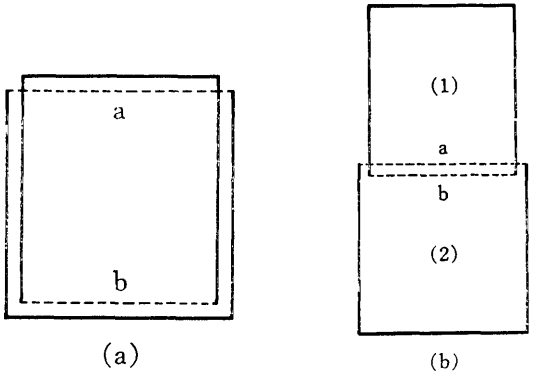


Fig. 2.10.

Now, in order to bring the gases back to the initial states, the separate gases are isothermally compressed from volume V to V_1 and V_2 respectively. By integrating $\mathrm{d}S=\mathrm{d}'Q/T=p\,\mathrm{d}V/T=nR\,\mathrm{d}V/V$, we obtain the change in entropy for each as

$$\Delta S_1 = n_1 R \log \frac{V_1}{V}, \qquad \Delta S_2 = n_2 R \log \frac{V_2}{V}. \tag{2}$$

Therefore, $\Delta S_1+\Delta S_2$ is the change in entropy for reversibly separating the mixed gases. Thus the entropy increase in the diffusion must have been equal to

$$\Delta S = -(\Delta S_1 + \Delta S_2) = -R\left\{n_1 \log \frac{V_1}{V} + n_2 \log \frac{V_2}{V}\right\}$$

$$= -R\left[n_1 \log \frac{n_1}{n_1+n_2} + n_2 \log \frac{n_2}{n_1+n_2}\right].$$

6. When a magnetic material obeys Curie's law $M = CH/T$ (where M is the magnetization, H is the field, T is the absolute temperature, and C is a constant), show that

$$\mathrm{d}T = (CH/C_H T)\,\mathrm{d}H$$

for an adiabatic change. C_H is the heat capacity per unit volume at constant magnetic field.

SOLUTION

Let the internal energy, entropy and the magnetization per unit volume be u, s and M respectively. (We do not consider a change in volume.) s is a function of T and H, so that we have

$$T\,\mathrm{d}s = T\left(\frac{\partial s}{\partial T}\right)_H \mathrm{d}T + T\left(\frac{\partial s}{\partial H}\right)_T \mathrm{d}H. \tag{1}$$

By definition, $C_H = T(\partial s/\partial T)_H$. Furthermore the relation

$$\left(\frac{\partial s}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \tag{2}$$

is obtained in the following way; from $\mathrm{d}u = T\,\mathrm{d}s + H\mathrm{d}M$ we have

$$\left(\frac{\partial u}{\partial T}\right)_H = T\left(\frac{\partial s}{\partial T}\right)_H + H\left(\frac{\partial M}{\partial T}\right)_H, \qquad \left(\frac{\partial u}{\partial H}\right)_T = T\left(\frac{\partial s}{\partial H}\right)_T + H\left(\frac{\partial M}{\partial H}\right)_T. \tag{3}$$

Differentiate the first equation with respect to H and the second with respect to T; then setting the two equal to each other gives (2). From (1) we have

$$T\,\mathrm{d}s = C_H\,\mathrm{d}T + T\left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H.$$

Under adiabatic conditions ($\mathrm{d}s = 0$), the relation

$$\mathrm{d}T = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H = \frac{CH}{C_H T}\,\mathrm{d}H$$

is obtained.

7. Show that when there is no exchange of matter with the environment, the minimum work $\mathrm{d}W_{\min}$ is

(i) equal to the increase in the Helmholtz free energy, $\mathrm{d}F$, for a change at constant temperature and volume;

(ii) equal to the increase in the Gibbs free energy $\mathrm{d}G$ for a change at constant temperature and constant pressure.

SOLUTION

For an isothermal process the temperature of the system is equal to the temperature $T^{(e)}$ of the environment so that eq. (2.24) gives

$$dW_{min} = dU - T\,dS + p^{(e)}\,dV = dF + p^{(e)}\,dV\,. \tag{1}$$

We have used the definition for the Helmholtz free energy in eq. (2.22). For the condition of constant volume ($dV=0$) (1) results in $dW_{min}=dF$. If the pressure of the system is constant and is equal to the external pressure, $p^{(e)}$, (1) gives $dW_{min}=dG$ by definition of the Gibbs free energy, eq. (2.23).

Problems

[A]

1. Using Clausius' principle, prove Clausius' inequality,

$$\sum_{i=1}^{n} \frac{Q_i}{T_i^{(e)}} \leqq 0\,. \tag{2.9}$$

2. When a system is returned to its original state through an isothermal reversible change, the net heat absorbed from its environment is zero and also the work done is zero. Prove this statement (i) by using Clausius' inequality and (ii) directly by Thomson's principle.

3. Show that, if two quasi-static adiabatics intersect, Thomson's principle is contradicted.

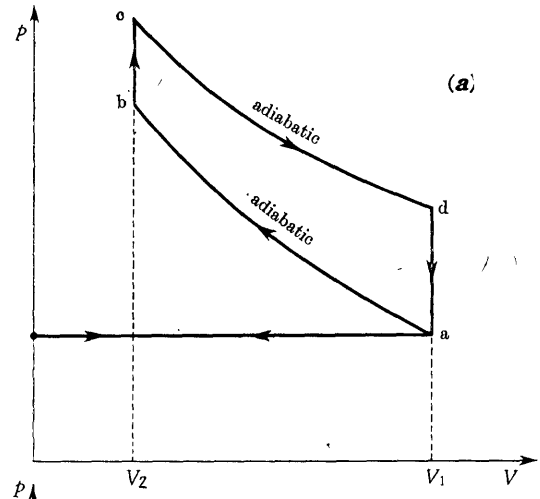
4. If T_{max} is the maximum temperature of the heat reservoirs from which a thermal engine receives heat and T_{min} is the minimum temperature of the heat reservoirs to which it gives up heat, show that the efficiency of the engine, η, never exceeds $1-(T_{min}/T_{max})$.

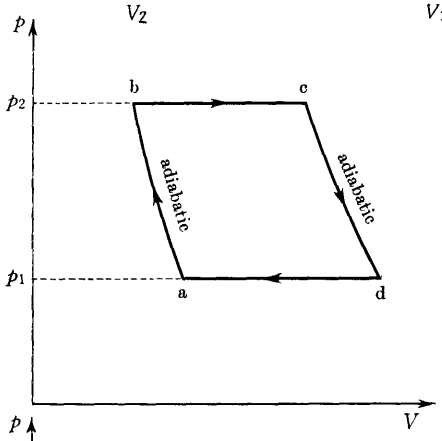
5. Show that the efficiencies of the three cycles listed below for an ideal gas are as given in the list.
   (i) Otto cycle (Figure a):

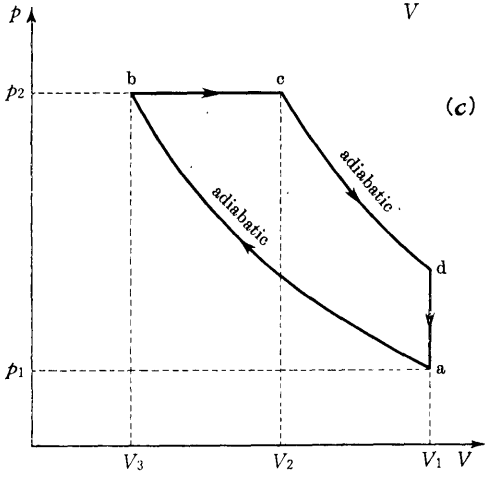
$$\eta = 1 - (V_2/V_1)^{\gamma-1}\,,$$

   (ii) Joule cycle (Figure b):

$$\eta = 1 - (p_1/p_2)^{(\gamma-1)/\gamma}\,,$$


p
c
b
(a)
adiabatic
adiabatic
d
a
V2
V1
V


p
b
c
p2
(b)
adiabatic
adiabatic
p1
a
d
V

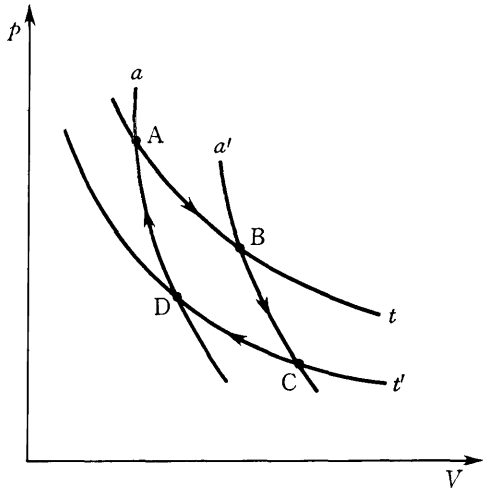

p
b
c
p2
(c)
adiabatic
adiabatic
d
p1
a
V3
V2
V1
V

(iii) Diesel cycle (Figure c):

$$\eta = 1 - \frac{1}{\gamma}\frac{(V_2/V_1)^\gamma - (V_3/V_1)^\gamma}{(V_2/V_1) - (V_3/V_1)}.$$

Assume that C_V, C_p and $C_p/C_V \equiv \gamma$ are constant.

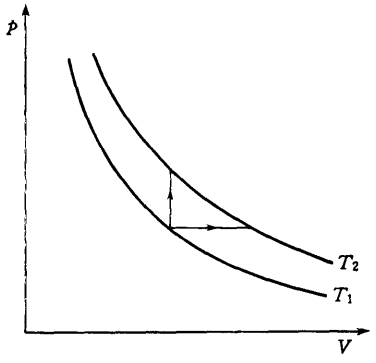
6. Let for a given material the intersections of adiabatics a, a' and isotherms t, t' be A, B, C and D in the p–V diagram. Show that in a cyclic process ABCD the ratio of the heat absorbed during AB to the heat given off during CD is determined by t, t' and is independent of the choice of the adiabatics.



7. Derive the entropy of an ideal gas when its molar specific heat at constant volume is constant, $C_V = C_V^0$.

8. An ideal gas of volume V_1 expands adiabatically in vacuum. Calculate the increase in entropy of the gas when the final volume is V_2 and show that this process is irreversible.

9. Consider the increase in entropy when an ideal gas is heated from T_1 to T_2 (i) at constant pressure and (ii) at constant volume. Show that the entropy increase in the first case is γ times that in the second case, where γ is the ratio of the specific heats at constant pressure and constant volume.



10. Experimentally it has been found for a given gas that the product of the pressure, p, and the specific volume, v, is a function only of the temperature and that the internal energy is also a function only of temperature. How much can be said about the equation of state of this gas from the viewpoint of thermodynamics?

11. The relations (a) $pV=f(\theta)$ and (b) $(\partial U/\partial V)_\theta=0$ are given for a gas. Show that $f(\theta)$ has the significance of an absolute temperature. Here θ is the temperature on some arbitrary temperature scale, p is the pressure, V is the volume and U is the internal energy.

12. Calculate the entropy density s of the radiation field using the following relations between the energy density, u, radiation pressure, p, and the absolute temperature T:

$$p = \tfrac{1}{3}u, \qquad u = \sigma T^4 \qquad (\sigma \text{ is a constant}).$$

Also draw the isothermal lines and adiabatic lines and consider a Carnot cycle.

13. The internal energy of a paramagnetic material is known to be independent of its magnetization M. Show that a temperature defined by the inverse of its magnetic susceptibility ($\theta=1/\chi$, $\chi=M/H$) is proportional to the absolute temperature.

14. (i) Prove that the ratio of the adiabatic compressibility to the isothermal compressibility is equal to the ratio of the specific heat at constant volume to that at constant pressure. (*Hint:* This is the same problem as example 7

in Chapter 1, but we use the entropy. For another solution, see the solution to problem 5 in Chapter 3.)
(ii) Show that the ratio of the adiabatic magnetic susceptibility to the isothermal susceptibility is equal to the ratio of the specific heat at constant magnetization to that at constant field.

15. Prove the following equations:

$$\text{(i)} \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

(*Hint*: $\mathrm{d}U$ is an exact differential.)

$$\text{(ii)} \quad \left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V.$$

(*Hint*: $\mathrm{d}S$ or $\mathrm{d}H$ is an exact differential.)

16. Prove the following equations:

$$\text{(i)} \quad \left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}, \qquad \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T},$$

$$\text{(ii)} \quad \frac{\partial^2 u}{\partial T \partial v} = T\frac{\partial^2 s}{\partial T \partial v}, \qquad \frac{\partial^2 h}{\partial T \partial p} = T\frac{\partial^2 s}{\partial T \partial p},$$

$$\text{(iii)} \quad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v, \qquad \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad \text{(Maxwell's relations)},$$

where u, h, s are the energy, enthalpy and entropy per unit mass respectively and c_v and c_p are the specific heats at constant volume and constant pressure.

17. Prove the following equations:

$$\text{(i)} \quad c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v = \frac{\alpha^2 v T}{\beta},$$

where

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p, \qquad \beta = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T;$$

$$\text{(ii)} \quad \left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p, \qquad \left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

18. Calculate the change in entropy, Helmholtz free energy and Gibbs free energy when a mole of ideal gas is compressed from 1 atm to 100 atm at 20 °C.

19. At 25 °C the volume of water V is given by

$$V = 18.066 - 0.000715p + 0.000000046p^2 \text{ cm}^3/\text{mol}$$

for p between 0 and 1000 atm and

$$\left(\frac{\partial V}{\partial T}\right)_p = 0.0045 + 0.0000014p \text{ cm}^3/\text{deg mol}.$$

Find the work necessary at 25 °C to compress 1 mole of water from 1 atm to 1000 atm and the increase in its internal energy.

20. The heat of fusion of ice at 1 atm and 0 °C is $\Delta H = 1436.3$ cal/mol and the heat of vaporization at 1 atm and 100 °C is $\Delta H = 9717.1$ cal/mol. Assuming an average heat capacity of 18.046 cal/deg mol at 1 atm between 0 °C and 100 °C for water, calculate the difference of the entropy of one mole of ice at 1 atm and 0 °C, and the entropy of one mole of steam at 100 °C and 1 atm.

21. A substance has a specific heat c_s in the solid state and a specific heat c_l in the liquid state. It absorbs a latent heat, Q_0, at a temperature, T_0, changing from solid to liquid. Assuming all specific heat values to be independent of the temperature, calculate how much more entropy M gram of this material has at temperature T_1 ($< T_0$) in the supercooled liquid state as compared with the solid state at the same temperature. (Assume the specific heat of the supercooled liquid to be also c_l.)

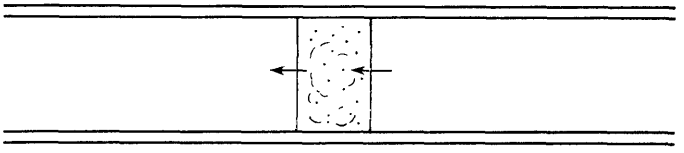
22. Suppose it is found experimentally for a solid that

$$(\partial V/\partial T)_p = a + bp + cp^2$$

at temperature T for $p_A \leqq p \leqq p_B$. How much will the entropy increase when the solid is compressed from a pressure p_A to p_B at a constant temperature T.

23. Express the coefficient $V(\partial T/\partial V)_S$, which indicates the temperature change for a quas-istatic adiabatic expansion of a gas, in terms of quantities that can be derived from the equation of state.

24. In the Joule-Thomson experiment, a gas is forced to flow under steady state conditions from the high pressure side of a cotton plug in a pipe with an adiabatic wall to the low pressure side of the plug, while the pressures at both sides are kept constant (see the figure). As a result of this, the temperature differs at the two sides of the plug. Show that this is an experiment at constant enthalpy and express $(\partial T/\partial p)_H$, which indicates the magnitude of this effect (Joule-Thomson coefficient), in terms of C_p and $(\partial V/\partial T)_p$. Also, when $pV = RT + B(T)p$ is a good approximation to the equation of state, express the Joule-Thomson coefficient in terms of B.



25. Gay-Lussac measured the change in the gas temperature when it underwent a free expansion into vacuum. Write the equation giving the temperature change $\mathrm{d}T$ when a gas makes a free expansion from V to $V + \mathrm{d}V$.

26. A paramagnetic substance has a magnetic susceptibility obeying the Curie law, $\chi = C/T$ (C is const.), and an internal energy given by $U = aT^4$ (a is a positive const.). (i) Obtain the heat of magnetization when this material is kept at T_1 and the field is increased from 0 to H_1. (ii) If the field is reduced adiabatically from H_1 to zero, what will be the change in temperature? (Adiabatic demagnetization.)

27. The magnetization M of a paramagnetic body was measured over a temperature range and it was found to depend only on H/T, i.e., $M = f(H/T)$. Show that the internal energy is independent of M and also find the functional form of the entropy S.

28. Consider all possible processes by which a body at temperature T_1 with a heat capacity, C, can lose heat and cool down to the temperature T_0 ($T_0 < T_1$) of a heat reservoir. How can one make the work done in this process to be maximum? What is the maximum value? For simplicity assume C to be a constant.

29. The heat of fusion of ice at 0 °C is 1436.3 cal/mol. A ton of ice is to be made by a refrigerator in a room at 25 °C. If the cost of electricity is 12 cents per kilowatt hour, what is the minimum cost of electricity necessary to make this ice?

[B]

30. Derive Carathéodory's principle from Thomson's principle.

31. Show that if the mixing of two different ideal gases by diffusion were a reversible process it would be inconsistent with Thomson's principle.

32. Two ideal gases, a mole each, with heat capacities C_V' and C_V'' are separated in a cylinder by an adiabatic movable piston. Show that this thermally inhomogeneous system is non-holonomic, i.e. there does not exist an integrating factor for $d'Q$ in this system.

33. If the internal energy of a material is independent of the volume, prove the following:

(i) the specific heat at constant volume C_V is a function of T only;

(ii) the volume V is a function of p/T only;

(iii) the difference between the specific heats at constant pressure and at constant volume is a function of p/T only.

34. Show that the specific heat at constant volume for a van der Waals gas is a function of T only and find the expression for its internal energy and the entropy.

35. Show that for a gas which obeys the van der Waals equation $(p+a/V^2)\times$ $\times(V-b)=RT$ and whose molar specific heat at constant volume C_V is constant and independent of temperature, the internal energy (per mole) U is given by

$$U = C_V T - a/V + \text{const}.$$

and that for an adiabatic quasi-static change

$$T(V-b)^{\gamma-1} = \text{const.} \qquad \text{or} \qquad (p + a/V^2)(V-b)^{\gamma} = \text{const.},$$

where $\gamma=(C_V+R)/C_V$. Also determine the temperature change when this gas undergoes a free expansion in vacuum.

36. Obtain the Joule-Thomson coefficient $(\partial T/\partial p)_H$ for a dilute van der Waals gas to second order in $nb/V(\ll 1)$ and $na/VRT(\ll 1)$. Also find the temperature T_i where the Joule-Thomson effect vanishes and express it in terms of the critical temperature $T_c=8a/27Rb$.

37. A real gas is not an ideal gas. The equations of state of a real gas can, for small values of p, be expressed by

$$(1)\quad pV = A + Bp + Cp^2 + \cdots \qquad \text{and} \qquad (2)\quad U = \alpha + \beta p + \gamma p^2 + \cdots$$

where $A, B, C, \ldots$ and $\alpha, \beta, \gamma, \ldots$ are known functions of temperature. Show that the absolute temperature can be measured using this gas.

38. The expansion coefficient $\alpha = V^{-1}(\partial V/\partial\theta)_p$ for a given substance is measured using an arbitrary temperature scale θ. The heat that is absorbed when the substance is expanded at constant temperature by changing the pressure p is also measured: $-\mathrm{d}'Q/\mathrm{d}p \equiv L_p$ (latent heat of expansion). Discuss the method and principles involved in connecting the empirical temperature θ to the absolute temperature.

39. Show that the internal energy U and the entropy S for a unit volume of a paramagnetic substance that obeys the Curie-Weiss law $\chi = C/(T-\theta)$ (where C and θ are constants, T is the absolute temperature and χ is the susceptibility) can be given by the following expressions:

$$U = \int^T C_M \,\mathrm{d}T - \tfrac{1}{2}(\theta/C)\, M^2 + \text{const.},$$

$$S = \int^T C_M \frac{\mathrm{d}T}{T} - \tfrac{1}{2}M^2/C + \text{const.},$$

where C_M is the heat capacity for constant M.

40. Prove the following relationship between the volume magnetostriction and the pressure coefficient of magnetization:

$$\left(\frac{\partial V}{\partial H}\right)_{p,T} = -\left(\frac{\partial I}{\partial p}\right)_{H,T}.$$

Next show that, when the field is increased isothermally from 0 to H, the change in volume ΔV (when $|\Delta V| \ll V$) is given by

$$\frac{\Delta V}{V} = \tfrac{1}{2}H^2\left\{\beta\chi - \left(\frac{\partial\chi}{\partial p}\right)_T\right\}.$$

Here I is the magnetic moment of the entire sample, $\beta = -(1/V)\,(\partial V/\partial p)_{H,T}$ is the isothermal compressibility and $\chi = I/HV$ is the isothermal magnetic

susceptibility. The magnetic field and magnetization are assumed to be uniform in the sample.

41. When there is no exchange of matter with the environment, show that the amount of heat, $\delta' Q$, received by a system is related to the minimum work $\delta W_{\min}$ by

$$\text{(i)} \quad \frac{\delta' Q}{T^2} = -\left(\frac{\partial}{\partial T}\left[\frac{\delta W_{\min}}{T}\right]\right)_V$$

in an isothermal change at constant volume; and that

$$\text{(ii)} \quad \frac{\delta' Q}{T^2} = -\left(\frac{\partial}{\partial T}\left[\frac{\delta W_{\min}}{T}\right]\right)_p$$

in an isothermal change at constant pressure. (These equations are called the Gibbs-Helmholtz equations or the Kelvin equations. They are used to derive $\delta W_{\min}$ from measured values of $\delta' Q$.)

[C]

42. How can one calculate the molar specific heat at constant pressure of a gas in its ideal gas condition ($p=0$) from actually measured values of specific heat for finite p?

43. Using Dieterici's equation, $p=nRT(V-nb)^{-1}\exp(-na/RTV)$, find the pressure dependence of the inversion point of the Joule-Thomson effect and illustrate this on a figure. (Show this using the law of corresponding states using critical quantities as units. See problem 12 of Chapter 1.) Do the same consideration for a van der Waals gas.

44. We would like to calibrate an empirical temperature θ obtained by using a constant pressure gas thermometer to give the absolute temperature. For this purpose, the density ρ, the specific heat, and the Joule-Thomson coefficient have been measured as functions of θ at that pressure. Derive the basic formula necessary to make this calibration.

45. The Joule-Thomson coefficient, μ, for air at a pressure of 1 kg cm^{-2} is given in the table. The density of air, ρ, is approximated by the formula

$$\rho = \frac{0.0012932}{1+0.003669\theta}\,\frac{p}{760}\ \text{g cm}^{-3},$$

where p is the pressure in mm Hg and θ is the temperature in °C. The specific heat at constant pressure between 0 °C and 100 °C is almost constant and is 0.240 cal g^{-1} deg^{-1}.

Using the above information, calculate the numerical value of 0 °C on the absolute temperature scale.

θ °C	μ
0	0.257
25	0.220
50	0.183
75	0.153
100	0.129

Solutions

1. The environment may be regarded as consisting of heat reservoirs $R_1, R_2, \ldots, R_n$ at temperature $T_1^{(e)}, T_2^{(e)}, \ldots$ and $T_n^{(e)}$, respectively. Now consider $n-1$ Carnot cycles, $C_1, C_2, \ldots, C_{n-1}$ which operate in the following manner (see § 2.6):

   C_1 operates between the reservoirs R_1 and R_2, receiving the heat Q_1' from R_1 and Q_2'' from R_2; C_2 operates between R_2 and R_3, receiving the heat Q_2' from R_2 and Q_3'' from R_3; ...; C_{n-1} operates between R_{n-1} and R_n, receiving Q_{n-1}' from R_{n-1} and Q_n'' from R_n.

Let C be the cycle followed by the system under consideration. When all the cycles $C, C_1, \ldots, C_{n-1}$ are completed, the heat lost by each heat reservoir is:

$$R_1: Q_1 + Q_1', \qquad R_2: Q_2 + Q_2' + Q_2'', \ldots,$$
$$R_{n-1}: Q_{n-1} + Q_{n-1}' + Q_{n-1}'', \qquad R_n: Q_n + Q_n''.$$

Therefore, according to the first law, the total work, A received by the system under consideration must be

$$A = -\{(Q_1 + Q_1') + (Q_2 + Q_2' + Q_2'') + \cdots + (Q_n + Q_n'')\}. \tag{1}$$

By suitably adjusting the Carnot cycles, $C_1, C_2, \ldots, C_n$, choose the $2(n-1)$ quantities of heat $Q_1', \ldots, Q_{n-1}'$; $Q_2'', \ldots, Q_n''$ in such a way that the following equations are satisfied:

$$\left.\begin{aligned} Q_2 + Q_2' + Q_2'' &= 0, \\ Q_3 + Q_3' + Q_3'' &= 0, \\ &\cdots\cdots \\ Q_{n-1} + Q_{n-1}' + Q_{n-1}'' &= 0, \\ A = 0 \text{ (therefore } Q_1 + Q_1' + Q_n + Q_n'' &= 0). \end{aligned}\right\} \tag{2}$$

There are, however, the following relations for the Carnot cycles:

$$\left.\begin{aligned} \frac{Q_1'}{T_1^{(e)}} + \frac{Q_2''}{T_2^{(e)}} &= 0, \\ &\cdots\cdots \\ \frac{Q_{n-1}'}{T_{n-1}^{(e)}} + \frac{Q_n''}{T_n^{(e)}} &= 0. \end{aligned}\right\} \tag{3}$$

Thus we have $2(n-1)$ equations all together, so that the above mentioned adjustment is in general possible. By multiplying each equation in (2) (except the last) by $-1/T_2^{(e)},\ldots,-1/T_{n-1}^{(e)}$, respectively, and adding them all to (3), we have the following relations:

$$\frac{Q_1'}{T_1^{(e)}}+\frac{Q_n''}{T_n^{(e)}}=\frac{Q_2}{T_2^{(e)}}+\frac{Q_3}{T_3^{(e)}}+\cdots+\frac{Q_n}{T_n^{(e)}}. \tag{4}$$

Since conditions (2) are satisfied, the net effect of the whole cycle is that R_1 and R_n have lost heat. If $T_n^{(e)}>T_1^{(e)}$ is assumed, Clausius' principle requires that

$$Q_n+Q_n''\geqq 0, \qquad Q_1+Q_1'\leqq 0. \tag{5}$$

On the other hand, since we have from (2),

$$Q_n+Q_n''=-(Q_1+Q_1'),$$

we must have that

$$\frac{Q_n+Q_n''}{T_n^{(e)}}\leqq-\frac{Q_1+Q_1'}{T_1^{(e)}}, \tag{6}$$

or

$$\frac{Q_1'}{T_1^{(e)}}+\frac{Q_n''}{T_n^{(e)}}\leqq-\left(\frac{Q_1}{T_1^{(e)}}+\frac{Q_n}{T_n^{(e)}}\right). \tag{6'}$$

From (6′) and (4) it is proved that

$$\sum_{i=1}^{n}\frac{Q_i}{T_i^{(e)}}\leqq 0. \tag{7}$$

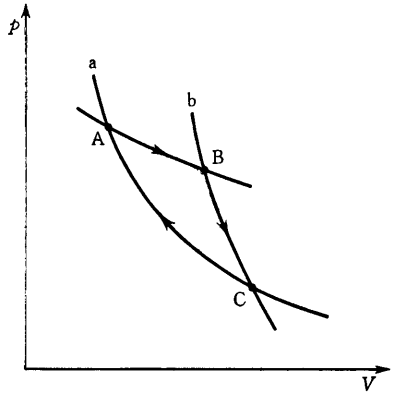
The inequality comes from eq. (5) and the equality holds when the process is reversible.

2. (i) For an isothermal reversible change, Clausius' inequality, $\oint d'Q/T\leqq 0$, becomes $(1/T)\oint d'Q=0$ ($d'Q$ is the infinitesimal heat and T is the temperature). Therefore, the total heat absorbed from the environment $Q=\oint d'Q$ is zero. Also, according to the first law, eq. (1.2), $U_2-U_1=Q+A$ (U_2-U_1 is the increase in internal energy, and A is the work done by the environment). Since $U_2-U_1=0$, $A=-Q=0$ and the work done is zero.

(ii) Assume that, for the given change, the total heat input from the environment, Q, is not zero and $Q>0$. Since the system had returned to its original state, the first law gives $Q+A=0$ and the work done by the environment is $A=-Q<0$. This means that in this reversible process, heat is taken

from one heat reservoir and converted into work with no other change. This contradicts Thomson's principle so that $Q>0$ is not permissible. In the same way, by considering the reverse process, $Q<0$ can be found to contradict Thomson's principle. Therefore, we must have $Q=0$ and $A=0$.

3. Assume that the two adiabatic lines a and b intersect at a point, C, in the p–V diagram. Consider an isothermal line which intersects with a and b at A and B respectively. (Such an isotherm can always be found because the slope of an isotherm is always less than that of an adiabatic line. See example 7, Chapter 1.) The process A→B→C→A can be considered as a reversible



cycle in which the system takes heat Q from its environment only during the isothermal process A→B. The work A done by the system is equal to the area ABC and positive. From the first law $Q=A$, and Q is also positive. This means that a positive amount of heat is taken from a heat reservoir and completely converted into work in this process. This contradicts Thomson's principle. Therefore we conclude that adiabatics cannot intersect.

4. According to Clausius' inequality, we have

$$\int_{(a)} \frac{d'Q_1}{T^{(e)}} - \int_{(b)} \frac{d'Q_2}{T^{(e)}} \leqq 0,$$

and therefore,

$$\int_{(a)} \frac{d'Q_1}{T^{(e)}} \leqq \int_{(b)} \frac{d'Q_2}{T^{(e)}}, \tag{1}$$

where heat is absorbed by the thermal engine through the process (a) ($d'Q_1>0$) and heat is given off in the process (b) ($d'Q_2>0$ is the amount given off). If T_{max} is the maximum value of $T^{(e)}$ in (a) and T_{min} is the minimum value of $T^{(e)}$ during (b), then from (1) we have

$$\frac{Q_1}{T_{max}} \leqq \frac{Q_2}{T_{min}}, \qquad \text{or} \qquad \frac{Q_2}{Q_1} \geqq \frac{T_{min}}{T_{max}}.$$

(The equal sign holds when there are only two heat reservoirs and the cycle is reversible. Even for a reversible cycle the equality does not hold if there are more than two reservoirs.) The work, W, done to the environment is $W=Q_1-Q_2$, so that

$$\text{Efficiency} = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \leqq 1 - \frac{T_{min}}{T_{max}}.$$

5. (i) From the results of example 6 in Chapter 1, the net work done by the system, which is equal to the work done by the gas in the process c→d minus the work given to the gas in the process a→b, is given by $W=C_V\{(T_c-T_d)-(T_b-T_a)\}$. On the other hand, the gas receives heat in the process b→c to an amount $Q=C_V(T_c-T_b)$. For an adiabatic process ((2a) of the solution to example 6 in Chapter 1) $TV^{\gamma-1}=\text{const.}$, so $T_cV_2^{\gamma-1}=T_dV_1^{\gamma-1}$ and $T_bV_2^{\gamma-1}=T_aV_1^{\gamma-1}$. The efficiency is

$$\eta = \frac{W}{Q} = \frac{T_c - T_b - T_d + T_a}{T_c - T_b} = 1 - \frac{T_d - T_a}{T_c - T_b}.$$

Since

$$\frac{T_d}{T_c} = \frac{T_a}{T_b} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_d - T_a}{T_c - T_b},$$

we obtain

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}.$$

(ii) Besides the work done in the adiabatic processes c→d and a→b, there is work done in the processes b→c and d→a. Hence

$$W = C_V\{(T_c - T_d) - (T_b - T_a)\} + p_2(V_c - V_b) - p_1(V_d - V_a).$$

Using $pV=nRT=(C_p-C_V)T=C_V(\gamma-1)T$ we have

$$W = C_p\{T_c - T_b - T_d + T_a\}.$$

In the process b→c the gas receives heat $Q=C_p(T_c-T_b)$. For an adiabatic

process $pV^\gamma = \text{const.}$, so that $Tp^{(1-\gamma)/\gamma} = \text{const.}$ and we have

$$\frac{T_a}{T_b} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma}, \qquad \text{and} \qquad \frac{T_d}{T_c} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma}.$$

Therefore

$$\eta = \frac{W}{Q} = 1 - \frac{T_d - T_a}{T_c - T_b} = 1 - \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma}.$$

(iii)
$$\begin{aligned} W &= C_V\{T_c - T_d - (T_b - T_a)\} + p_2(V_c - V_b) \\ &= C_V\{T_c - T_d - T_b + T_a + (\gamma - 1)(T_c - T_b)\} \\ &= C_V\{\gamma(T_c - T_b) - (T_d - T_a)\}. \end{aligned}$$

The heat absorbed during the process b→c is $Q = C_p(T_c - T_b)$. Therefore

$$\eta = 1 - \frac{1}{\gamma}\frac{T_d - T_a}{T_c - T_b}.$$

Using the relations

$$\frac{T_c}{T_b} = \frac{V_2}{V_3}, \qquad T_a V_1^{\gamma-1} = T_b V_3^{\gamma-1}, \qquad \text{and} \qquad T_c V_2^{\gamma-1} = T_d V_1^{\gamma-1},$$

the answer is obtained.

NOTE: According to the results of problem 4, all of these efficiencies must be less than $1 - T_a/T_c$.

6. This is obvious, if the absolute temperature has been defined, using Clausius' inequality (2.9) (the equality sign holds for a quasi-static process). If the absolute temperature has not yet been defined, use the proof of eq. (2.8) in § 2.5.

7. When a quasi-static change takes place in a mole of ideal gas the change in entropy, dS, is given by eq. (2.16)

$$dS = \frac{dU + p\,dV}{T},$$

where U is the internal energy, p the pressure and V the volume. Using $dU = C_V^0\,dT$ and $pV = RT$, we have

$$dS = \frac{C_V^0}{T}dT + \frac{R}{V}dV.$$

Therefore

$$S = C_V^0 \log T + R \log V + S_0, \tag{1}$$

where S_0 is an integration constant.

NOTE: For n moles of gas, we have

$$S(T, V, n) = n\left(C_V^0 \log T + R \log \frac{V}{n} + S_0\right) \tag{2}$$

because S is extensive.

8. Since the gas is undergoing an adiabatic expansion into a vacuum, there is no interchange of work, nor heat exchange; i.e. $d'A=0$ and $d'Q=0$. Therefore, from the first law, the change in the internal energy, U, is also zero. By (1.12) we know that $dU=nC_V^0\,dT$ for an ideal gas and therefore $dT=0$, i.e., there is no temperature change. The entropy of an ideal gas is given as

$$S = n\left(C_V^0 \log T + R \log \frac{V}{n} + S_0\right)$$

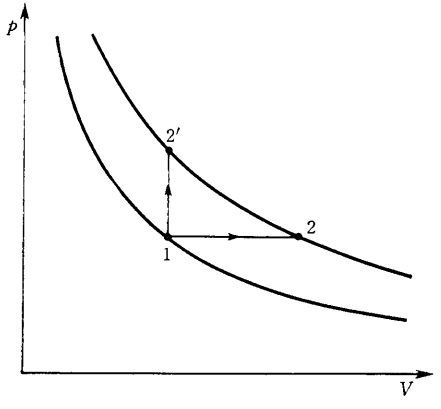
(see the note to the previous problem). Thus the entropy change in this process is

$$\Delta S = S(T, V_2) - S(T, V_1) = nR \log \frac{V_2}{V_1},$$

which means $\Delta S>0$, since $V_2>V_1$. Therefore this process is an adiabatic process which increases the entropy. According to the second law it is an irreversible process.

9. In a quasi-static process of an ideal gas (see (1) and (3) in example 3 of Chapter 1) we have

$$d'Q = C_V\,dT + p\,dV = C_p\,dT - V\,dp. \tag{1}$$



The entropy increase, $(\Delta S)_p$, for a constant pressure process is found to be

$$(\Delta S)_p = \int_{T_1}^{T_2} \frac{C_p \, \mathrm{d}T}{T}$$

and that for a constant volume process to be

$$(\Delta S)_V = \int_{T_1}^{T_2} \frac{C_V \, \mathrm{d}T}{T}.$$

Therefore the ratio of the two entropy increases is equal to C_p/C_V if C_V and C_p are constants.

10. We have been told that

$$pv = f(T) \qquad \text{and} \qquad u = u(T).$$

From the fundamental equation of thermodynamics,

$$\mathrm{d}s = (\mathrm{d}u + p \, \mathrm{d}v)/T,$$

we get (see example 2)

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p = 0. \tag{1}$$

Multiply this equation by v, and we see that

$$T\frac{\mathrm{d}f(T)}{\mathrm{d}T} - f(T) = 0. \tag{2}$$

Integration gives

$$f(T) = \text{const.} \times T. \tag{3}$$

The constant is independent of the temperature and volume and therefore the equation of state has the form

$$pv = AT \qquad (A \text{ is a constant}). \tag{4}$$

11. From $(\partial U/\partial V)_\theta = 0$ we find $\mathrm{d}U = g(\theta)\,\mathrm{d}\theta$. Divide the equation

$$\mathrm{d}'Q = \mathrm{d}U + p\,\mathrm{d}V = g(\theta)\,\mathrm{d}\theta + p\,\mathrm{d}V$$

for a quasi-static process by $f(\theta)$ and we have

$$\frac{\mathrm{d}'Q}{f} = \frac{g(\theta)\,\mathrm{d}\theta}{f} + \frac{p\,\mathrm{d}V}{f} = \frac{g(\theta)\,\mathrm{d}\theta}{f(\theta)} + \frac{\mathrm{d}V}{V},$$

which is clearly a complete differential. Hence if we set

$$d'Q/f = dS,$$

S is a function of state. By considering a Carnot cycle we see that the ratio of the heat Q_1 obtained from the hot heat reservoir at θ_1 to the heat Q_2 given to the cold heat reservoir at θ_2, is given by

$$\oint dS = Q_1/f(\theta_1) - Q_2/f(\theta_2) = 0,$$

i.e.,

$$Q_2/Q_1 = f(\theta_2)/f(\theta_1).$$

Therefore, according to the definition of the absolute temperature (2.5), $f(\theta) = \text{const.} \times T$.
(For an alternative solution, see problem 10.)

12. Let the internal energy be U and the entropy S for a volume, V, of radiation field. Then

$$dS = \frac{dU + p\,dV}{T} = \frac{d(\sigma T^4 V) + \frac{1}{3}\sigma T^4\,dV}{T}$$

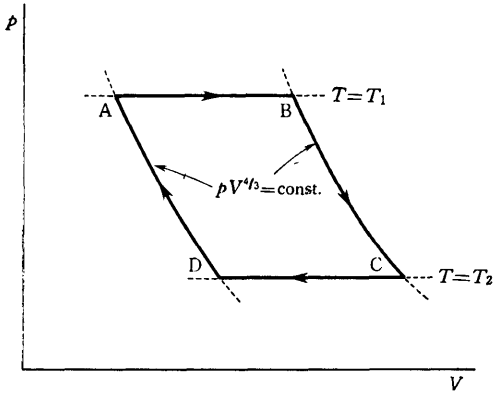
$$= 4\sigma T^2 V\,dT + \tfrac{4}{3}\sigma T^3\,dV = d(\tfrac{4}{3}\sigma T^3 V), \tag{1}$$

$$S = \tfrac{4}{3}\sigma T^3 V + \text{const.}.$$

Therefore

$$\text{entropy density} \qquad s = \tfrac{4}{3}\sigma T^3. \tag{2}$$

For an isothermal process, we have $u = \text{const.}$ and $p = \text{const.}$, and for an adiabatic process $T^3 V = \text{const.}$ and, hence, $pV^{\frac{4}{3}} = \text{const.}$ Therefore the Carnot



cycle is as shown in the figure. The heat absorbed or given off during the isothermal processes A→B and C→D, Q_1 and Q_2, are found to be (see problem 20, Chapter 1)

$$Q_1 = \int_A^B (\mathrm{d}U + p\,\mathrm{d}V)$$
$$= \tfrac{4}{3}\sigma T_1^4 (V_B - V_A),$$
$$Q_2 = \tfrac{4}{3}\sigma T_2^4 (V_C - V_D).$$

Using the relations $V_B T_B^3 = V_C T_C^3$ and $V_A T_A^3 = V_D T_D^3$ or $V_B T_1^3 = V_C T_2^3$, $V_A T_1^3 = V_D T_2^3$ for the adiabatic processes, we obtain

$$Q_1/T_1 = Q_2/T_2.$$

The work done during a cycle is $\tfrac{4}{3}\sigma T_1^3 (T_2 - T_1)(V_A - V_B)$ and is equal to $Q_1 - Q_2$.

13. The first law, $\mathrm{d}'Q = \mathrm{d}U - \mathrm{d}'A$, for a quasi-static process of a paramagnetic body is (see example 1 in Chapter 1)

$$\mathrm{d}'Q = \mathrm{d}U - H\,\mathrm{d}M, \tag{1}$$

(we consider a unit volume) where U is a function of temperature only and independent of M. From the relation $M = \chi H$ we have $H = M/\chi = M\theta$. Here χ or θ is also independent of M and a function of temperature only. Divide (1) by θ and we have

$$\mathrm{d}'Q/\theta = \mathrm{d}U/\theta - M\,\mathrm{d}M = \mathrm{d}S, \tag{2}$$

where S is a complete differential. Hence $\theta = 1/\chi$ is the integrating denominator for $\mathrm{d}'Q$. Since this is a function of temperature, it must be proportional to the absolute temperature. In fact, if we perform a Carnot cycle with this paramagnetic body, the ratio of the heat absorbed, Q_1, from the hot reservoir to the heat given, Q_2, to the cool reservoir is θ_1/θ_2 as can be seen from the equation

$$0 = \oint \mathrm{d}S = \oint \frac{\mathrm{d}'Q}{\theta} = \frac{Q_1}{\theta_1} - \frac{Q_2}{\theta_2}.$$

14. (See example 7 in Chapter 1 for an alternative solution.)
(i) If we let the entropy be S, then

$$\left.\begin{aligned} &\text{adiabatic compressibility} \qquad \kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S, \\ &\text{isothermal compressibility} \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T. \end{aligned}\right\} \tag{1}$$

Using (1.23) we can write κ_S as

$$\kappa_S = +\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_V \Big/ \left(\frac{\partial S}{\partial V}\right)_p. \tag{2}$$

If S is considered to be a function of T and V, i.e., $S(T,V)=S(T(p, V), V)$, we have

$$\left(\frac{\partial S}{\partial p}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V = \frac{C_V}{T}\left(\frac{\partial T}{\partial p}\right)_V. \tag{3}$$

Similarly, by considering $S(T,p)=S(T(p, V), p)$, we have

$$\left(\frac{\partial S}{\partial V}\right)_p = \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p = \frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p. \tag{4}$$

Substituting (3) and (4) in (2)

$$\kappa_S = \frac{C_V}{VC_p}\left(\frac{\partial T}{\partial p}\right)_V \Big/ \left(\frac{\partial T}{\partial V}\right)_p = -\frac{C_V}{C_p V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{C_V}{C_p}\kappa_T. \tag{5}$$

We again used (1.23) in (5).

(ii) If the same operation as in (i) is applied to the adiabatic magnetic susceptibility, $\chi_S=(\partial M/\partial H)_S$ and the isothermal susceptibility, $\chi_T=(\partial M/\partial H)_T$ (substitutions $V\to M$ and $-p\to H$), obviously we get $\chi_S=(C_M/C_H)\chi_T$.

15. (i) The solution of example 2 is one proof. Here we give another proof:

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left\{T\left(\frac{\partial S}{\partial V}\right)_T - p\right\}\mathrm{d}V. \tag{1}$$

Therefore

$$\frac{\partial}{\partial V}\left\{T\left(\frac{\partial S}{\partial T}\right)\right\} = \frac{\partial}{\partial T}\left\{T\left(\frac{\partial S}{\partial V}\right) - p\right\}, \qquad \text{i.e.,} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V. \tag{2}$$

Substitute this into $\partial U/\partial V$ obtained from (1) and we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

(ii) Substitute $H=U+pV$ in (2.16) and we have

$$\mathrm{d}S = \frac{1}{T}(\mathrm{d}H - V\,\mathrm{d}p), \tag{3}$$

therefore

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p, \qquad \left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{T}\left(\frac{\partial H}{\partial p}\right)_T - \frac{V}{T}.$$

Since $\partial^2 S/\partial p\,\partial T = \partial^2 S/\partial T\,\partial p$,

$$\left(\frac{\partial H}{\partial p}\right)_T = -T^2 \frac{\partial}{\partial T}\left(\frac{V}{T}\right) = -T\left(\frac{\partial V}{\partial T}\right)_p + V.$$

For another method of solution, start from $\mathrm{d}H = \mathrm{d}(U+pV) = T\,\mathrm{d}S + V\,\mathrm{d}p$ and follow the method of (i).

6. (i) By definition, $c_v = (\mathrm{d}'q)_v/\mathrm{d}T$, and by the second law (2.12), $\mathrm{d}'q = T\,\mathrm{d}s$, we have

$$c_v = T(\partial s/\partial T)_v.$$

Similarly,

$$c_p = T(\partial s/\partial T)_p.$$

(ii) Equation (2.16),

$$\mathrm{d}u = T\,\mathrm{d}s - p\,\mathrm{d}v \tag{1}$$

gives $(\partial u/\partial T)_v = T(\partial s/\partial T)_v$, $\partial^2 u/\partial v\,\partial T = T\partial^2 s/\partial v\,\partial T$. Also, since $h = u + pv$ we have

$$\mathrm{d}h = T\,\mathrm{d}s + v\,\mathrm{d}p, \tag{2}$$

and similarly $\partial^2 h/\partial T\,\partial p = T\partial^2 s/\partial T\,\partial p$.
(iii) The first equation is proved by (2) of the solution of problem 15. The second equation is proved as follows: from (1)

$$\left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T, \qquad \left(\frac{\partial u}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial T}\right)_p.$$

Since $\partial^2 u/\partial T\,\partial p = \partial^2 u/\partial p\,\partial T$, we have $(\partial s/\partial p)_T = -(\partial v/\partial T)_p$. Alternative solution: Taking p and T as independent variables, one may use eq. (2) and proceed in parallel to example 2.

7. (i) By (i) of the previous problem, we have

$$c_p - c_v = T\left\{\left(\frac{\partial s}{\partial T}\right)_p - \left(\frac{\partial s}{\partial T}\right)_v\right\}. \tag{1}$$

Considering $s = s(T, v(T,p))$ as a function of T and p,

$$\left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial s}{\partial T}\right)_v + \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p. \tag{2}$$

Now substitute Maxwell's relation $(\partial s/\partial v)_T = (\partial p/\partial T)_v$ ((iii) of problem 16)

to get

$$c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v . \tag{3}$$

Then use $(\partial p/\partial T)_v = -(\partial v/\partial T)_p/(\partial v/\partial p)_T$ and substitute α and β to obtain the answer.

Alternative solution: Substitute (i) of problem 15, Chapter 1, into (ii) of problem 16, Chapter 1.

(ii)
$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p ,$$

so that

$$\left(\frac{\partial c_p}{\partial p}\right)_T = T\,\frac{\partial^2 s}{\partial p \partial T} = -\,T\,\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_p = -\,T\left(\frac{\partial^2 v}{\partial T^2}\right)_p ,$$

where we have used Maxwell's relation $(\partial s/\partial p)_T = -(\partial v/\partial T)_p$ (iii) of problem 16. Similarly, using $(\partial s/\partial v)_T = (\partial p/\partial T)_v$, we obtain

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\,\frac{\partial^2 s}{\partial v \partial T} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v .$$

18. For 1 mole of an ideal gas, the internal energy is $U = C_V T + U_0$ (C_V is the molar heat at constant volume) and the entropy is $S(T, p) = C_p \log T - R \log p + S_0$ (see solution to problem 7). U_0 and S_0 are constants. Therefore, the Helmholtz free energy is $F = U - TS = C_V T - C_p T \log T + RT \log p + U_0 - TS_0$ and the Gibbs free energy, $G = U - TS + pV = C_p T - C_p T \log T + RT \log p + U_0 - TS_0$. The changes in these quantities from $p = 1$ atm to $p = 100$ atm ($T =$ const. $= 293$ °K) are

$$\begin{aligned} \Delta S &= S(T, 100) - S(T, 1) \\ &= -\,R \log 100 = -\,R \log_{10} 100/\log_{10} \mathrm{e} \fallingdotseq -\,4.6R \fallingdotseq -\,9.2 \text{ cal/deg}, \\ \Delta F &= \Delta G = RT \log 100 = 293R \log 100 \fallingdotseq 2.7 \text{ kcal}. \end{aligned}$$

NOTE: Here we have assumed that C_V is a constant, but this assumption is not necessary.

19. Writing

$$V = a - bp + cp^2 \tag{1}$$

and

$$\mathrm{d}V = (b + 2cp)\,\mathrm{d}p , \tag{2}$$

the desired work, A, is given by

$$A = -\int p\,\mathrm{d}V = -\left(\tfrac{1}{2}bp^2 + \tfrac{2}{3}cp^3\right)\Big|_{p=1000}^{p=0} . \tag{3}$$

Substitute $b = -715 \times 10^{-6}$ and $c = 46 \times 10^{-9}$ to obtain $A = 326.83$ atm cm^3/mol $= 33.116$ joule/mol. If the heat adsorbed during this change is Q, the increase in the internal energy ΔU is

$$\Delta U = A + Q. \tag{4}$$

For a quasi-static process

$$Q = \int T\,\mathrm{d}S = T\int \mathrm{d}S = T\int \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p = -T\int \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p. \tag{5}$$

(We have used Maxwell's relation $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$, (iii) of problem 16.) Therefore

$$Q = -298 \times (4.5 + \tfrac{1}{2} \times 1.4)\,(\text{atm. cm}^3/\text{mol}) \fallingdotseq -157.0\,(\text{joule/mol}), \tag{6}$$

so that $\Delta U \fallingdotseq -123.9$ joule/mol.

20. By definition, the entropy change is $\Delta S = S_v - S_i = \int_{i\to v} \mathrm{d}'Q/T$. Here the integration means the total sum of the heat absorbed, $\mathrm{d}'Q$, divided by the temperature at each instant, T, as the system changes quasi-statically from state i (ice at 0 °C and 1 atm) to the state v (steam at 100 °C and 1 atm). The process i to v may be divided into i→w_0 (water at 0 °C and 1 atm)→w_{100} (water at 100 °C and 1 atm)→v. In process i→w_0

$$\int_{i\to w_0} \frac{\mathrm{d}'Q}{T} = (1436/273)\ \text{cal/deg mol} \fallingdotseq 5.26\ \text{cal/deg mol}. \tag{1}$$

Assuming the average specific heat to be C_p, the process $w_0 \to w_{100}$ gives

$$\int_{w_0\to w_{100}} \frac{\mathrm{d}'Q}{T} = C_p \int_{w_0\to w_{100}} \frac{\mathrm{d}T}{T} = 18.05 \log (373/273)\ \text{cal/deg mol}$$
$$\fallingdotseq 5.63\ \text{cal/deg mol}, \tag{2}$$

where we put $\log (373/273) = \log 1.366 \fallingdotseq 0.312$. For $w_{100} \to$ v, we have

$$\int_{w_{100}\to v} \frac{\mathrm{d}'Q}{T} = 972 \times 10/373\ \text{cal/deg mol} \fallingdotseq 26.1\ \text{cal/deg mol}. \tag{3}$$

Adding (1), (2) and (3), we obtain

$$\Delta S = 37.0\ \text{cal/deg mol}.$$

21. Consider the following quasi-static change of the substance from a solid state at temperature T_1 to a supercooled liquid state at temperature T_1: solid at

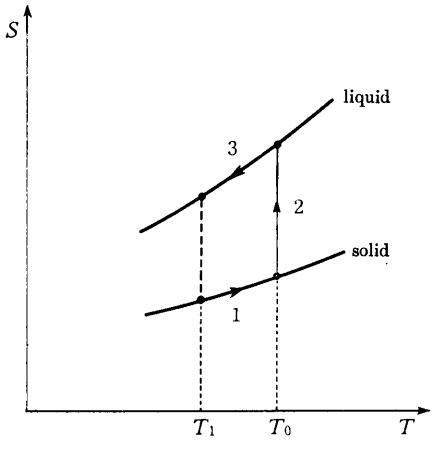
$T_1 \xrightarrow{1}$ solid at $T_0 \xrightarrow{2}$ liquid at $T_0 \xrightarrow{3}$ liquid at T_1. The entropy increase in process 1 is

$$\int_{T_1}^{T_0} \frac{d'Q}{T} = Mc_s \log \frac{T_0}{T_1}.$$

The entropy increase in process 2 is MQ_0/T_0. The entropy increase in process 3 is

$$\int_{T_0}^{T_1} \frac{d'Q}{T} = -Mc_l \log \frac{T_0}{T_1}.$$

Therefore the entropy of the supercooled liquid state at T_1 is greater than the entropy of the solid state at T_1 by $\Delta S = MQ_0/T_0 - M(c_l - c_s)\log(T_0/T_1)$.



22. Using the Maxwell relation, $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$, the desired entropy increase is given by

$$\int dS = \int_{p_A}^{p_B} \left(\frac{\partial S}{\partial p}\right)_T dp = -\int_{p_A}^{p_B} \left(\frac{\partial V}{\partial T}\right)_p dp$$
$$= -\{a(p_B - p_A) + \tfrac{1}{2}b(p_B^2 - p_A^2) + \tfrac{1}{3}c(p_B^3 - p_A^3)\}.$$

23. From the condition $dS = (\partial S/\partial T)_V\, dT + (\partial S/\partial V)_T\, dV = 0$, we obtain

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_V$$

(see (1.23)). Now use the specific heat at constant volume, $C_V = T(\partial S/\partial T)_V$, and the Maxwell relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ ((iii) of problem 16), to obtain

$$V\left(\frac{\partial T}{\partial V}\right)_S \equiv \left(\frac{\partial T}{\partial \log V}\right)_S = -\frac{VT}{C_V}\left(\frac{\partial p}{\partial T}\right)_V .$$

(Since $(\partial p/\partial T)_V > 0$ for a gas, the temperature decreases in an adiabatic expansion. The gas cools down because work is done on the environment during the expansion.)

24. We have shown that $H = \text{const.}$ in example 9 of Chapter 1. The temperature change due to a small pressure change is obtained from the condition $dH = 0$, i.e.

$$\left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial H}{\partial p}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_p .$$

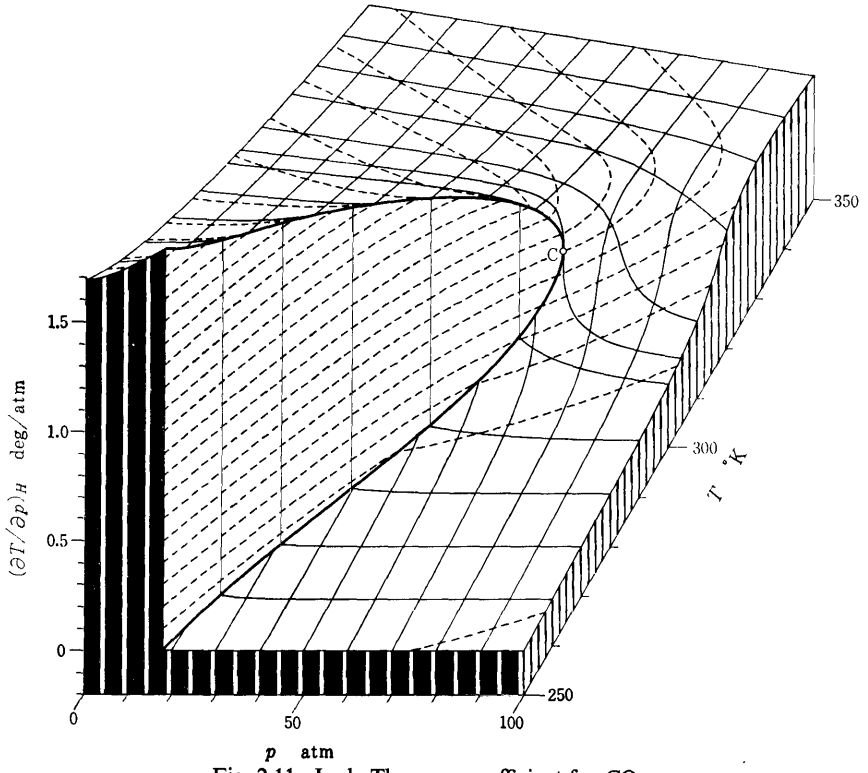


Fig. 2.11. Joule-Thomson coefficient for CO_2.

Using $C_p = (\partial H/\partial T)_p$ and the formula $(\partial H/\partial p)_T = -T(\partial V/\partial T)_p + V$ ((ii) in problem 15), we obtain

$$\left(\frac{\partial T}{\partial p}\right)_H = \left\{T\left(\frac{\partial V}{\partial T}\right)_p - V\right\}\Big/C_p. \tag{1}$$

When the equation of state $pV = RT(1 + Bp)$ is substituted, eq. (1) becomes

$$(\partial T/\partial p)_H = \left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right)\Big/C_p. \tag{2}$$

If I is the point of contact of the tangent drawn from the origin on the graph of the second virial coefficient, B, versus T, the Joule-Thomson coefficient changes sign at T_I. T_I is a function of the pressure, p, and is called the *inversion point* of the Joule-Thomson coefficient.

Figure 2.11 shows the dependence of the Joule-Thomson coefficient on p and T.

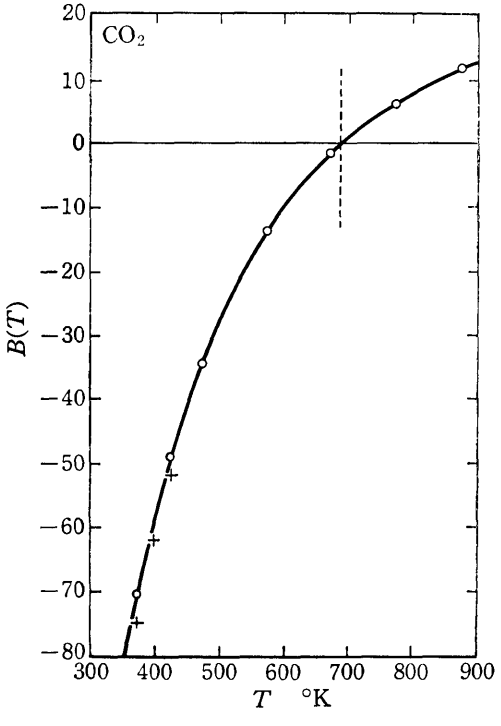


Fig. 2.12.

25. For free expansion into a vacuum (this is adiabatic and irreversible), U is constant. The solution is similar to those for problems 23 and 24. (Use (1.23), and (ii) of problem 15.) We obtain

$$\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_T \Big/ \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{C_V}\left\{p - T\left(\frac{\partial p}{\partial T}\right)_V\right\}.$$

26. Considering a unit volume of the material, we have

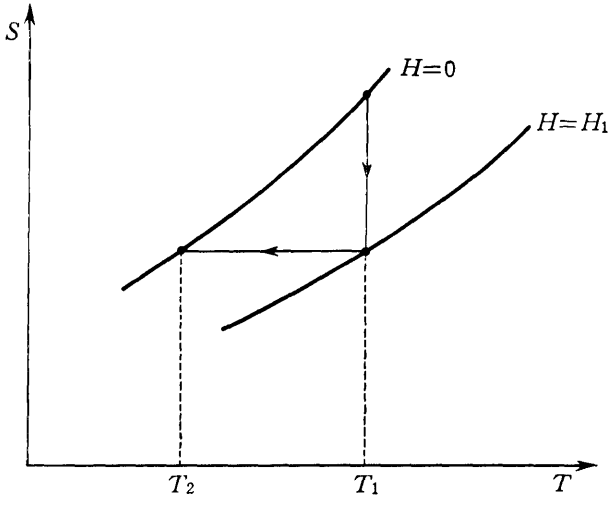
$$\mathrm{d}'Q = \mathrm{d}U - H\,\mathrm{d}M \tag{1}$$

for a quasi-static process. When the substance is magnetized isothermally, we know that $\mathrm{d}U=0$ and $M=CH/T$. Hence

$$Q = -\int_0^{H_1} H\,\mathrm{d}\left(\frac{CH}{T_1}\right) = -\frac{C}{2T_1}H_1^2,$$

i.e. only heat $-Q=CH_1^2/2T_1$ is developed. By the relation

$$\begin{aligned}\mathrm{d}S &= \frac{1}{T}\{\mathrm{d}U - H\,\mathrm{d}M\}\\ &= 4aT^2\,\mathrm{d}T - C\frac{H}{T}\,\mathrm{d}\left(\frac{H}{T}\right),\end{aligned}$$



the entropy is obtained as

$$S = \tfrac{4}{3}aT^3 - \tfrac{1}{2}C\left(\frac{H}{T}\right)^2 + \text{const.} \tag{2}$$

In the adiabatic demagnetization from $H=H_1$ to $H=0$, S is unchanged so that we have

$$\tfrac{4}{3}aT_2^3 = \tfrac{4}{3}aT_1^3 - \tfrac{1}{2}C\left(\frac{H_1}{T_1}\right)^2,$$

and thus

$$T_2^3 = T_1^3 - \frac{3C}{8a}\left(\frac{H_1}{T_1}\right)^2. \tag{3}$$

Since $C>0$ and $a>0$, we have $T_2<T_1$. If H_1 is small, the temperature difference is small, and we have the approximation

$$\Delta T = T_2 - T_1 \doteqdot -\frac{CH_1^2}{8aT_1^4}.$$

NOTE: Adiabatic demagnetization is used to attain temperatures below 1 °K. Fig. 2.13 shows a relief of the entropy (due to the electronic spin) of iron ammonium alum as a function of magnetic field and temperature. A mag-

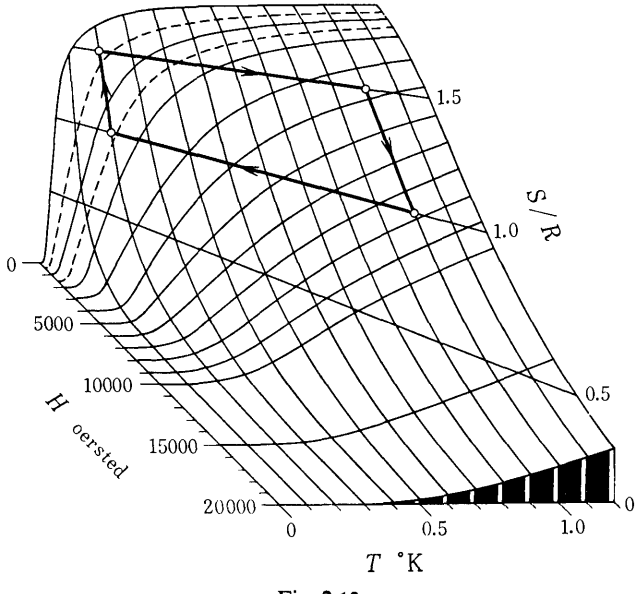


Fig. 2.13.

netic refrigerator can be made by using a paramagnetic salt such as this in a Carnot cycle (operating along the cycle as shown by the thick line in the figure). These have actually been used to maintain temperatures of the order of 0.2 °K.

According to (3), if H_1 is made sufficiently large for a given T_1, T_2 will become negative. However, (2) is inconsistent with the third law of thermodynamics and is not correct near 0 °K, so that it cannot be used when it gives a negative T_2. Actually, one can never reach absolute zero by adiabatic demagnetization or by any other means. The lowest temperature attained so far by adiabatic demagnetization is about 0.003 °K.

27. We consider a unit volume. The equation

$$\mathrm{d}S = (\mathrm{d}U - H\,\mathrm{d}M)/T \tag{1}$$

gives

$$\left(\frac{\partial S}{\partial T}\right)_M = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_M \qquad \text{and} \qquad \left(\frac{\partial S}{\partial M}\right)_T = \frac{1}{T}\left(\frac{\partial U}{\partial M}\right)_T - \frac{H}{T}. \tag{2}$$

The condition $\partial^2 S/\partial M\,\partial T = \partial^2 S/\partial T\,\partial M$ (integrability condition) then yields

$$(\partial U/\partial M)_T = -\,T^2(\partial(H/T)/\partial T)_M \tag{3}$$

(see problem 15, (i)). As $M = f(H/T)$ the right side is zero (because H/T must be constant when M is constant), so that

$$(\partial U/\partial M)_T = 0.$$

Eq. (1) becomes

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U(T) - \frac{H}{T}f'\left(\frac{H}{T}\right)\mathrm{d}\left(\frac{H}{T}\right)$$

and, when integrated,

$$S = \int \frac{\mathrm{d}U(T)}{T} - \int_0^{H/T} xf'(x)\,\mathrm{d}x + \text{const.}$$

$$= g(T) - \frac{H}{T}f\left(\frac{H}{T}\right) + \int_0^{H/T} f(x)\,\mathrm{d}x + \text{const.} \tag{4}$$

28. By the principle of maximum work the work obtained through a reversible process is a maximum. (No work is obtained if the body is directly put in contact with the cold reservoir.) To take heat reversibly from the body and

do work we consider a Carnot cycle which absorbs heat $d'Q = C|dT| = -C\,dT\,(dT<0)$ from a reservoir at temperature T, while giving heat $d'Q_0 = d'Q \times T_0/T$ to a reservoir at temperature T_0, and which does work

$$d'W = d'Q - d'Q_0 = \left(1 - \frac{T_0}{T}\right) d'Q.$$

By repeating the above cycle, the body can be reduced eventually to T_0. Then the total work done is

$$W = \int d'W = \int \left(1 - \frac{T_0}{T}\right) d'Q = -\int_{T_1}^{T_0} \left(1 - \frac{T_0}{T}\right) C\,dT$$

$$= C\left\{(T_1 - T_0) - T_0 \log \frac{T_1}{T_0}\right\}.$$

29. (This is the reverse of the previous prob m.) We consider the room at 25 °C as a heat reservoir at 298 °K. In order to cool water initially at 298 °K to ice at 273 °K, we have to take heat from it and give the heat to the reservoir which is hotter than the water. This can be done only when work is also done. This work is a minimum when the process is reversible. Use a Carnot cycle, in which the heat $d'Q$ is taken from the water at T and heat $d'Q' = d'Q + d'W$ is given to the reservoir at $T'(>T)$. Since $d'Q/d'Q' = T/T'$, $d'W = d'Q(T'-T)/T$, where $d'Q = -C\,dT$, C being the total heat capacity of the water. The work necessary to cool the water to 273 °K from 298 °K is

$$W_1 = \int_{298}^{273} \left(\frac{298}{T} - 1\right) d\,Q = \int_{298}^{273} \left(\frac{298}{T} - 1\right)(-C\,dT)$$

$$= C\left\{298 \log \frac{298}{273} - (298 - 273)\right\}. \tag{1}$$

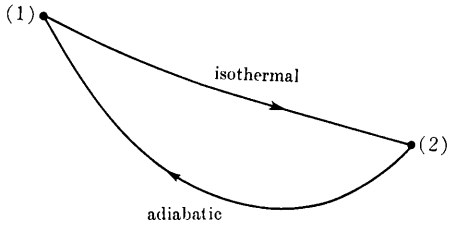
The minimum work necessary to give the latent heat of freezing, L, to the reservoir at 298 °K is

$$W_2 = L \times (298 - 273)/273.$$

Using the given latent heat for water, the specific heat $C_{H_2O} = 18.05$ cal/deg mol and the work equivalent of heat 4.18 joule/cal, we have $W_1 = 4.64 \times 10^6$ joule and $W_2 = 35.8 \times 10^6$ joule. The total work $W = W_1 + W_2 = 4.04 \times 10^6$ joule which corresponds to $40.4 \times 10^6/3.6 \times 10^6 = 11.2$ kilowatt hours at a cost of \$ 1.35.

30. It is sufficient to show that Thomson's principle is violated when Carathéodory's principle is violated. Let us assume that a thermally uniform system changed isothermally from a state (1) to a state (2) and absorbs a positive heat quantity Q. Letting the internal energy of the two states be U_1 and U_2 and the amount of work received be A, the first law states that

$$Q = U_2 - U_1 - A. \tag{1}$$



We next change the system from (2) back to (1) adiabatically. This is possible if Carathéodory's principle is not true. If the work received during the adiabatic process is A', the first law states that

$$0 = U_1 - U_2 - A'. \tag{2}$$

From (1) and (2)

$$Q = -(A + A'). \tag{3}$$

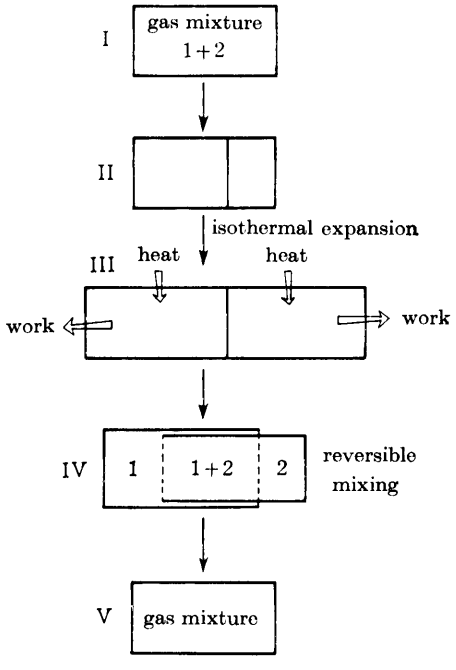
Therefore in the cycle (1)→(2)→(1), the system absorbs heat, Q, from the environment and does an equivalent amount of work $-(A+A')$. This is a violation of Thomson's principle.

Alternative solution: The validity of Clausius' (or Thomson's) principle means that there exists a state quantity, S, and, if T is the absolute temperature, $\mathrm{d}'Q/T = \mathrm{d}S$. For an adiabatic process, $\mathrm{d}'Q = 0$, $\mathrm{d}S = 0$ and since $\mathrm{d}S$ is a total differential of S, it means that $S = a$ (constant). That is, there is a set of surfaces in the space of state variables (e.g. x, y, z). If the initial state is (x_0, y_0, z_0), it lies on the surface defined by $S(x_0, y_0, z_0) = a$. Therefore all adiabatic reversible changes which start from (x_0, y_0, z_0) must be on this surface and any point outside this surface cannot be reached by an adiabatic reversible change. Thus in any neighborhood of a given state (x_0, y_0, z_0) there exist always states such that they cannot be reached by an adiabatic change. This means that Carathéodory's principle is valid.

NOTE: Carathéodory's principle further includes adiabatic irreversible processes. Starting from Clausius' or Thomson's principle one can prove that the entropy, S, increases in an adiabatic irreversible process by Clausius' inequality. Therefore, for an initial state (x_0, y_0, z_0), the states which have

smaller values of entropy and so lie on one side of the surface $S(x, y, z) = S(x_0, y_0, z_0)$ cannot be reached by any adiabatic irreversible process. Hence we can state that for any state there exists an arbitrarily close neighbouring state which cannot be reached either by reversible or irreversible adiabatic processes.

31. Consider a mixture of two gases, n_1 mole of gas 1 and n_2 mole of gas 2 at volume V, temperature T and pressure, p. Assume that mixing by diffusion is a reversible process. Then it is possible to separate the mixture to become pure gas 1 at $V_1 = Vn_1/(n_1+n_2)$, T and p and pure gas 2 at $V_2 = Vn_2/(n_1+n_2)$,



T and p, without leaving any other change (I→II in the figure). Next, increase isothermally the volume of each to V. The heat absorbed from the reservoir at temperature T is converted to work in this process (II→III). Then, by making one wall of each container semipermeable (example 5), it is possible to combine the two containers and reversibly (without the exchange of heat or work) mix the two gases to their original state (III→IV→V=I). In this whole process, heat was obtained from the heat reservoir at the stage II→III and it was all converted to work without leaving any other change. This is in contradiction to Thomson's principle.

32. The heat received by this system, $d'Q$, is the sum of $d'Q'$ and $d'Q''$. By the first law we have

$$d'Q' = C'_V\,dT' + p'\,dV' \qquad \text{and} \qquad d'Q'' = C''_V\,dT'' + p''\,dV''.$$

The pressure p' and p'' of the two parts are always equal ($p'=p''=p$) since they are in a mechanical equilibrium. Now express dV' and dV'' in terms of dT', dp and dT'' and dp using the ideal gas equation, $pV=RT$. (Multiply $dV/V=dT/T-dp/p$ by $pV=RT$ to obtain $p\,dV=R\,dT-RT\,dp/p$.) Thus we have

$$d'Q = d'Q' + d'Q'' = (C'_V + R)\,dT' + (C''_V + R)\,dT'' - \frac{R}{p}(T' + T'')\,dp. \tag{1}$$

In this system $d'Q$ is a differential form of three variables, T', T'' and p. We now apply the condition that

$$X_1\,dx_1 + X_2\,dx_2 + X_3\,dx_3 \tag{2}$$

has an integrating factor, i.e.

$$X_1\left(\frac{\partial X_3}{\partial x_2} - \frac{\partial X_2}{\partial x_3}\right) + X_2\left(\frac{\partial X_1}{\partial x_3} - \frac{\partial X_3}{\partial x_1}\right) + X_3\left(\frac{\partial X_2}{\partial x_1} - \frac{\partial X_1}{\partial x_2}\right) = 0 \tag{3}$$

(see Note 1). Setting $x_1=T'$, $x_2=T''$, $x_3=p$, $X_1=C'_V+R$, $X_2=C''_V+R$ and $X_3=-(R/p)\,(T'+T'')$ we get the left side of (3)

$$-(C'_V + R)\frac{R}{p} + (C''_V + R)\frac{R}{p} = \frac{R}{p}(C''_V - C'_V), \tag{4}$$

which cannot be zero since $C'_V \neq C''_V$. Therefore $d'Q$ of (1) does not have any integrating factor.

NOTE 1: If there exists an integrating factor, $\lambda(x_1, x_2, x_3)$, such that $\lambda(X_1\,dx_1 + X_2\,dx_2 + X_3\,dx_3) = d\phi(x_1, x_2, x_3)$, then we have

$$\partial\phi/\partial x_1 = \lambda X_1, \qquad \partial\phi/\partial x_2 = \lambda X_2, \qquad \partial\phi/\partial x_3 = \lambda X_3.$$

By setting $\partial^2\phi/\partial x_1\,\partial x_2 = \partial^2\phi/\partial x_2\,\partial x_1$, etc. and eliminating λ from them, eq. (3) is derived as the condition of integrability.

NOTE 2: This is an example showing that, for a system in which the temperature is not uniform, an integrating factor does not necessarily exist for $d'Q$. In order to deduce from the second law that a system has an integrating factor, we have generally to require that the system is *thermally uniform.*

33. Let the internal energy and entropy per unit mass be u and s respectively. If

$$du = \left(\frac{\partial u}{\partial T}\right)_V dT = g(T)\,dT \qquad (g(T) \text{ is a function of } T \text{ only}), \tag{1}$$

we find from

$$\mathrm{d}u = T\,\mathrm{d}s - p\,\mathrm{d}v, \tag{2}$$

that

$$T\,\mathrm{d}s = g(T)\,\mathrm{d}T + p\,\mathrm{d}v,$$

and also

$$c_v = T(\partial s/\partial T)_v = g(T) \tag{3}$$

by definition. Therefore c_v is a function of T only (proof of (i)).

Next, rewrite (2) as

$$\mathrm{d}v = (T/p)\,\mathrm{d}s - (g(T)/p)\,\mathrm{d}T$$

using (1). This gives the equation

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{T}{p}\left(\frac{\partial s}{\partial T}\right)_p - \frac{g(T)}{p} \tag{4}$$

and

$$\left(\frac{\partial v}{\partial p}\right)_T = \frac{T}{p}\left(\frac{\partial s}{\partial p}\right)_T. \tag{5}$$

Eq. (2) also gives the Maxwell relation

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p, \tag{6}$$

which is obtained from (2) by first writing the equations

$$\left(\frac{\partial u}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial T}\right)_p \quad \text{and} \quad \left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T$$

and then by equating $\partial^2 u/\partial p\,\partial T$ and $\partial^2 u/\partial T\,\partial p$. Eqs. (5) and (6) give

$$\left(\frac{\partial v}{\partial p}\right)_T = -\frac{T}{p}\left(\frac{\partial v}{\partial T}\right)_p, \tag{7}$$

which in fact means (ii) in the problem. In order to see this, consider v as a function of the variables, $x = p/T$ and T. Then we have

$$\begin{aligned}\left(\frac{\partial v}{\partial T}\right)_p &= \left(\frac{\partial v}{\partial x}\right)_T\left(\frac{\partial x}{\partial T}\right)_p + \left(\frac{\partial v}{\partial T}\right)_x \\ &= -\frac{p}{T^2}\left(\frac{\partial v}{\partial x}\right)_T + \left(\frac{\partial v}{\partial T}\right)_x,\end{aligned} \tag{8}$$

$$\left(\frac{\partial v}{\partial p}\right)_T = \left(\frac{\partial v}{\partial x}\right)_T\left(\frac{\partial x}{\partial p}\right)_T = \frac{1}{T}\left(\frac{\partial v}{\partial x}\right)_T. \tag{9}$$

Eq. (7) thus means that

$$(\partial v/\partial T)_x = 0$$

or that v depends only on $x=p/T$ (proof of (ii)). By the definition, $c_p=T(\partial s/\partial T)_p$, eqs. (3) and (4) give

$$c_p - c_v = p(\partial v/\partial T)_p.$$

Since v depends only on $x=p/T$, eq. (8) gives

$$p\left(\frac{\partial v}{\partial T}\right)_p = -\frac{p^2}{T^2}\left(\frac{\partial v}{\partial x}\right)_T = -x^2\frac{\mathrm{d}v}{\mathrm{d}x}.$$

Therefore $c_p - c_v$ is also a function of x only.

34. Let $C_V=(\partial U/\partial T)_V$ be the molar specific heat at constant volume, U the internal energy per mole and V the molar volume. Then we have

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial^2 U}{\partial V\,\partial T} = \frac{\partial}{\partial T}\left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V \tag{1}$$

(using (i) of problem 15). Since the van der Waals equation (1.17) can be written as

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \tag{2}$$

the right side of (1) is zero so that C_V is independent of V and depends only on T. Using eq. (1) of problem 15, we have

$$\begin{aligned}\mathrm{d}U &= \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = C_V\,\mathrm{d}T + \left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\}\mathrm{d}V \\ &= C_V\,\mathrm{d}T + \frac{a}{V^2}\,\mathrm{d}V.\end{aligned} \tag{3}$$

This is integrated to give

$$U = \int^T C_V\,\mathrm{d}T - \frac{a}{V} + U_0 \qquad (U_0 \text{ is a constant}). \tag{4}$$

With the use of (2) and (3), the entropy differential is written as

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p\,\mathrm{d}V}{T} = \frac{C_V}{T}\mathrm{d}T + \frac{R}{V-b}\mathrm{d}V, \tag{5}$$

which is integrated to give

$$S = \int^T \frac{C_V}{T}\mathrm{d}T + R\log(V-b) + S_0 \qquad (S_0 \text{ is a constant}). \tag{6}$$

35. Assuming $C_V = \text{const.}$, the equation for U is obvious from (4) in the solution to the previous problem. In the case of an adiabatic quasi-static change, eq. (5) of the previous solution gives

$$dS = \frac{C_V}{T}\,dT + \frac{R}{V-b}\,dV = \frac{C_V}{T}\,dT + \frac{C_p - C_V}{V-b}\,dV = 0$$

(using Mayer's relation), which is written as

$$\frac{dT}{T} + \frac{(\gamma-1)\,dV}{V-b} = 0$$

and results in

$$T(V-b)^{\gamma-1} = \text{const.}$$

This can be written as

$$\left(p + \frac{a}{V^2}\right)(V-b)^{\gamma} = \text{const.}$$

when the van der Waals equation is substituted. In the case of an adiabatic expansion into a vacuum (irreversible!) $U = \text{const.}$, so that

$$T_2 - T_1 = \frac{a}{C_V}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

must clearly hold.

36. As given in the solution of problem 24 the Joule-Thomson coefficient is

$$\left(\frac{\partial T}{\partial p}\right)_H = \left\{T\left(\frac{\partial V}{\partial T}\right)_p - V\right\}\Big/ C_p. \tag{1}$$

By approximating the van der Waals equation as $p = nRT/V + n^2(RTb - a)/V^2$ to the order of $1/V^2$, we have

$$\left(\frac{\partial V}{\partial T}\right)_p \doteqdot \frac{V}{T}\,\frac{(1 + nb/V)}{\{1 + (2n/V)(b - a/RT)\}} \doteqdot \frac{V}{T}\left\{1 + \frac{n}{V}\left(\frac{2a}{RT} - b\right)\right\} \tag{2}$$

and

$$\left(\frac{\partial T}{\partial p}\right)_H \doteqdot \frac{1}{C_p}\left(\frac{2a}{RT} - b\right), \tag{3}$$

where C_p is the molar specific heat for constant pressure. If $(\partial T/\partial p)_H = 0$ at T_i (inversion temperature), we have from eq. (3)

$$T_i = 2a/Rb. \tag{4}$$

The critical temperature is $T_c = 8a/27Rb$ (example 8, Chapter 1), so that $T_i = 27\,T_c/4$.

37. The simplest way is to use $(\partial H/\partial p)_T = V - T(\partial V/\partial T)_p$ ((ii) of problem 15). We substitute $H = U + pV$ and the given expansion formula for V to obtain

$$(B+\beta) + 2(C+\gamma)p + \cdots = \frac{1}{p}(A - TA') + (B - TB') + (C - TC')p + \cdots,$$

where $A' = \mathrm{d}A/\mathrm{d}T$, etc. The limit as $p \to 0$ gives $A - TA' = 0$ with the solution $A = \text{const.} \times T$. Thus, the absolute temperature can be determined in the following way. Measure the quantity pV for a gas at different pressures but at a given temperature and extrapolate them to get $\lim_{p\to 0} pV = A$ (cf. Fig. 1.5). Do the same thing at a temperature of a reference point such as the triple point of water for which the numerical value $T_0 = 273.16$ is fixed. Then the desired value of the absolute temperature is given by $A/A_{\text{triple point}} = T/T_0$.

38. From $\delta Q = T\delta S$ the latent heat of expansion, L_p, is defined as

$$L_p \equiv T\left(\frac{\partial S}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p \tag{1}$$

(using Maxwell's relation (iii) of problem 16). If we use T instead of θ,

$$\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial V}{\partial \theta}\right)_p \frac{\mathrm{d}\theta}{\mathrm{d}T}.$$

Substituting this into (1), we get $L_p = -(\partial V/\partial\theta)_p T\,\mathrm{d}\theta/\mathrm{d}T$, or

$$\frac{\mathrm{d}\log T}{\mathrm{d}\theta} = -\left(\frac{\partial V}{\partial \theta}\right)_p \Big/ L_p = -\frac{V\alpha(\theta)}{L_p(\theta)}.$$

This is integrated to give

$$\log\left(\frac{T}{T_0}\right) = -V\int_{\theta_0}^{\theta} \frac{\alpha(\theta)\,\mathrm{d}\theta}{L_p(\theta)} = f(\theta, \theta_0). \tag{2}$$

The right side can be obtained by numerical calculation, using measured values. Then θ can be converted to T by this relation.

39. Substitute

$$H = \frac{M(T-\theta)}{C} \qquad \left(\text{as} \quad M = \chi H = \frac{CH}{T-\theta}\right) \tag{1}$$

into eq. (3) of the solution to problem 27. Then we have

$$(\partial U/\partial M)_T \doteq -\theta M/C. \tag{2}$$

Multiply the two equations in (2) of the solution to problem 27 by T and differentiate them with respect to M and T to obtain Maxwell's relation $(\partial S/\partial M)_T = -(\partial H/\partial T)_M$. Therefore we find that

$$\left(\frac{\partial C_M}{\partial M}\right)_T = \frac{T\partial^2 S}{\partial T\,\partial M} = -T\left(\frac{\partial^2 H}{\partial T^2}\right)_M = 0$$

and that C_M is independent of M and depends on T only. Hence, integrating

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_M \mathrm{d}T + \left(\frac{\partial U}{\partial M}\right)_T \mathrm{d}M = C_M\,\mathrm{d}T - \frac{\theta M\,\mathrm{d}M}{C},$$

we obtain

$$U = \int^T C_M\,\mathrm{d}T - \frac{\theta M^2}{2C} + \text{const.},$$

and integrating

$$\mathrm{d}S = \frac{\mathrm{d}U - H\,\mathrm{d}M}{T} = C_M\frac{\mathrm{d}T}{T} - \frac{M\,\mathrm{d}M}{C},$$

we find

$$S = \int^T C_M\frac{\mathrm{d}T}{T} - \frac{M^2}{2C} + \text{const.}.$$

40. Let U be the internal energy and S the entropy of the system. The first and the second laws state that

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + H\,\mathrm{d}I, \tag{1}$$

where I is the magnetic moment of the system. From (1) we have

$$\left.\begin{aligned}\left(\frac{\partial U}{\partial p}\right)_H &= T\left(\frac{\partial S}{\partial p}\right)_H - p\left(\frac{\partial V}{\partial p}\right)_H + H\left(\frac{\partial I}{\partial p}\right)_H,\\ \left(\frac{\partial U}{\partial H}\right)_p &= T\left(\frac{\partial S}{\partial H}\right)_p - p\left(\frac{\partial V}{\partial H}\right)_p + H\left(\frac{\partial I}{\partial H}\right)_p.\end{aligned}\right\} \tag{2}$$

Since $\partial^2 X/\partial p\,\partial H = \partial^2 X/\partial H\,\partial p$ $(X = U, S, V, I)$,

$$\left(\frac{\partial V}{\partial H}\right)_p = -\left(\frac{\partial I}{\partial p}\right)_H. \tag{3}$$

Substitute $I = \chi H V$ into (3) to obtain

$$\left(\frac{\partial V}{\partial H}\right)_p = -H\left\{V\left(\frac{\partial \chi}{\partial p}\right)_T + \chi\left(\frac{\partial V}{\partial p}\right)_T\right\}$$

or

$$\frac{1}{V}\left(\frac{\partial V}{\partial H}\right)_p = +H\left\{\beta\chi - \left(\frac{\partial \chi}{\partial p}\right)_T\right\}. \tag{4}$$

Integrate both sides with respect to H from 0 to H, neglecting the dependence of χ and $(\partial\chi/\partial p)_T$ on H, to obtain

$$\log\frac{V+\Delta V}{V} = \frac{1}{2}H^2\left\{\beta\chi - \left(\frac{\partial \chi}{\partial p}\right)_T\right\}, \tag{5}$$

where ΔV is the volume change. We may usually assume that $\Delta V/V \ll 1$. Expanding the left side, keeping only the first term, we have

$$\frac{\Delta V}{V} = \frac{1}{2}H^2\left\{\beta\chi - \left(\frac{\partial \chi}{\partial p}\right)_T\right\}.$$

41. By example 5, (i) for an isothermal change at constant volume we have $\delta W_{\min} = \delta F$, so that

$$\left(\frac{\partial[\delta W_{\min}/T]}{\partial T}\right)_V = -\frac{\delta F}{T^2} - \frac{\delta S}{T} = -\frac{\delta U}{T^2},$$

for which the condition of constant volume (no work) gives

$$\delta U = \delta' Q.$$

(ii) For an isothermal change at constant pressure we have $\delta W_{\min} = \delta G$, so that

$$\left(\frac{\partial[\delta W_{\min}/T]}{\partial T}\right)_p = -\frac{\delta G}{T^2} - \frac{\delta S}{T^2} = -\frac{\delta H}{T^2},$$

for which the condition of constant pressure gives

$$\delta H = \delta' Q.$$

42. Let the equation of state for the real gas be

$$pV = f(p, T) = A + Bp + Cp^2 + \cdots.$$

Using the relation $(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p$ ((ii) of problem 17) we get

$$C_p - C_p^{(0)} = \int_0^p \left(\frac{\partial C_p}{\partial p}\right)_T \mathrm{d}p = -\int_0^p \frac{T}{p}\left(\frac{\partial^2 f}{\partial T^2}\right)_p \mathrm{d}p.$$

$C_p^{(0)}$ is the molar specific heat at zero pressure. Insert here the equation of

state and carry out the integration noticing that $A \propto T$ and $A''(T)=0$ (see solution to problem 37). Thus we have

$$C_p^{(0)} = C_p + TB''p + \tfrac{1}{2}TC''p^2 + \cdots. \tag{1}$$

Therefore, the measured values C_p for different values of p at a given temperature T can be extrapolated to $C_p^{(0)}$ by this equation.

43. Let the critical point be (p_c, V_c, T_c) and set $\mathfrak{p}=p/p_c$, $\mathfrak{v}=V/V_c$ and $\mathfrak{t}=T/T_c$. Then Dieterici's equation becomes

$$\mathfrak{p}(2\mathfrak{v}-1) = \mathfrak{t}\exp\left(2-\frac{2}{\mathfrak{t}\mathfrak{v}}\right) \tag{1}$$

(see problem 12, Chapter 1). The condition that the Joule-Thomson coefficient $(\partial T/\partial p)_H=0$ is $T(\partial V/\partial T)_p - V=0$ or

$$\left(\frac{\partial \mathfrak{v}}{\partial \mathfrak{t}}\right)_{\mathfrak{p}} = \frac{\mathfrak{v}}{\mathfrak{t}}. \tag{2}$$

Differentiate (1) with respect to $\mathfrak{t}$ at constant $\mathfrak{p}$ and substitute (2) for $\partial\mathfrak{v}/\partial\mathfrak{t}$ to get

$$\mathfrak{v} = 4/(8-\mathfrak{t}). \tag{3}$$

Eliminate $\mathfrak{v}$ in (1) with this to get

$$\mathfrak{p} = (8-\mathfrak{t})\exp\left(\frac{5}{2}-\frac{4}{\mathfrak{t}}\right). \tag{4}$$

Fig. 2.14 shows the plot of this relation. On one side of the inversion temperature curve, $(\partial T/\partial p)_H>0$; cooling takes place in a Joule-Thomson expansion. On the other side of the curve, $(\partial T/\partial p)_H<0$: heating occurs. The figure also shows the experimental curve for H_2.

Similar considerations can be applied to a van der Waals gas. The equation of state is

$$\left(\mathfrak{p}+\frac{3}{\mathfrak{v}^2}\right)\left(\mathfrak{v}-\frac{1}{3}\right) = \frac{8}{3}\mathfrak{t} \tag{5}$$

in terms of the reduced variables (see example 8 in Chapter 1). This gives

$$-\frac{6}{\mathfrak{v}^3}\left(\frac{\partial \mathfrak{v}}{\partial \mathfrak{t}}\right)_{\mathfrak{p}}\left(\mathfrak{v}-\frac{1}{3}\right) + \left(\mathfrak{p}+\frac{3}{\mathfrak{v}^2}\right)\left(\frac{\partial \mathfrak{v}}{\partial \mathfrak{t}}\right)_{\mathfrak{p}} = \frac{8}{3},$$

and hence

$$\left(\frac{\partial \mathfrak{v}}{\partial \mathfrak{t}}\right)_{\mathfrak{p}} = \frac{8}{3}\bigg/\left(\mathfrak{p}-\frac{3}{\mathfrak{v}^2}+\frac{2}{\mathfrak{v}^3}\right). \tag{6}$$

Substituting the condition $T(\partial V/\partial T)_p - V = 0$ or

$$\mathfrak{t}\left(\frac{\partial \mathfrak{v}}{\partial \mathfrak{t}}\right)_{\mathfrak{p}} - \mathfrak{v} = 0 \tag{7}$$

into (6), we have with (5)

$$\left(\mathfrak{p} + \frac{3}{\mathfrak{v}^2}\right)\left(\mathfrak{v} - \frac{1}{3}\right) = \frac{8}{3}\mathfrak{t} = \mathfrak{v}\left(\mathfrak{p} - \frac{3}{\mathfrak{v}^2} + \frac{2}{\mathfrak{v}^3}\right),$$

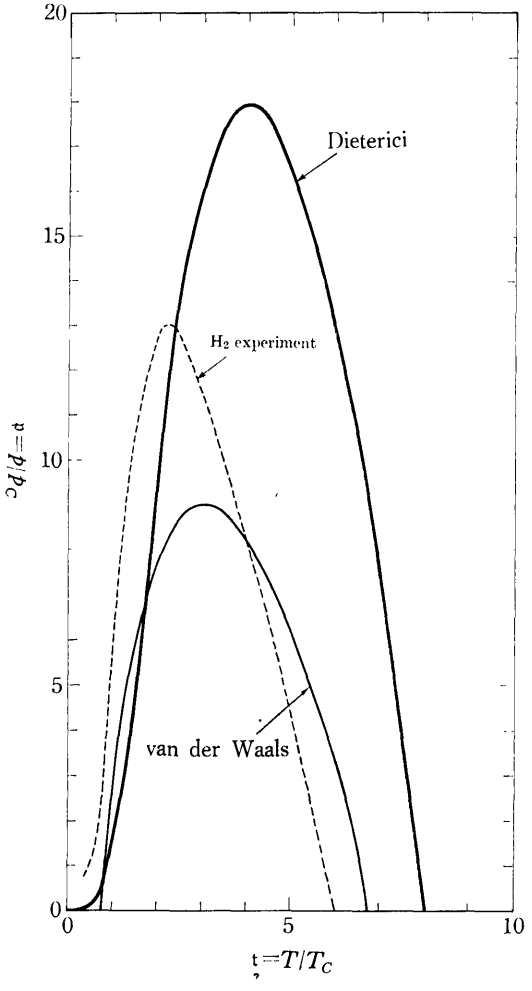


Fig. 2.14.

and hence

$$\mathfrak{p} = \frac{9}{\mathfrak{v}}\left(2 - \frac{1}{\mathfrak{v}}\right). \tag{8}$$

Equations (8) and (5) then give

$$\frac{18}{\mathfrak{v}^2}\left(\mathfrak{v} - \frac{1}{3}\right)^2 = \frac{8}{3}\mathfrak{t},$$

or

$$\mathfrak{v} = 1/(3 - 2\sqrt{\tfrac{1}{3}\mathfrak{t}}). \tag{9}$$

Substituting (9) into (8) we find

$$\mathfrak{p} = 24\sqrt{3\mathfrak{t}} - 12\mathfrak{t} - 27. \tag{10}$$

This is the locus of the inversion point on the $\mathfrak{p}$–$\mathfrak{t}$ diagram. As shown in Fig. 2.14 this locus has a maximum of $\mathfrak{p}=9$ at $\mathfrak{t}=3$.

44. If the volume for a unit mass is $v(=1/\rho)$, the Joule-Thomson coefficient, μ, is given by (problem 24)

$$\mu c_p = T\left(\frac{\partial v}{\partial T}\right)_p - v, \tag{1}$$

where T is the absolute temperature. If c_p' and μ' are the values of c_p and μ referred to an empirical temperature scale θ, they are related to c_p and μ by

$$c_p' = c_p\frac{\mathrm{d}T}{\mathrm{d}\theta}, \tag{2a}$$

$$\mu' = \left(\frac{\partial\theta}{\partial p}\right)_h = \mu\frac{\mathrm{d}\theta}{\mathrm{d}T}. \tag{2b}$$

Similarly,

$$\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial v}{\partial\theta}\right)_p\frac{\mathrm{d}\theta}{\mathrm{d}T}. \tag{3}$$

If θ is the temperature by this gas thermometer, it is defined by $\theta=\text{const.}\times v$, so that $\partial v/\partial\theta = v/\theta$. Therefore, with (3), (1) becomes

$$\mu' c_p' = \frac{T}{\theta}\frac{\mathrm{d}\theta}{\mathrm{d}T}v - v,$$

or

$$\frac{\mathrm{d}\log\theta}{\mathrm{d}\log T} = 1 + \mu' c_p'\rho \equiv f(\theta), \tag{4}$$

which is integrated to give

$$\log\frac{T_1}{T_0} = \int_{\theta_0}^{\theta_1} \frac{\mathrm{d}\theta}{\theta f(\theta)}, \tag{5}$$

where $f(\theta)$ is defined by (4) and is known from the measured values of the density, ρ, the specific heat, c_p', and the Joule-Thomson coefficient, μ'. If T_0 is known for a standard point θ_0, the calibration of T_1 and θ_1 can be done by numerical integration of (5).

45. According to (1) in the solution to the previous problem, we have

$$T\left(\frac{\partial v}{\partial T}\right)_p = v + \mu c_p,$$

and therefore

$$\frac{\mathrm{d}T}{T} = \frac{\mathrm{d}v}{v + \mu c_p} = \frac{\mathrm{d}v}{v}\,\frac{1}{1 + \rho\mu c_p} = -\frac{\mathrm{d}\rho}{\rho}\,\frac{1}{1 + \rho\mu c_p}.$$

Insert

$$\mathrm{d}\log\rho/\mathrm{d}\theta = -\alpha(1 + \alpha\theta)^{-1} \qquad (\alpha = 0.003\,669)$$

into this equation and carry out the integration:

$$\log\frac{T}{T_0} = \int_0^t \frac{\alpha\,\mathrm{d}\theta}{1 + \alpha\theta}\,\frac{1}{1 + \rho\mu c_p}.$$

Put $T = 100 + T_0$ $(t = 100)$:

$$\log\left(1 + \frac{100}{T_0}\right) = \int_0^{100} \frac{\alpha\,\mathrm{d}\theta}{1 + \alpha\theta}\,\frac{1}{1 + \rho\mu c_p}. \tag{1}$$

The first approximation would be to use $(1 + \rho\mu c_p)^{-1} \doteqdot 1$, which gives $T_0 \doteqdot 1/\alpha$. Therefore to improve the approximation, we put

$$(1 + \rho\mu c_p)^{-1} = 1 + f \tag{2}$$

and write (1) as

$$\log\left(1 + \frac{100}{T_0}\right) = \log(1 + 100\alpha) + \alpha\int_0^{100} \frac{f(\theta)}{1 + \alpha\theta}\,\mathrm{d}\theta. \tag{3}$$

Further, we may put $T_0 = \alpha^{-1} + x$ and rewrite (3) as

$$\log\left\{\left(1 + \frac{x\alpha}{1 + 100\alpha}\right)\Big/(1 + x\alpha)\right\} = \alpha\int_0^{100} \frac{f(\theta)}{1 + \alpha\theta}\,\mathrm{d}\theta. \tag{4}$$

Since x and $x\alpha/(1+100\alpha)$ are small numbers compared to α, we may expand the left-hand side of (4), take only the first order term in x, and obtain

$$x\left(\frac{1}{1+100\alpha}-1\right)=\int_0^{100}\frac{f(\theta)}{1+\alpha\theta}\,d\theta\equiv\int_0^{100}g(\theta)\,d\theta\,. \tag{5}$$

The function $g(\theta)=f(\theta)/(1+\alpha\theta)$ is obtained from the given data as shown in the table. Note the necessary conversion of units. 1 cal$=4.18\times10^7$ erg, 1 kg/cm$^2=0.98\times10^6$ c.g.s., so that $\rho\mu c_p=\rho\mu' c_p'\cdot4.18\times10^7/0.98\times10^6$ (where μ' and c_p' are the given values in the units in the problem). Since the given value of α has only four significant figures, only two figures are necessary for x. Thus, a crude integration is sufficient for this problem. Then eq. (5) gives

$$-0.269x=-0.00183\,,$$

or

$$x=0.68\,,$$

thus

$$T_0=(0.003669)^{-1}+0.68=273.2\,.$$

θ	$f(\theta)$	$g(\theta)$
0°	− 0.00329	− 0.00329
25	− 0.00258	− 0.00235
50	− 0.00198	− 0.00167
75	− 0.00153	− 0.00120
100	− 0.00121	− 0.00088

DIVERTISSEMENT 7

Kapitza's helium liquefier. Helium, the last of the "permanent gases", was liquefied in 1908 by H. Kamerlingh Onnes. The reason why it is so difficult to liquefy helium is that the inversion temperature of the Joule-Thomson effect is extremely low for helium. Precooling to liquid hydrogen temperature is therefore necessary for the Joule-Thomson effect to be effective. In the original method the Joule-Thomson effect was used in cascade first for hydrogen and then for helium. In the method, most commonly used at present, hydrogen is not used and the first step is replaced by an adiabatic expansion. The use of adiabatic expansion was first applied by Claude-Heylandt for liquefaction of air and later by P. L. Kapitza for helium. The Collins machine is an example of a liquefier of this type.

In order to understand the basic processes of liquefaction, let us look at the figures showing schematic sketches of the liquefier and of the entropy-temperature diagram of helium. For simplicity, we assume that the heat insulation of the system is perfect and that the drop of pressure along the pipes is negligible. In the process a → b, the helium gas of temperature T_1 (~ 300 °K) and pressure p_1 (~ 1 atm) is compressed to a higher pressure p_2 (for example, 15 atm). This is an adiabatic compression so that the gas heats up. It is then cooled back to T_1 by water (b → c). The gas is further cooled to T_3 (~ 77 °K) by liquid nitrogen as it flows through the heat exchanger I and the liquid nitrogen bath (c → d).

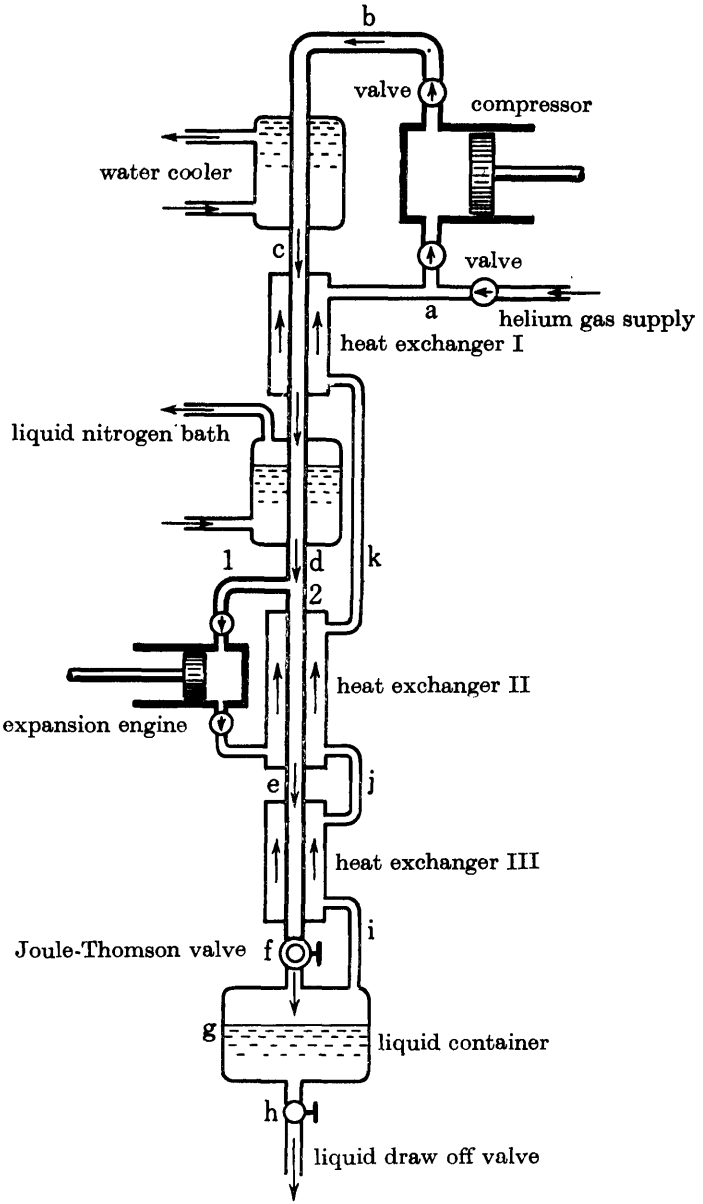


Fig. 2.15. Kapitza system of helium liquefier.

Then the gas is divided into two streams, 1 and 2. Stream 1 is introduced to an "expansion" engine where the gas expands under adiabatic conditions. By the adiabatic expansion (constant entropy, $\Delta S = 0$) the gas is cooled down from T_3 to T_4 (d → j) and goes through the heat exchanger II, cooling the other stream (2) of helium gas. It is then returned to the compressor (j → a). The stream 2, which passes through the heat exchanger II, is cooled to the temperature T_4 (d → e). It is then led

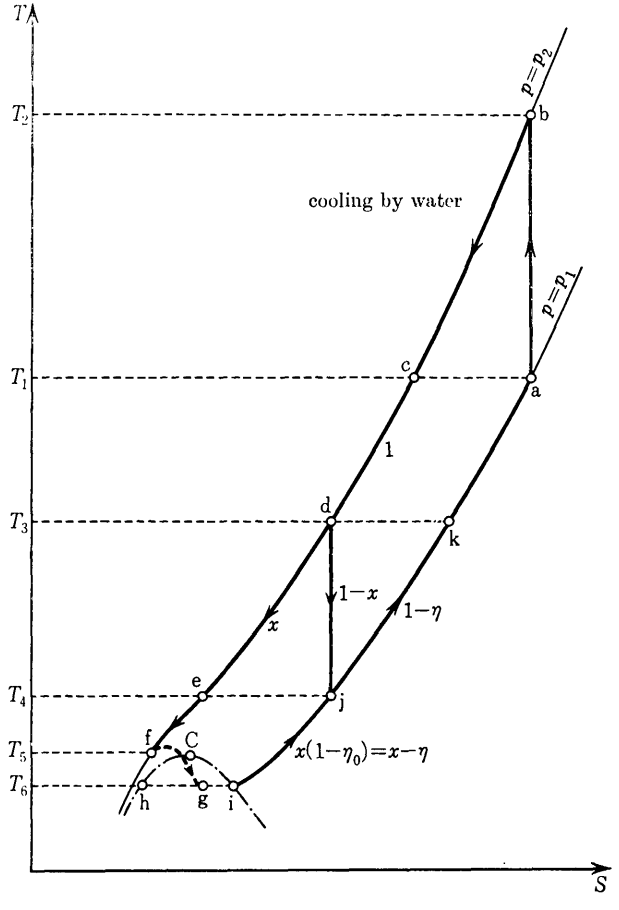


Fig. 2.16 *T-S* diagram of the liquefier.

to the liquid container through the Joule-Thomson valve. The temperature at which it enters the valve must be lower than the inversion temperature, so that the Joule-Thomson effect can lower the temperature, and thereby liquefy some part of the gas (h). The rest of the gas

goes through the heat exchanger III (i → j), which serves to cool the incoming stream to T_5 (e → f) at the Joule-Thomson valve, and then joins stream 1 at the point j and goes back to the compressor (j → a).

The liquefying efficiency of the whole process can be calculated as follows. If H is the enthalpy per 1 mol of helium gas, the Joule-Thomson process (f → g) is characterized by

$$H_f = H_g \quad (\Delta H = 0),$$

where the subscripts denote to the points in diagram. If η_0 is the fraction of gas liquefied at g, then

$$H_g = \eta_0 H_h + (1 - \eta_0) H_i,$$

where point h is in the liquid state and i is in the gas state. When the gas is cooled down in going from e to f, an amount of heat, $H_e - H_f$, must be

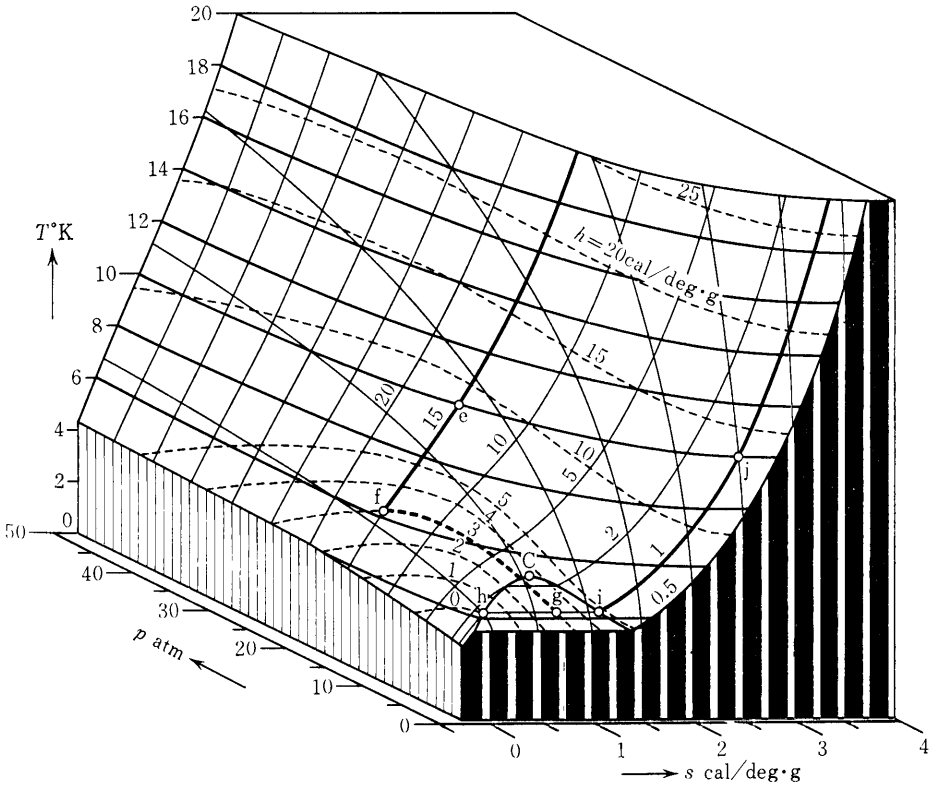


Fig. 2.17 Entropy of helium.

transferred to the gas coming out of the liquid container. Thus we have

$$H_e - H_f = (1 - \eta_0)(H_j - H_l).$$

By eliminating H_f and H_g from these equations we obtain

$$\eta = x\eta_0 = x\frac{H_j - H_e}{H_j - H_h},$$

where x is the fraction of gas in stream 2.

CHAPTER 3

THERMODYNAMIC FUNCTIONS AND EQUILIBRIUM CONDITIONS

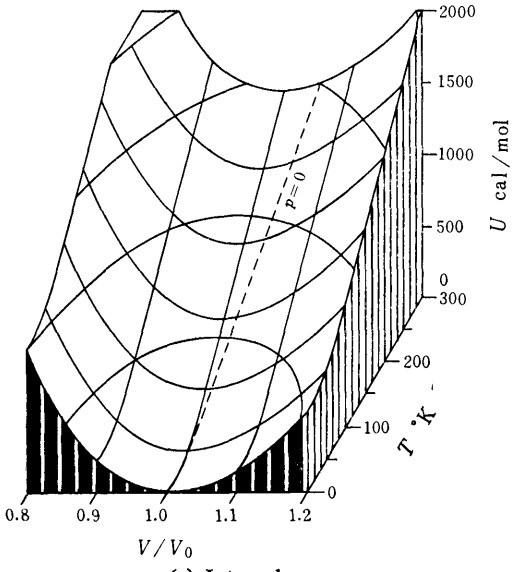
The third law of thermodynamics is introduced in this chapter as a new principle, but the most important thing is to clearly understand the structure of thermodynamics. The use of the various thermodynamic functions and the thermodynamic equations which can be derived therefrom seems somewhat like an exercise in mathematics. It is to be hoped that the reader will not lose himself in the calculations but will give some thought to the physics involved. The thermal equilibrium conditions are repeated here since they form the basis for applications of thermodynamics. In relation to this, the thermodynamic inequalities and Le Chatelier-Brown's principle will be discussed and will be applied to simple systems.

Fundamental topics

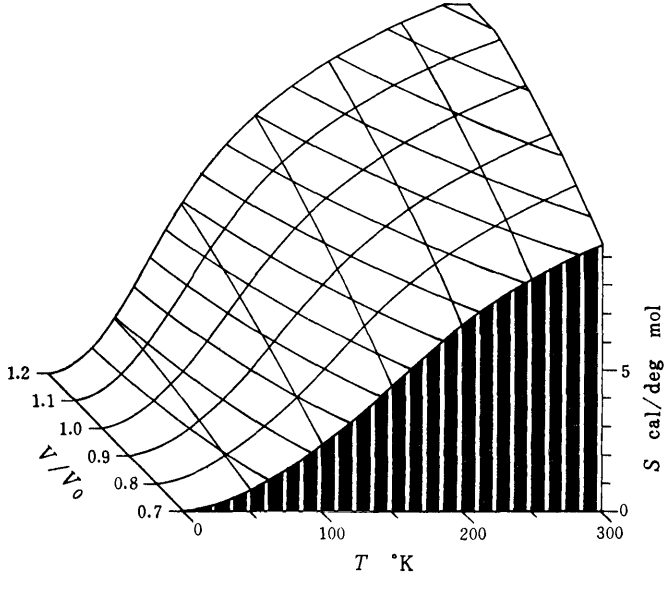
§ 3.1. THERMODYNAMIC FUNCTIONS

A system in thermal equilibrium is characterized by *thermodynamic functions* (or *thermodynamic potentials*) which are extensive quantities expressed as functions of suitable independent variables. The thermodynamic quantities concerning the system are all derived as various partial derivatives of thermodynamic functions and the so-called thermodynamic relations are derived as relations between these quantities (the *analytical formulation of thermodynamics*). Thermodynamics can only make general statements about the form of the thermodynamic functions (§ 3.8), but it cannot determine the concrete functional form for each particular system. This must be determined empirically or by statistical mechanics.

There is a particular set of variables which is convenient for each thermodynamic function. These are called the *natural independent variables*. If a thermodynamic function is given as a function of its natural independent variables, the thermodynamic properties are completely determined, but if it is given as a function of another set of independent variables, this is not sufficient to determine all the thermodynamic properties. (Example: compare the two cases where $U(S, V)$ is given and where $U(T, V)$ is given.) We will summarize in the following table the typical thermodynamic functions for a homogeneous system, their natural variables and the related total differential.

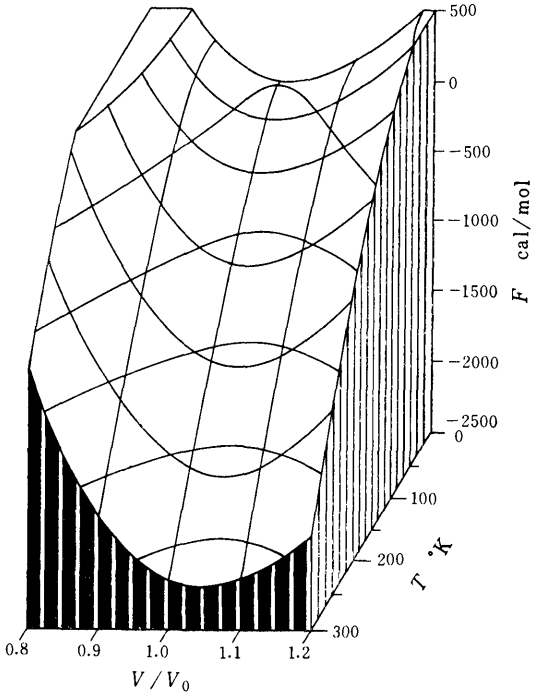


(a) Internal energy

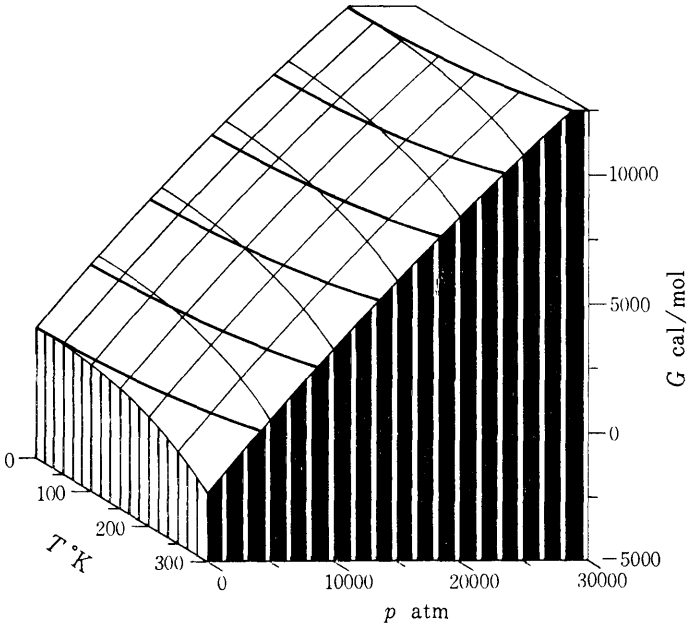


(b) Entropy

Fig. 3.1. Some examples of thermodynamic functions for solid sodium.



(c) Helmholtz free energy.



(d) Gibbs free energy.

Table 3.1

Thermodynamic functions (Definition)	Natural variables	Total differential	
Internal energy U	S, V, N_i	$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \Sigma\,\mu_i\,\mathrm{d}N_i$	(3.1)
Enthalpy $H = U + pV$	S, p, N_i	$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \Sigma\,\mu_i\,\mathrm{d}N_i$	(3.2)
Helmholtz free energy $F = U - TS$	T, V, N_i	$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \Sigma\,\mu_i\,\mathrm{d}N_i$	(3.3)
Gibbs free energy (thermodynamic potential) $G = F + pV = \Sigma\,N_i\mu_i$	T, p, N_i	$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \Sigma\,\mu_i\,\mathrm{d}N_i$	(3.4)
Grand potential* $J = -pV = F - G$	T, V, μ_i	$\mathrm{d}J = -S\,\mathrm{d}T - p\,\mathrm{d}V - \Sigma\,N_i\,\mathrm{d}\mu_i$	(3.5)
Entropy S	U, V, N_i	$\mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{p}{T}\mathrm{d}V - \Sigma\frac{\mu_i}{T}\mathrm{d}N_i$	(3.6)
Massieu function $\Psi = -F/T$	$\frac{1}{T}, V, N_i$	$\mathrm{d}\Psi = -U\,\mathrm{d}\left(\frac{1}{T}\right) + \frac{p}{T}\mathrm{d}V - \Sigma\frac{\mu_i}{T}\mathrm{d}N_i$	(3.7)
Planck function $\Phi = -G/T$	$\frac{1}{T}, p, N_i$	$\mathrm{d}\Phi = -H\,\mathrm{d}\left(\frac{1}{T}\right) - \frac{V}{T}\mathrm{d}p - \Sigma\frac{\mu_i}{T}\mathrm{d}N_i$	(3.8)
Kramers function $q = -J/T$	$\frac{1}{T}, V, \frac{\mu_i}{T}$	$\mathrm{d}q = -U\,\mathrm{d}\left(\frac{1}{T}\right) + \frac{p}{T}\mathrm{d}V + \Sigma\,N_i\,\mathrm{d}\left(\frac{\mu_i}{T}\right)$	(3.9)

* This function has no particular name widely accepted. In recent literature of statistical thermodynamics it is sometimes called this way because it is related to the grand canonical partition function.

§ 3.2. LEGENDRE TRANSFORMATION

In general a thermodynamic function, L, with $x, y, z, \ldots$ as its natural independent variables has the following total differential (Pfaffian form):

$$\mathrm{d}L = X\,\mathrm{d}x + Y\,\mathrm{d}y + Z\,\mathrm{d}z + \cdots, \tag{3.10}$$

where $X, Y, Z, \ldots$ are all functions of $x, y, z, \ldots$. The following transformation of L and the independent variables

$$\left.\begin{aligned} &L \to \bar{L} = L - Xx, \\ &x, y, z, \ldots \to X, y, z, \ldots, \\ \text{and thus}\quad &\mathrm{d}\bar{L} = -x\,\mathrm{d}X + Y\,\mathrm{d}y + Z\,\mathrm{d}z + \cdots \end{aligned}\right\} \tag{3.11}$$

is called the *Legendre transformation.* The various thermodynamic functions shown in Table 3.1 are derived by successive Legendre transformations from U or S. Besides the functions listed in Table 3.1, there are a variety of thermodynamic functions which are derived, for instance, from the internal energy $U(S, V, x_1, x_2, \ldots, N_1, N_2, \ldots)$ by successive Legendre transformations with respect to the variables $x_1, x_2, \ldots, X_1, X_2, \ldots$ representing such variables as electric field strength, magnetic field strength, strain and so forth. It is rather difficult to give a proper name to each of such thermodynamic functions.

§ 3.3. GIBBS-DUHEM RELATION

$$S\,\mathrm{d}T - V\,\mathrm{d}p + \sum_j N_j\,\mathrm{d}\mu_j = 0. \tag{3.12}$$

Here we explicitly consider work with respect to V only. Since the Gibbs free energy has the particle numbers $N_1, N_2, \ldots$ as extensive variables, it is obvious that

$$G(T, p, \alpha N_1, \alpha N_2, \ldots) = \alpha G(T, p, N_1, N_2, \ldots).$$

Differentiate this with respect to α and setting $\alpha = 1$, we have*

$$\sum_j N_j \left(\frac{\partial G}{\partial N_j}\right)_{T,p,N_j'} = G \qquad \text{(Euler's equation)}.$$

Since

$$\left(\frac{\partial G}{\partial N_j}\right)_{T,p,N_j'} = \mu_j$$

from eq. (3.4), this can be written as

$$G = \sum N_j \mu_j \left(= \sum n_j \tilde{G}_j\right). \tag{3.13}$$

By substituting this into $\mathrm{d}G$ of (3.4) we have eq. (3.12).

§ 3.4. DEFINITIONS OF THERMODYNAMIC QUANTITIES AND THERMODYNAMIC RELATIONS

1) *Heat capacity, specific heat.* By eqs. (1.10) and (2.12) we have:
heat capacity at constant volume:

$$C_V = \left(\frac{\mathrm{d}'Q}{\mathrm{d}T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V, \tag{3.14a}$$

* N_j' means the set of N_i, $i = 1, 2, \ldots$, other than N_j.

heat capacity at constant pressure:

$$C_p = \left(\frac{\mathrm{d}'Q}{\mathrm{d}T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p . \tag{3.14b}$$

2) *First partial differential coefficients of thermodynamic functions.* From (3.1)–(3.9) we have,

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p, \qquad \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_{j'}} = \mu_j, \tag{3.15*}$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}, \qquad \left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_{j'}} = -\frac{\mu_j}{T}, \tag{3.16}$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \qquad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -p, \qquad \left(\frac{\partial F}{\partial N_j}\right)_{T,V,N_{j'}} = \mu_j, \tag{3.17}$$

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S, \qquad \left(\frac{\partial G}{\partial p}\right)_{T,N} = V, \qquad \left(\frac{\partial G}{\partial N_j}\right)_{T,p,N_{j'}} = \mu_j . \tag{3.18}$$

Derivatives are not listed here for other thermodynamic functions.

3) *Partial molar quantities.* In a *multi-component system* with components $j = 1, 2, \ldots$, the quantity defined by

$$\frac{\partial \Phi}{\partial n_j} = \bar{\Phi}_j \tag{3.19}$$

is the partial molar quantity where n_j is the mole number of component j and Φ is an extensive variable. For example

$$\bar{U}_j = \frac{\partial U}{\partial n_j} \quad \text{(partial molar energy)},$$

$$\bar{H}_j = \frac{\partial H}{\partial n_j} \quad \text{(partial molar enthalpy)},$$

$$\bar{S}_j = \frac{\partial S}{\partial n_j} \quad \text{(partial molar entropy)},$$

$$\bar{V}_j = \left(\frac{\partial V}{\partial n_j}\right)_p \quad \text{(partial molar volume)},$$

$$\bar{G}_j = \frac{\partial G}{\partial n_j} \quad \text{(partial molar free energy)}.$$

* Subscripts, N, indicates differentiation, all N_1, N_2, ... being kept constant.

In particular, $\bar{G}_j$ is none other than the chemical potential per mole.*

4) *Reciprocity theorems* (Maxwell's relations). From the total differential (3.10) we have

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x}, \quad \text{etc.} \tag{3.20}$$

This is the condition for the left-hand side of eq. (3.10) to be a total exact differential, $\mathrm{d}L$ (integrability condition, or existence condition of L). The relation corresponding to eq. (3.20) can easily be written for eqs. (3.1)–(3.9). These *Maxwell relations* are, of course, not all independent (see note to example 2). For example, from eqs. (3.17) and (3.18) we have

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}, \qquad \left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{3.21a}$$

and from (3.7),

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = -\frac{\partial}{\partial(1/T)}\left(\frac{p}{T}\right)_{V,N} = T\left(\frac{\partial p}{\partial T}\right)_{V,N} - p. \tag{3.21b}$$

Some of these have already been obtained in the examples and problems of Chapter 2, but, in this chapter, we can treat them more systematically.

5) *Relations derived by transformation of variables.* Thermodynamic functions and the thermodynamic quantities that are derived from them are not always considered as functions of their natural variables. It is often necessary in thermodynamics to suitably change independent variables and derive relations between related differential coefficients. One of the formulae often used is eq. (1.23),

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \Big/ \left(\frac{\partial z}{\partial x}\right)_y, \tag{3.22a}$$

or, in a form more convenient for memorising,

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{3.22b}$$

It is also convenient to make use of the Jacobian transformation

$$\frac{\partial(u, v, \ldots)}{\partial(x, y, \ldots)} = \frac{\partial(u, v, \ldots)}{\partial(\xi, \eta, \ldots)} \Big/ \frac{\partial(x, y, \ldots)}{\partial(\xi, \eta, \ldots)}, \tag{3.23}$$

especially

$$\left(\frac{\partial u}{\partial x}\right)_{y,z,\ldots} = \frac{\partial(u, y, z, \ldots)}{\partial(x, y, z, \ldots)}. \tag{3.24}$$

* In this respect there are various names for $\bar{G}_j$ (partial molar free energy, Gibbs free energy per mole, molar free energy, etc).

§ 3.5. THE THIRD LAW OF THERMODYNAMICS (NERNST-PLANCK THEOREM)

The entropy of a chemically uniform body of finite density approaches a limiting value as the temperature goes to absolute zero regardless of pressure, density or phase. It is therefore convenient to take the state at 0 °K as the standard state (see eq. (2.11)) by assuming

$$\lim_{T \to 0} S = S_0 \equiv 0. \tag{3.25}$$

Then the entropy at any state is uniquely determined. The entropy defined in this way is sometimes called the absolute entropy.

Some important conclusions may be drawn from this theorem. First of all, *one can never attain the absolute zero of temperature by any means* (unattainability of absolute zero), and second, the specific heat, the thermal expansion coefficient and some other similar quantities are bound to approach zero as the temperature approaches zero. This theorem also has great significance for chemical reactions (see Chapter 4, § 4.15).

Historically, this theorem was deduced from a number of experimental facts, and therefore, like the other principles of thermodynamics, it is a principle established as an empirical law. Together with the zeroth, the first, and the second law, it forms a system of principles of axioms on which the whole logic of thermodynamics is based.

From the more atomistic viewpoint of statistical mechanics, the third law is a consequence of the quantum-mechanical nature of the microscopic motion of matter.

§ 3.6. EQUILIBRIUM BETWEEN TWO SYSTEMS

When two systems A and B are in thermodynamic contact, the equilibrium condition may be stated as follows, depending on the nature of the contact:

1) mechanical action (mechanical equilibrium): $p_A = p_B$, etc.* (3.26a)
2) thermal action (heat exchange): $T_A = T_B$, (3.26b)
3) mass action (material exchange): $\mu_j^A = \mu_j^B$. (3.26c)

PROOF: If we consider an isolated system, the equilibrium condition of the composite is (see § 2.10, a_1))

$$S_A + S_B = \max. \tag{3.27}$$

We also have the following auxiliary conditions from the fact that A + B is isolated

* When the boundary is not flat and surface tension is present, the pressure is not the same. Such cases are omitted here (see Chapter 4, § 4.3).

$$U_A + U_B = \text{const.}, \quad V_A + V_B = \text{const.}, \quad N_j^A + N_j^B = \text{const.}, \quad j = 1, 2, \ldots.$$

So the conditions are written as

$$\delta S_A + \delta S_B = 0, \tag{3.27'}$$

$$\delta U_A + \delta U_B = 0, \delta V_A + \delta V_B = 0, \delta N_j^A + \delta N_j^B = 0, \qquad j = 1, 2, \ldots. \tag{3.27''}$$

By (3.6), (3.27′) gives

$$\frac{\delta U_A}{T_A} + \frac{p_A}{T_A}\delta V_A - \sum \frac{\mu_j^A}{T_A}\delta N_j^A + \frac{\delta U_B}{T_B} + \frac{p_B}{T_B}\delta V_B - \sum \frac{\mu_j^B}{T_B}\delta N_j^B = 0,$$

which becomes, by (3.27″),

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\delta U_A + \left(\frac{p_A}{T_A} - \frac{p_B}{T_B}\right)\delta V_A - \sum\left(\frac{\mu_j^A}{T_A} - \frac{\mu_j^B}{T_B}\right)\delta N_j^A = 0.$$

Conditions (3.26a)–(3.26c) are obtained from this by considering possible variations under the prescribed restrictions.

§ 3.7. EQUILIBRIUM CONDITION FOR A GIVEN ENVIRONMENT

The condition for thermal equilibrium was given in § 2.10 and § 3.6. Here we summarize it again in a general form.

General equilibrium condition. The system under consideration is in contact with the environment at temperature $T^{(e)}$, pressure $p^{(e)}$, chemical potential of the j-th chemical component $\mu_j^{(e)}(j=1, 2, \ldots)$ and is acted on by forces $X_i^{(e)}$. When the system makes a virtual displacement defined by δU, δS, δV, $\delta N_j(j=1, 2, \ldots)$ and $\delta x_i(i=1, 2, \ldots)$ under the above-mentioned circumstances, the first law (see (1.5)) gives

$$\delta' Q = \delta U + p^{(e)}\delta V - \sum_i X_i^{(e)}\delta x_i - \sum_j \mu_j^{(e)}\delta N_j.$$

By the second law, such a displacement will be unrealizable if

$$\delta U - T^{(e)}\delta S + p^{(e)}\delta V - \sum_i X_i^{(e)}\delta x_i - \sum_j \mu^{(e)}\delta N_j > 0. \tag{3.28}$$

This is the equilibrium condition in its most general form.

The condition (3.28) demands of $U(S, V, x_1, x_2, \ldots, N_1, N_2, \ldots)$

$$\left.\begin{aligned} &\frac{\partial U}{\partial S} = T = T^{(e)}, && -\frac{\partial U}{\partial V} = p = p^{(e)}, \\ &\frac{\partial U}{\partial x_i} = X_i = X^{(e)}, && i = 1, 2, \ldots \\ &\frac{\partial U}{\partial N_j} = \mu_j = \mu_j^{(e)}, && j = 1, 2, \ldots \end{aligned}\right\} \tag{3.29}$$

as the *equilibrium condition between the system and the environment.* This results from the condition that the first order variation of the left-hand side of (3.28) is zero. See § 3.8, for remarks on the second order variation.

Relation (3.28) can be expressed in the following form for special cases.

The equilibrium conditions for a closed system involving no work other than that due to change in volume are:

a) $\delta U > 0$, for constant volume, V, and entropy, S, of the system; (3.30a)

b) $\delta H > 0$, for constant pressure $p = p^{(e)}$ and entropy, S, of the system; (3.30b)

c) $\delta S < 0$, for an adiabatic change; (3.30c)

d) $\delta F > 0$, for constant V and $T = T^{(e)}$ of the system; (3.30d)

e) $\delta G > 0$, for constant pressure $p = p^{(e)}$ and temperature $T = T^{(e)}$. (3.30e)

Stability of thermal equilibrium. The maximum of the potential in statics represent unstable equilibrium but unstable equilibrium does not exist in thermodynamics. Condition (3.28) or conditions (3.30a–e) require that the first-order variation is zero as a necessary condition which does not, however, guarantee the equilibrium to be stable. It is necessary that the condition of minimum or maximum be satisfied for second order (or higher order) variations (cf. § 3.8).

Metastable equilibrium. If, for example, in a case where T and V are constant, F has more than two minima, the state which gives the least value of the minima is the *most stable equilibrium state.* In contrast to this, the

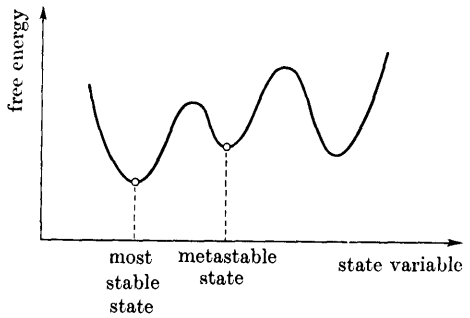


Fig. 3.2.

state corresponding to a larger value of minima is a metastable equilibrium state. A metastable state is often realized in nature almost like a stable state (example: supercooled states or supersaturation), but it will be broken spontaneously or by some triggering action, the system then transferring to the stable state with the least free energy.

§ 3.8. INEQUALITIES OF THERMODYNAMICS

In order that the state determined by eq. (3.29) be an equilibrium state, the left-hand side of (3.28) must be positive with respect to any variation in its neighborhood. For simplicity we write (see (2.15))

$$(S, V, x_1, x_2, \ldots, N_1, N_2, \ldots) = (Y_1, Y_2, \ldots), \tag{3.31a}$$

$$(T, -p, X_1, X_2, \ldots, \mu_1, \mu_2, \ldots) = (y_1, y_2, \ldots), \qquad (y_i = \partial U/\partial Y_i). \tag{3.31b}$$

Since the second order variation is

$$\delta_2 U = \frac{1}{2}\sum_i\sum_k \frac{\partial^2 U}{\partial Y_i \partial Y_k}\,\delta Y_i\,\delta Y_k = \frac{1}{2}\sum_i \delta y_i\,\delta Y_i$$

the above condition is

$$\sum_i\sum_k \frac{\partial^2 U}{\partial Y_i \partial Y_k}\,\delta Y_i\,\delta Y_k \geqq 0 \tag{3.32a}$$

or

$$\sum_i \delta y_i\,\delta Y_i \equiv \delta T\,\delta S - \delta p\,\delta V + \sum \delta X_i\,\delta x_i + \sum \delta\mu_j\,\delta N_j \geqq 0. \tag{3.32b}$$

Relation (3.32b) is more general than (3.32a); for example, when the set $(y_1, y_2, \ldots, y_r, Y_{r+1}, Y_{r+2}, \ldots)$ is used for the independent variables instead of (3.31a), it gives

$$\sum_{i=1}^{r}\sum_{j=1}^{r}\left(\frac{\partial Y_i}{\partial y_j}\right)_{y_j' Y_{r+1}\ldots}\delta y_i\,\delta y_j + \sum_{i=1}^{r}\sum_{k\geqq r+1}\left(\frac{\partial Y_i}{\partial Y_k}\right)_{y, Y_k'}\delta y_i\,\delta Y_k +$$
$$+\sum_{i=1}^{r}\sum_{k\geqq r+1}\left(\frac{\partial y_k}{\partial y_i}\right)_{y_i' Y_{r+1}\ldots}\delta y_i\,\delta Y_k + \sum_{k\geqq r+1}\sum_{l\geqq r+1}\left(\frac{\partial y_k}{\partial Y_l}\right)_{y, Y_l'}\delta Y_k\,\delta Y_l \geqq 0. \tag{3.32c}$$

Condition that the second order variation is positive. In order that the second order variation such as the quadratic form (3.32a) or (3.32c) be positive, the principal minors of the matrix of the coefficients must be positive*. For example, for (3.32a)

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* A quadratic form

$$\Phi = \sum_{i;\,k=1}^{m}\sum a_{ik}x_i x_k$$

can be brought into a diagonal form

$$\Phi = \sum_{i=1}^{m} a_i y_i^2$$

by an orthogonal transformation, $x_i = \sum T_{ik} y_k$. The positive definiteness of Φ means that

$$\begin{vmatrix} \dfrac{\partial^2 U}{\partial Y_{k_1}^2} & \dfrac{\partial^2 U}{\partial Y_{k_1}\,\partial Y_{k_2}} & \cdots & \dfrac{\partial^2 U}{\partial Y_{k_1}\,\partial Y_{k_n}} \\ \dfrac{\partial^2 U}{\partial Y_{k_2}\,\partial Y_{k_1}} & \dfrac{\partial^2 U}{\partial Y_{k_2}^2} & \cdots & \dfrac{\partial^2 U}{\partial Y_{k_2}\,\partial Y_{k_n}} \\ \cdots & & \cdots & \\ \dfrac{\partial^2 U}{\partial Y_{k_n}\,\partial Y_{k_1}} & \cdots & \cdots & \dfrac{\partial^2 U}{\partial Y_{k_n}^2} \end{vmatrix} \geqq 0, \quad (n = 1, 2, \ldots), \tag{3.33}$$

where $Y_{k_1}, \ldots, Y_{k_n}$ are n arbitrary members of the set $Y_1, Y_2, \ldots$. The same applies to (3.32c).

Thermodynamic inequalities (1).

i) The simplest of the conditions, (3.33), is that any diagonal element of the coefficient matrix of (3.32a) or (3.32c) must be positive:

$$\frac{\partial^2 U}{\partial Y_k^2} = \left(\frac{\partial y_k}{\partial Y_k}\right)_{Y_{k'}} \geqq 0, \tag{3.34a}$$

or

$$\left(\frac{\partial Y_i}{\partial y_i}\right)_{y'_i, Y_{r+1} \ldots} \geqq 0, \qquad \left(\frac{\partial y_k}{\partial Y_k}\right)_{y_1 \ldots y_r, Y_{k'}} \geqq 0. \tag{3.34b}$$

Examples are:

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \geqq 0 \quad (C_V \geqq 0), \qquad \left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p} \geqq 0 \quad (C_p \geqq 0), \tag{3.35a}$$

$$\left(\frac{\partial p}{\partial V}\right)_S \leqq 0, \qquad \left(\frac{\partial p}{\partial V}\right)_T \leqq 0, \tag{3.35b}$$

$$\left(\frac{\partial \mu_i}{\partial N_i}\right)_{S,V,N_{i'}} \geqq 0, \qquad \left(\frac{\partial \mu_i}{\partial N_i}\right)_{T,p,N_{i'}} \geqq 0. \tag{3.35c}$$

ii) The next simplest condition is that a two-by-two minor determinant is positive. For example,

$$\frac{\partial^2 U}{\partial S^2}\,\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S\,\partial V}\right)^2 = -\frac{T}{C_V}\left(\frac{\partial p}{\partial V}\right)_T \geqq 0 \tag{3.36}$$

(see example 5).

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the eigenvalues $a_1, \ldots, a_n$ of the matrix $A = (a_{ik})$ are all positive. Since we have

$$a_1 \ldots a_n = \det T^{-1}AT = \det T^{-1} \det A \det T = \det A \qquad (\text{since } \det T = \det T^{-1} = 1)$$

det A must be positive. A principal minor of the matrix A is the determinant of an n by n matrix constructed from A by choosing n corresponding columns and rows $(i_1, i_2, \ldots, i_n)$. The corresponding quadratic form is a special case of Φ in which only the corresponding x's are allowed to take finite values. Thus it must be positive. By applying the previous argument, one finds that the principal minor itself must be positive. Therefore, for a positive definite form Φ, every principal minor must be positive.

Thermodynamic inequalities (2). If $(Y_1, Y_2, \ldots)$ and $(y_1, y_2, \ldots)$ are the variables in (3.31a) or (3.31b), the inequalities

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{y_k} < \left(\frac{\partial y_i}{\partial Y_i}\right)_{Y_k}, \tag{3.37a}$$

$$\left(\frac{\partial Y_i}{\partial y_i}\right)_{Y_k} < \left(\frac{\partial Y_i}{\partial y_i}\right)_{y_k} \tag{3.37b}$$

must hold; e.g.

$$\left(\frac{\partial T}{\partial S}\right)_p < \left(\frac{\partial T}{\partial S}\right)_V \quad \text{or} \quad \left(\frac{\partial S}{\partial T}\right)_V < \left(\frac{\partial S}{\partial T}\right)_p, \quad \text{so that} \quad C_V < C_p; \tag{3.38a}$$

$$\left(\frac{\partial p}{\partial V}\right)_T > \left(\frac{\partial p}{\partial V}\right)_S, \qquad \left|\left(\frac{\partial p}{\partial V}\right)_S\right| > \left|\left(\frac{\partial p}{\partial V}\right)_T\right|. \tag{3.38b}$$

PROOF of (3.37a):

$$\begin{aligned}\left(\frac{\partial y_i}{\partial Y_i}\right)_{y_k} &= \frac{\partial(y_i, y_k)}{\partial(Y_i, y_k)} = \frac{\partial(y_i, y_k)}{\partial(Y_i, Y_k)}\,\frac{\partial(Y_i, Y_k)}{\partial(Y_i, y_k)} \\ &= \left\{\left(\frac{\partial y_i}{\partial Y_i}\right)_{Y_k}\left(\frac{\partial y_k}{\partial Y_k}\right)_{Y_i} - \left(\frac{\partial y_i}{\partial Y_k}\right)_{Y_i}\left(\frac{\partial y_k}{\partial Y_i}\right)_{Y_k}\right\}\Big/\left(\frac{\partial y_k}{\partial Y_k}\right)_{Y_i} \\ &= \left(\frac{\partial y_i}{\partial Y_i}\right)_{Y_k} - \frac{(\partial y_i/\partial Y_k)^2_{Y_i}}{(\partial y_k/\partial Y_k)_{Y_i}} < \left(\frac{\partial y_i}{\partial Y_i}\right)_{Y_k},\end{aligned} \tag{3.39}$$

where the relation (Maxwell's relation)

$$\left(\frac{\partial y_i}{\partial Y_k}\right)_{Y_i} = \left(\frac{\partial y_k}{\partial Y_i}\right)_{Y_k} = \frac{\partial^2 U}{\partial Y_i\,\partial Y_k}$$

and equation (3.34a) were used. Equation (3.37b) is proved in a similar fashion (problem 11).

§ 3.9. LE CHATELIER-BROWN'S PRINCIPLE

Le Chatelier's principle. When a given system in an equilibrium state is disturbed by the application of an action, A, a direct reaction, a, occurs in such a way as to diminish A. This principle is a physical interpretation of the inequality (3.34a, b), which is a condition for stability of the equilibrium. EXAMPLE: Suppose two bodies, 1 and 2, are in equilibrium at the same temperature, T. If the equilibrium is disturbed by an increase of the temperature of 1 (action A), heat starts to flow from 1 to 2 (reaction a). This tends to reduce the temperature difference, ΔT. The transfer of heat, δQ, means a

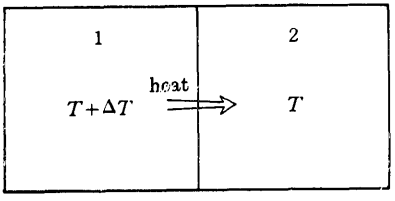


Fig. 3.3.

decrease in entropy, $\delta S = -\delta Q/T$, of 1: since $(\partial T/\partial S)_V = T/C_V > 0$, the temperature of 1 decreases by $\delta T = (T/C_V)\delta S = -\delta Q/C_V$.

NOTE: The action, A, and its direct reaction, a, are defined by changes in conjugate thermodynamic quantities (y_i and Y_i or Y_i and y_i).

Le Chatelier-Brown's principle. When a system in equilibrium is disturbed by an action, A, the indirect reaction, b, due to A occurs in the direction which tends to decrease the action, A. This principle is the physical interpretation of the inequality (3.37a, b).

EXAMPLE. A material is enclosed in a cylinder and piston, both of a thermally conducting material. The piston is in equilibrium with an external pressure, p. Now heat, ΔQ, is supplied (action, A) and the equilibrium is disturbed. The direct reaction is a temperature rise, ΔT, of the material (reaction, a). Besides this, the pressure may change and also the volume may change, the piston being displaced (indirect reaction, b). The inequality (3.38a) means that

$$(\Delta T)_V > (\Delta T)_p, \qquad (\Delta S = \Delta Q/T).$$

This means that the temperature change is larger when the volume change is inhibited (fixed piston) than when it is allowed (movable piston). This also means that the piston moves, if it is movable, in such a way as to diminish the effect of the action, A.

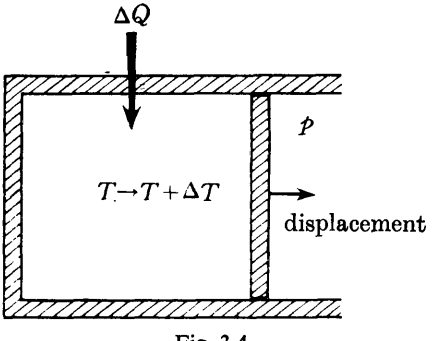


Fig. 3.4.

DIVERTISSEMENT 8

On the names of thermodynamic functions. The word "energy ἐνέργεια" can be seen in the works of Aristotle but "internal energy" is due to W. Thomson (1852) and R. J. E. Clausius (1876). The portion "en" means Inhalt=capacity and "ergy", like the unit "erg", derives from ἔργον= work. "Entropy" is also attributed to Clausius (1865) who took it from ἐντρέπειν=verwandeln and means Verwandlungsinhalt=change quantity. "Enthalpy" was introduced by H. Kamerlingh Onnes (1909) from ἐνθάλπειν=sich erwärmen which means Wärmeinhalt. W. Gibbs called it the heat function (for constant pressure). "Free energy" is due to H. von Helmholtz (1882), and means that part of the internal energy that can be converted into work, as seen in the equation $dF = d'A$ for an isothermal quasi-static process. It was customary to call the remaining part, TS, of the internal energy, $U = F + TS$, the gebundene Energie (bound energy), but this is not so common now. The Gibbs free energy (for constant pressure) was introduced by Gibbs, but German scientists used to call it die freie Enthalpie. Thus the thermodynamic functions often have different names in German and in English.

Further, on the equation of state: Kamerlingh Onnes gave the names, "thermische Zustandsgleichung" to $p = p(T, V)$ and the name "kalorische Zustandsgleichung" to $U = U(S, V)$. M. Planck (1908) called the latter "kanonische Zustandsgleichung".

Examples

1. Prove the following two statements which give a physical meaning to the concept of enthalpy.

(i) The enthalpy of a system is equal to the internal energy of the system and of the work source which exerts on the system a pressure, $p^{(e)}$, equal to the uniform pressure of the system, p.

(ii) If the state of the system changes under the constant pressure $p^{(e)}$, and it is in thermal equilibrium before and after the change, the heat absorbed by the system is equal to the increase in enthalpy, regardless of whether the change was reversible or irreversible.

SOLUTION

(i) Consider a cylinder with a cross-sectional area, σ, as shown in Figure 3.5. A weight is placed on a weightless piston so that the external pressure, $p^{(e)}$, due to the weight is equal to the internal pressure of the gas. Then if g is the gravitational acceleration and M is the mass of the weight, the pressure is

$$p = p^{(e)} = Mg/\sigma. \tag{1}$$

If the height of the piston is z, the volume of the gas is $V = \sigma z$. Consider the

weights on top of the piston and on the side at a constant level as the external work source. Taking the level of the weights on the side as the zero point, the potential energy of the weight on the piston becomes $U_e = Mgz$. (This energy is in fact the energy of the system composed of the weights and the earth, but as far as we implicitly accept the earth's existence and the constancy of its state it is permissible to call U_e the energy of the weights.)

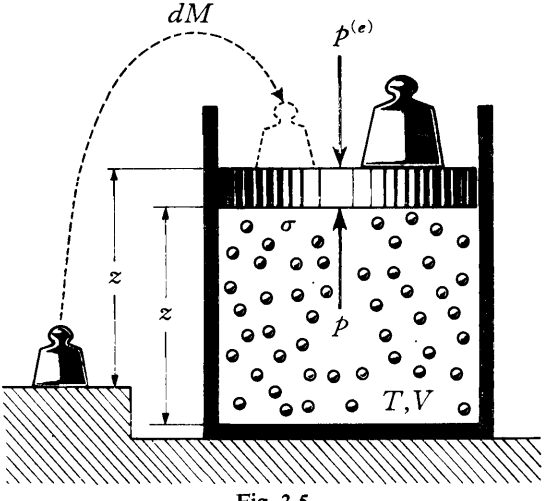


Fig. 3.5.

Now consider the change in the internal energy U^* of the entire system, gas plus weights. If the internal energy of the gas is U, we have by (1)

$$dU^* = dU + dU_e = dU + d(Mgz) = dU + d(p\sigma z) = d(U + pV),$$

or $dU^* = dH$. Except for an arbitrary constant we may suppose $U^* = H$. When the auxiliary weight on the side, dM, is put on the piston, the work done by our hands, $dM \cdot g(z + dz) = dM \cdot gz$ (neglect second order terms like $dM\, dz$), is equal to $V dp$. The first term dU in

$$dU^* = dU + p\, dV + V\, dp$$

is the change in the internal energy of the gas and $p\, dV$ (due to the change of the height of the piston) combined with $V\, dp$ is the change in the energy of the work source. Note that the gas pressure p and the external pressure, $p^{(e)}$, are always assumed to be in equilibrium and thus the variables (M and z) which describe the state of the purely mechanical work source are uniquely determined by the state variables of the thermal system (gas).

(ii) According to the first law (assuming that there is no exchange of work with the surroundings except that due to volume change) we have

$$U_2 - U_1 = Q + A = Q - p^{(e)}(V_2 - V_1)$$

for a change from an equilibrium state 1 to another state 2, where the pressure $p^{(e)}$ is constant. (Even if the pressure of the system p is not always equal to $p^{(e)}$, the work $A = -p^{(e)}(V_2 - V_1)$ is the proper expression.) Since $p^{(e)} = p$ holds both at the state 1 and the state 2, obviously we have

$$(U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = Q.$$

(This is the reason why H is called the *heat function*.)

Although gases were taken as an example, the argument is general. The work source could be something different.

NOTE: Figure 3.6 shows the relief of the enthalpy, $H(p, T)$, of air. C is the critical point. $(\partial H/\partial T)_p = C_p$ is the heat capacity at constant pressure. What is $(\partial H/\partial p)_T$?

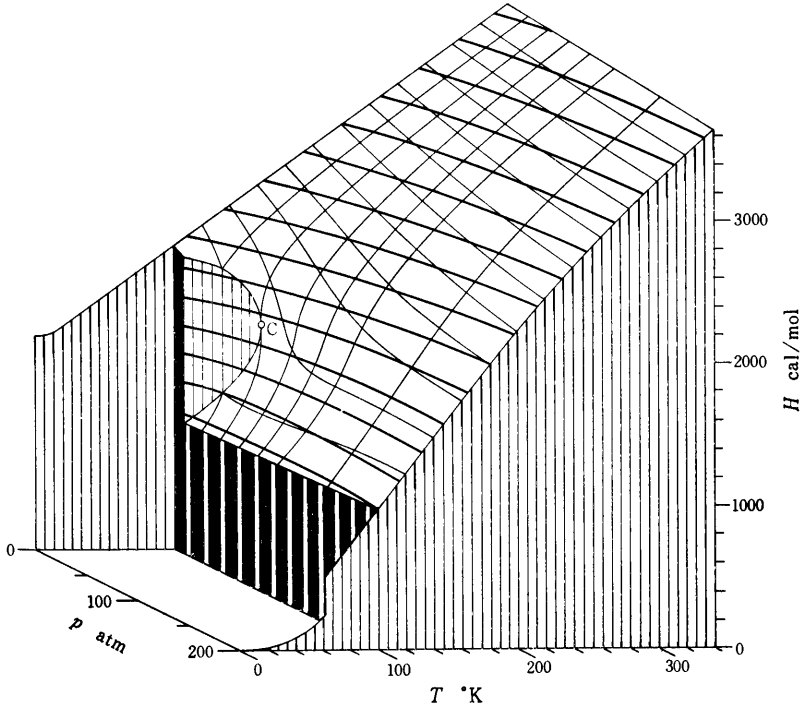


Fig. 3.6. Enthalpy of air.

2. Show that for the internal energy U, entropy S, the volume V, the absolute temperature T, the pressure p and the heat capacity C_V at constant volume, the following relation holds:

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} + p = T\left(\frac{\partial p}{\partial T}\right)_{V,N} = -C_V\left(\frac{\partial T}{\partial V}\right)_{S,N}.$$

SOLUTION

The first equation is proved in (3.21b) (also see examples 2 and 4 and problem 15 in Chapter 2). To prove the second equality we rewrite the left side of Maxwell's relation (3.21a), $(\partial S/\partial V)_{T,N} = (\partial p/\partial T)_{V,N}$. Using formula (3.22b) we have

$$\left(\frac{\partial S}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial T}\right)_{S,N}\left(\frac{\partial T}{\partial S}\right)_{V,N} = -1.$$

By (3.14a) $(\partial S/\partial T)_{V,N} = C_V/T$, and therefore

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial T}{\partial V}\right)_{S,N}\frac{C_V}{T}.$$

NOTE: Although the first equality was proved from (3.7) in Fundamental Topics, it can be proved from other equations, in which case it becomes a problem of transformation of variables in Maxwell's relation. This shows that the Maxwell equations are not all independent. For example, in example 2 of Chapter 2 we started from eq. (3.6). Another proof is shown in the solution of problem 5.

3. Show that the equation of state, $p = f(T, V)$, determines the dependence of the heat capacity at constant pressure, $C_p(T, p)$, on the pressure p, and the dependence of the heat capacity at constant volume, $C_V(T, V)$, on the volume V. In particular, when the equation of state is expanded in the form $pV = A(T) + B(T)p + C^*(T)p^2 + \cdots$, derive the expansion formula for the heat capacity using the temperature dependence of A, B, $C^*, \ldots$. Further, prove that $(\partial C_p/\partial p)_T = 0$ for a gas with an ideal gas type equation of state. Show that it is possible to derive the temperature dependence of C_p from that of C_V (or vice versa), if the equation of state is known.

SOLUTION

As shown in the solution to problem 17, the Maxwell relations are

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p, \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V,$$

which gives

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p, \quad \text{so that} \quad C_p(T, p) = C_p(T, p_0) - T\int_{p_0}^{p}\left(\frac{\partial^2 V}{\partial T^2}\right)_p \mathrm{d}p. \tag{1}$$

The second term can be calculated from the equation of state. In particular, if

$$pV = A(T) + B(T)\,p + C^*(T)\,p^2 + \cdots, \tag{2}$$

we have

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_p = A''(T)\,p^{-1} + B''(T) + C^{*\prime\prime}(T)\,p + \cdots,$$

and thus

$$C_p(T, p) = C_p(T, p_0) - T\left\{A''(T)\log\frac{p}{p_0} + B''(T)(p - p_0) + \right.$$
$$\left. + \tfrac{1}{2}C^{*\prime\prime}(T)(p^2 - p_0^2) + \cdots\right\}, \tag{3}$$

where the value of $C_p(T, p_0)$ is the experimental value at the pressure p_0. For an ideal gas, $A \propto T$, and $B = C = \cdots = 0$, so that $(\partial^2 V/\partial T^2)_p = 0$. Hence from (1) we have $(\partial C_p/\partial p)_T = 0$.

Similarly, for C_V we have

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V,$$

and thus

$$C_V(T, V) = C_V(T, V_0) + T\int_{V_0}^{V}\left(\frac{\partial^2 p}{\partial T^2}\right)_V \mathrm{d}V, \tag{4}$$

where V_0 is some arbitrarily chosen standard volume. A convenient expansion of the equation of state for this case is the virial expansion

$$pV = A(T) + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \cdots. \tag{5}$$

The reader may expand C_V using this expression.

To obtain either C_p or C_V from the other, we can use (i) of problem 17. An alternative method is to follow the calculation of (3.39) and proceed in the following manner:

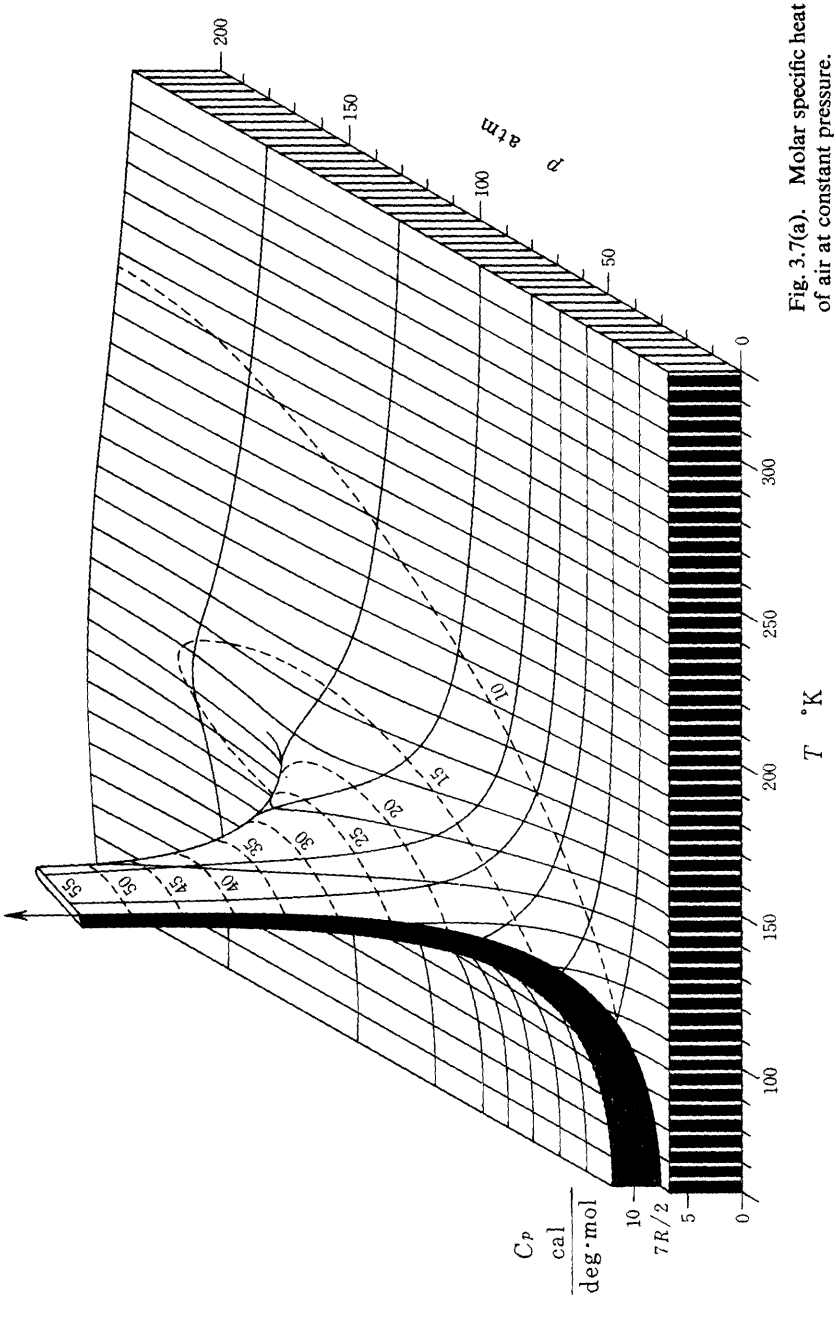
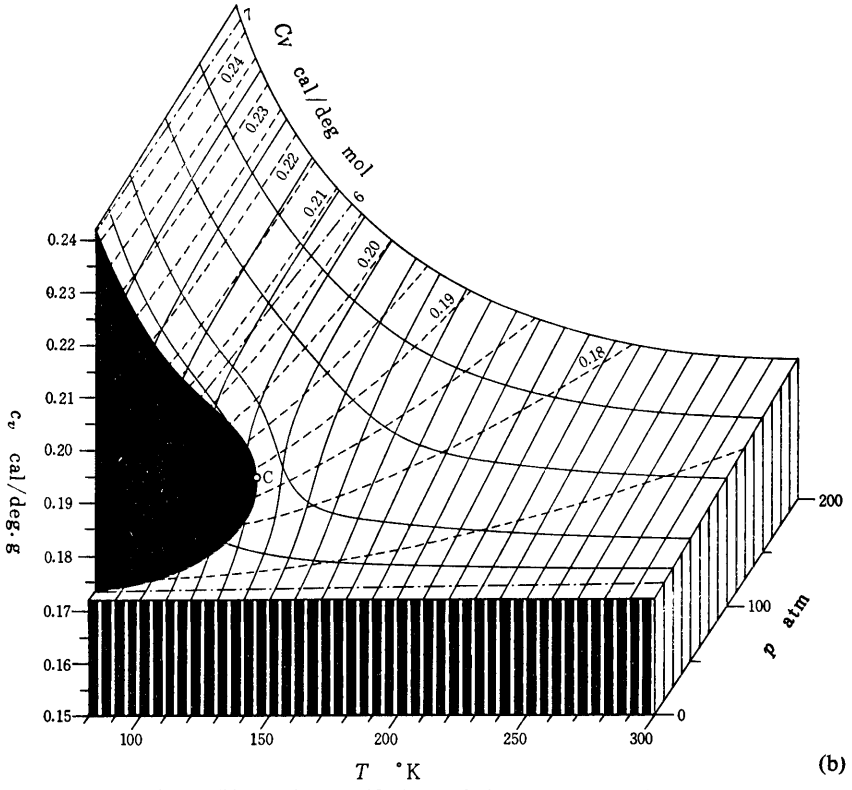


Fig. 3.7(a). Molar specific heat of air at constant pressure.

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\frac{\partial(S,p)}{\partial(T,p)} = T\frac{\partial(S,p)}{\partial(T,V)}\bigg/\frac{\partial(T,p)}{\partial(T,V)}$$
$$= T\left\{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial S}{\partial V}\right)_T\right\}\bigg/\left(\frac{\partial p}{\partial V}\right)_T$$
$$= T\left\{\left(\frac{\partial S}{\partial T}\right)_V - \left(\frac{\partial p}{\partial T}\right)_V^2\bigg/\left(\frac{\partial p}{\partial V}\right)_T\right\} = C_V - T\left(\frac{\partial p}{\partial T}\right)_V^2\bigg/\left(\frac{\partial p}{\partial V}\right)_T, \tag{6}$$

where we have used Maxwell's relation $(\partial p/\partial T)_V = (\partial S/\partial V)_T$. Similarly

$$C_V = T\frac{\partial(S,V)}{\partial(T,V)} = T\frac{\partial(S,V)}{\partial(T,p)}\bigg/\frac{\partial(T,V)}{\partial(T,p)} = T\left\{\left(\frac{\partial S}{\partial T}\right)_p + \left(\frac{\partial V}{\partial T}\right)_p^2\bigg/\left(\frac{\partial V}{\partial p}\right)_T\right\}$$
$$= C_p + T\left(\frac{\partial V}{\partial T}\right)_p^2\bigg/\left(\frac{\partial V}{\partial p}\right)_T. \tag{7}$$



(b)

Fig. 3.7(b). Molar specific heat of air at constant volume.

$C_p - C_V$ can be obtained in a concrete form using (2) in eq. (6) and (5) in eq. (7).

NOTE: The method outlined above uses Jacobians. This is a systematic method of transformation, which is very much worth learning well. The equivalence of eqs. (6) and (7) can be seen directly from

$$\left(\frac{\partial p}{\partial T}\right)_V \Big/ \left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p, \qquad -\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial V}{\partial T}\right)_p \Big/ \left(\frac{\partial V}{\partial p}\right)_T.$$

NOTE: Figures 3.7a and b illustrate the dependence on p and T of the molar specific heats, C_p, at constant pressure and C_V, at constant volume for air.

4. For internal energy U, absolute temperature T, volume V and pressure p, show that $(\partial U/\partial p)_T = 0$ if $(\partial U/\partial V)_T = 0$.

SOLUTION

This is a problem of transforming the independent variables from p, T to V, T. Using (3.24) and (3.23)

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{\partial(U, T)}{\partial(p, T)} = \frac{\partial(U, T)}{\partial(V, T)} \Big/ \frac{\partial(p, T)}{\partial(V, T)} = \left(\frac{\partial U}{\partial V}\right)_T \Big/ \left(\frac{\partial p}{\partial V}\right)_T.$$

(One can also prove this by considering $U(V, T)$ to be $U(V(p, T), T)$ and differentiating with respect to p.) Therefore if $(\partial U/\partial V)_T = 0$, $(\partial U/\partial p)_T = 0$ unless $(\partial p/\partial V)_T = 0$.

5. For a uniform closed system, prove that the heat capacities at constant pressure and at constant volume are always positive and that the volume decreases if the pressure is increased isothermally. Further, show that the heat capacity at constant pressure is never less than that at constant volume.

SOLUTION

This was treated from a more general point of view in § 3.8. Here a solution will be given for this specific problem. According to (3.32b), the stability condition is

$$\delta T\, \delta S - \delta p\, \delta V \geqq 0. \tag{1}$$

If T and V are taken as the independent variables, (1) becomes

$$\left(\frac{\partial S}{\partial T}\right)_V \delta T^2 + \left(\frac{\partial S}{\partial V}\right)_T \delta V\, \delta T - \left(\frac{\partial p}{\partial T}\right)_V \delta T\, \delta V - \left(\frac{\partial p}{\partial V}\right)_T \delta V^2 \geqq 0. \tag{2}$$

Now, from $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$, we have $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ (Maxwell's relation), so that (2) can be written as

$$\frac{C_V}{T}\delta T^2 - \left(\frac{\partial p}{\partial V}\right)_T \delta V^2 \geqq 0, \quad \text{so that} \quad C_V \geqq 0, \quad \left(\frac{\partial p}{\partial V}\right)_T \leqq 0. \tag{3}$$

Also, if T and p are chosen as independent variables, (1) becomes

$$\left(\frac{\partial S}{\partial T}\right)_p \delta T^2 + \left(\frac{\partial S}{\partial p}\right)_T \delta p\,\delta T - \left(\frac{\partial V}{\partial T}\right)_p \delta T\,\delta p - \left(\frac{\partial V}{\partial p}\right)_T \delta p^2 \geqq 0. \tag{4}$$

Using Maxwell's relation $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$, (4) becomes

$$\frac{C_p}{T}\delta T^2 - 2\left(\frac{\partial V}{\partial T}\right)_p \delta T\,\delta p - \left(\frac{\partial V}{\partial p}\right)_T \delta p^2 \geqq 0,$$

$$\text{and thus} \quad C_p \geqq 0, \quad \left(\frac{\partial V}{\partial p}\right)_T \leqq 0. \tag{5}$$

Following (3.39), we calculate

$$\begin{aligned}\left(\frac{\partial S}{\partial T}\right)_p &= \frac{\partial(S,p)}{\partial(T,p)} = \frac{\partial(S,p)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(T,p)} \\ &= \left\{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\right\}\Big/\left(\frac{\partial p}{\partial V}\right)_T \\ &= \left(\frac{\partial S}{\partial T}\right)_V - \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\Big/\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V - \left(\frac{\partial p}{\partial T}\right)_V^2\Big/\left(\frac{\partial p}{\partial V}\right)_T\end{aligned}$$

(where we have used Maxwell's relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V$). Since $(\partial p/\partial V)_T < 0$, we have

$$\left(\frac{\partial S}{\partial T}\right)_p \geqq \left(\frac{\partial S}{\partial T}\right)_V, \qquad \text{or} \qquad C_p \geqq C_V.$$

NOTE 1: Since $(\partial p/\partial V)_S \leqq 0$ can be easily derived from (1), $C_p/C_V = \kappa_T/\kappa_S > 0$ gives $C_p = 0$ if $C_V = 0$.

NOTE 2: Equations similar to (3) and (5) can be proved for a heat capacity defined by an arbitrary specified process. It should be noted, however, that a heat capacity can be negative for a non-uniform system. For instance, if the density is high in the centre due to gravitational force, or if an open system is exchanging matter with the outside, the specific heat can be negative. (See problem 39 in Chapter 4.)

6. In the quasi-static expansion of a uniform body under constant pressure, show that the entropy of the body increases or decreases depending on

whether the volume thermal expansion coefficient at constant pressure is positive or negative.

SOLUTION

This can be shown by examining the sign of the volume derivative of the entropy at constant pressure $(\partial S/\partial V)_p$. The volume expansion coefficient at constant pressure is defined by $\alpha=(\partial V/\partial T)_p/V$, for which it is convenient to consider T and p as the independent variables. Thus the problem reduces to that of changing the independent variables V, p to T, p in $(\partial S/\partial V)_p$. This is done as follows (application of (3.23) and (3.24)):

$$\left(\frac{\partial S}{\partial V}\right)_p=\frac{\partial(S,p)}{\partial(V,p)}=\frac{\partial(S,p)}{\partial(T,p)}\bigg/\frac{\partial(V,p)}{\partial(T,p)}=\left(\frac{\partial S}{\partial T}\right)_p\bigg/\left(\frac{\partial V}{\partial T}\right)_p=\frac{C_p}{T}\bigg/V\alpha.$$

As proved in example 5, $C_p \geqq 0$ for a uniform body and since $T \geqq 0$ and $V \geqq 0$, the sign of $(\partial S/\partial V)_p$ is the same as the sign of α.

7. The heat capacity at constant volume $C_V=Nf(T)$ (where N is the number of molecules) is known for an ideal gas. Find the free energy F, the internal energy U, the entropy S, and the chemical potential μ. (See problem 12.)

SOLUTION

Integration of $(\partial S/\partial T)_V=C_V/T$ gives

$$S=\int^T \frac{C_V(T')}{T'}\,\mathrm{d}T'+g_1(V,N)=N\int^T \frac{f(T')}{T'}\,\mathrm{d}T'+g_1(V,N), \qquad (1)$$

where $g_1(V, N)$ is a function of V and N. Since $(\partial F/\partial T)_V=-S$, integrating (1) gives

$$\begin{aligned} F &= -\int^T S(T')\,\mathrm{d}T'+g_2(V,N) \\ &= -N\int^T \mathrm{d}T'\int^{T'}\frac{f(T'')\,\mathrm{d}T''}{T''}-Tg_1(V,N)+g_2(V,N), \end{aligned} \qquad (2)$$

where $g_2(V, N)$ is a function of V and N. Integrating by parts, we get

$$\int^T \mathrm{d}T'\int^{T'}\frac{f(T'')\,\mathrm{d}T''}{T''}=T\int^T\frac{f(T')\,\mathrm{d}T'}{T'}-\int^T f(T')\,\mathrm{d}T' \qquad (3)$$

and

$$U = F + TS = N \int^{T} f(T')\,\mathrm{d}T' + g_2(V, N). \tag{4}$$

Substitute eq. (2) into the condition (1.11), $(\partial F/\partial V)_T = -p = -NkT/V$, to obtain

$$\frac{\partial g_1}{\partial V} = \frac{Nk}{V}, \qquad \frac{\partial g_2}{\partial V} = 0,$$

and hence

$$g_1 = Nk \log V + k\phi_1(N), \qquad g_2 = \phi_2(N), \tag{5}$$

which are inserted into F in (2), and give, by differentiation with respect to N,

$$\mu = \frac{\partial F}{\partial N} = -\int^{T} \mathrm{d}T' \int^{T'} \frac{f(T'')}{T''}\,\mathrm{d}T'' - kT \log V - kT\,\frac{\mathrm{d}\phi_1}{\mathrm{d}N} + \frac{\mathrm{d}\phi_2}{\mathrm{d}N}. \tag{6}$$

Since μ must be a function of V/N, we must have

$$\frac{\mathrm{d}\phi_1}{\mathrm{d}N} = -\log N + \alpha, \quad \text{or} \quad \phi_1 = -N \log N + N + N\alpha$$

$$(\alpha \text{ is a constant}), \tag{7}$$

$$\frac{\mathrm{d}\phi_2}{\mathrm{d}N} = 0, \quad \text{or} \qquad \phi_2 = N\phi_0 \qquad (\phi_0 \text{ is a constant}). \tag{8}$$

Having thus obtained g_1 and g_2, we substitute them in eqs. (1), (2), (4) and (6):

$$F = -\int^{T} \mathrm{d}T' \int^{T'} C_V(T'')\,\frac{\mathrm{d}T''}{T''} - NkT \log \frac{V}{N} - NkT + N\phi_0 - NkT\alpha, \tag{9}$$

$$U = \int^{T} C_V(T')\,\mathrm{d}T' + N\phi_0, \tag{10}$$

$$S = \int^{T} C_V(T')\,\frac{\mathrm{d}T'}{T'} + Nk \log \frac{V}{N} + Nk + Nk\alpha, \tag{11}$$

$$\mu = -\int^{T} \mathrm{d}T' \int^{T'} f(T'')\,\frac{\mathrm{d}T''}{T''} - kT \log \frac{V}{N} + \phi_0 - kT\alpha$$

$$= -\int^{T} \mathrm{d}T' \int^{T'} f(T'')\,\frac{\mathrm{d}T''}{T''} + kT \log \frac{p}{kT} + \phi_0 - kT\alpha, \tag{12}$$

$$G \equiv N\mu. \tag{13}$$

NOTE: The form of G usually used for an ideal gas is given by eq. (5) in the solution of problem 12.

8. Consider a spring which follows Hooke's law; namely the elongation x is proportional to the tension X when it is pulled at a constant temperature. The proportionality constant (spring constant) k, is temperature-dependent. Determine the free energy F, the internal energy U, and the entropy S, as a function of x. Neglect the thermal expansion.

SOLUTION

If F is given as a function of the strain x and the temperature T, we have

$$\mathrm{d}F = -S\,\mathrm{d}T + X\,\mathrm{d}x, \tag{1}$$

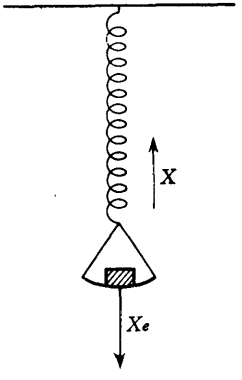


Fig. 3.8.

where X is the tension of the spring which is in balance with the external force X_e, and is equal to X_e for a quasi-static process. Hence the work done by the external force was expressed as $\mathrm{d}'A = X_e\,\mathrm{d}x = X\,\mathrm{d}x$. From (1) follows

$$\left(\frac{\partial F}{\partial x}\right)_T = X = kx. \tag{2}$$

Integrating this we have

$$F(T, x) = F(T, 0) + \tfrac{1}{2}kx^2, \tag{3}$$

which gives

$$S(T, x) = -\frac{\partial F}{\partial T} = -\frac{\mathrm{d}F(T, 0)}{\mathrm{d}T} - \tfrac{1}{2}k'x^2 = S(T, 0) - \tfrac{1}{2}k'x^2 \qquad \left(k' = \frac{\mathrm{d}k}{\mathrm{d}T}\right), \tag{4}$$

$$U(T, x) = F + TS = U(T, 0) + \tfrac{1}{2}(k - Tk')x^2. \tag{5}$$

NOTE: Usually, in mechanics the potential energy of the spring is written as $U_m = \frac{1}{2}kx^2$ and the elastic force as $K = -\partial U_m/\partial x = -kx$. The signs of K and of X are different because $-K\,dx = X\,dx$ is the work done by the external force. In mechanics, the conditions under which elongation or contraction of the spring occurs are not always clearly specified; U_m is defined only as a mechanical potential energy without reference to thermodynamics. If the elongation takes place isothermally, U_m is the free energy F. On the other hand, if it takes place adiabatically, U_m is the internal energy U.

9. Show from the third law of thermodynamics that the heat capacity tends to zero as the temperature approaches the absolute zero.

SOLUTION

The heat capacity for a given process may be written as $C_x = T(\partial S/\partial T)_x$, where $(\partial S/\partial T)_x$ is the partial derivative with respect to the absolute temperature, the quantity x being kept constant. By the third law, as $T \to 0$, we have

$$\lim_{T\to 0} S = \lim_{T\to 0} \frac{TS}{T} = \lim_{T\to 0} \left(\frac{\partial(TS)}{\partial T}\right)_x \Big/ \left(\frac{\partial T}{\partial T}\right)_x = \lim_{T\to 0}\left(S + T\left(\frac{\partial S}{\partial T}\right)_x\right)$$
$$= \lim_{T\to 0} S + \lim_{T\to 0} C_x$$

and $\lim_{T\to 0} S = 0$. Thus $\lim_{T\to 0} C_x = 0$.

Problems

[A]

1. Prove the following properties of the Helmholtz free energy, F:

(i) Consider a system (A) in thermal contact with a single heat reservoir (R) at a temperature $T^{(e)}$ equal to the uniform internal temperature, T, of the system. The change in the Helmholtz free energy, F, of the system A is equal to the change in the internal energy of the system A and the heat reservoir R, provided that the heat reservoir R supplies heat only to the system A and no work is done on the reservoir from the outside.

(ii) When a system changes isothermally, the work received by the system is equal to the increase in the free energy of the system.

2. There is a system whose internal energy U, and enthalpy H, are determined by its pressure p, and volume V. Prove the following relations for this

system:

$$\text{(i)}\quad dU = C_V(\kappa/\alpha)\,dp + (C_p/\alpha - pV)\,dV/V,$$
$$\text{(ii)}\quad dH = (C_V(\kappa/\alpha) + V)\,dp + (C_p/\alpha)\,dV/V,$$

where C_p and C_V are the heat capacity at constant pressure and constant volume respectively, κ is the isothermal compressibility and α is the volume expansion coefficient.

3. Express the rate of temperature change, $\chi_S = (\partial T/\partial p)_S$, for a system subject to an adiabatic and quasi-static compression (adiabatic temperature coefficient), in terms of the expansion coefficient at constant pressure α, and the heat capacity at constant pressure C_p. Also, find the expression for the increase in entropy in terms of χ_S when the system is quasi-statically expanded at constant pressure.

4. Find the formula for calculating the Gibbs free energy G, the enthalpy H, and the entropy S, when experimentally determined expansion coefficients, $A(T)$, $B(T)$, $C(T)$,... are given for the equation of state

$$pV = A(T) + B(T)\,p + C(T)\,p^2 + \cdots.$$

5. Prove the following equations using the Helmholtz free energy F, and the Gibbs free energy G:

$$\left(\frac{\partial U}{\partial V}\right)_T + p = T\left(\frac{\partial p}{\partial T}\right)_V, \qquad \left(\frac{\partial H}{\partial p}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_p.$$

6. Show that

$$\left(\frac{\partial H}{\partial p}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_p = -C_p\left(\frac{\partial T}{\partial p}\right)_S.$$

7. Show that the entropy, S, increases with the volume, V, for a gas whose pressure, p, is known to be proportional to the absolute temperature when the volume is kept constant.

8. Prove the following inequalities:

$$\text{(i)}\quad \left(\frac{\partial S}{\partial p}\right)_H < 0, \qquad \text{(ii)}\quad \left(\frac{\partial S}{\partial V}\right)_U > 0,$$

where U, H, S, P and V are the internal energy, enthalpy, entropy, pressure and volume, respectively.

9. Show that the following processes are irreversible: (a) a gas makes a free adiabatic expansion from a volume V to $V+\mathrm{d}V$ ($\mathrm{d}V>0$) and (b) a gas expands adiabatically by the Joule-Thomson process from a pressure p, to $p+\mathrm{d}p$ ($\mathrm{d}p<0$).

10. The volume expansion coefficient at constant pressure is positive for gases. Show that the temperature always decreases for a quasi-static adiabatic expansion and that this decrease is greater than the temperature decrease which results from a corresponding decrease of the pressure by the adiabatic Joule-Thomson effect.

11. (i) Show that the ratio of the adiabatic compressibility to the isothermal compressibility is equal to the ratio of the specific heat at constant volume to the specific heat at constant pressure (use a Jacobian).

(ii) Prove inequality (3.37b), and use it to discuss the relative magnitudes of the compressibilities at constant entropy and at constant temperature.

(iii) Give a physical interpretation of this using Le Chatelier-Brown's principle.

12. The heat capacity at constant pressure C_p (for n moles) of an ideal gas is usually expressed as

$$C_p = nC_p^0 + nC_{\mathrm{vib}}(T),$$

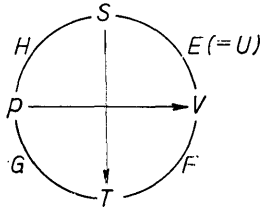
where C_p^0 is the specific heat at constant pressure due to the translational and rotational motion of the molecules ($C_p^0=\frac{5}{2}R$ for a gas of monatomic molecules, $C_p^0=\frac{7}{2}R$ for a gas of diatomic molecules and $C_p^0=4R$ for a gas of polyatomic molecules) and $C_{\mathrm{vib}}(T)$ is the molar specific heat due to molecular vibrations ($\lim_{T\to 0} C_{\mathrm{vib}}(T)=0$). Derive the formulae giving the Gibbs free energy and the entropy.

DIVERTISSEMENT 9

Thermodynamic mnemonic diagrams. The Gibbs relation (3.1) is the consequence of the first and the second laws of thermodynamics applied to an infinitesimal quasi-static process, and eqs. (3.2)–(3.4) are then obtained by repeated application of the Legendre transformation (3.11). If you have mastered the two fundamental laws and keep in mind the definition of thermodynamic potentials, you ought to be able easily to write down eqs. (3.1)–(3.4) in the way described above. However, you had better remember the following method, as a sort of rainyday fund.

The method of writing eqs. (3.1)–(3.4) automatically is based on a diagram, which was devised by Max Born or someone before 1929. You first

draw two arrows perpendicular to each other: one from S to T going downward, while the other, from p to V, goes from left to right, as shown in the figure. Drawing a cross of arrows, you might say to yourself that the *S*un is pouring down his rays upon the *T*rees, and the brook is flowing from the *p*eak to the *V*alley. Next you complete the diagram by adding four quarters of a circle named $E(=U)$, F, G and H clockwise. Then you can write, for instance, eq. (3.4) in the following way. The natural variables corresponding to the Gibbs free energy G are given by T and p,



which stand at the ends of the G-quarter of the circle. In the expression of $\mathrm{d}G$, you write $-S$ and $+V$ as the coefficients of $\mathrm{d}T$ and $\mathrm{d}p$, respectively. The minus sign of $-S$ comes from the fact that you have to trace the ST-arrow in a reverse sense to arrive at S, starting from T.

In the diagram mentioned above, the mass-action term $\Sigma\mu_i \mathrm{d}N_i$ has been dropped, because the diagram is two-dimensional, and because that term is common to all of eqs. (3.1)–(3.4). If necessary, you can generalize the diagram to include the mass-action term and other types of the work term. You will find some examples in a text book by H. B. Callen: *Thermodynamics* (John Wiley and Sons, Inc., New York, 1960), which shows application of the diagram method to the Maxwell reciprocal relations.

13. Derive the Gibbs free energy of an ideal gas mixture consisting of n_1 moles of one and n_2 moles of a second component.

14. Measuring the tension X, of a rubber band stretched at a constant length l we have found that $X = AT$, where $A\,(>0)$ is a constant depending only on l, and T is the absolute temperature. Show that the internal energy, U, of such a rubber band is a function of the temperature only and that its entropy S decreases with increasing length.

15. For a rubber band as described in the previous problem show that the temperature rises if the rubber band is stretched adiabatically. Also show that it will contract if the temperature is raised while maintaining a constant tension.

16. Derive the Gibbs-Duhem relation (3.12) from the Helmholtz free energy.

17. Show that, according to the third law of thermodynamics, the thermal expansion coefficient $(\partial V/\partial T)_p/V$ and the pressure coefficient $(\partial p/\partial T)_V$ approach zero as $T \to 0$.

18. If the tension of a wire is X and its length is x, show that

$$\left(\frac{\partial X}{\partial x}\right)_{S,p} > 0 \qquad \text{and} \qquad \left(\frac{\partial X}{\partial x}\right)_{T,p} > 0.$$

19. Show that

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,p} > 0.$$

20. Consider a paramagnetic body with an isothermal magnetic susceptibility, χ_T. Obtain the free energy F, as a function of the magnetization M, and the temperature T, and from this derive the internal energy U, and the entropy S.

[B]

21. Consider a system of N particles of a single kind; U, T, V and μ are the internal energy, the absolute temperature, the volume and the chemical potential per particle, respectively. Prove the following equations:

$$\text{(i)} \quad \left(\frac{\partial U}{\partial N}\right)_{T,V} - \mu = -T\left(\frac{\partial \mu}{\partial T}\right)_{V,N},$$

$$\text{(ii)} \quad \left(\frac{\partial N}{\partial T}\right)_{V,\mu/T} = \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \left(\frac{\partial U}{\partial N}\right)_{T,V} \Big/ T,$$

$$\text{(iii)} \quad \left(\frac{\partial U}{\partial T}\right)_{V,\mu/T} - \left(\frac{\partial U}{\partial T}\right)_{V,N} = \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \left(\frac{\partial U}{\partial N}\right)^2_{T,V} \Big/ T \geqq 0.$$

22. Derive a formula which would be convenient for calculating the heat capacity at constant volume C_V, as a function of the absolute temperature T, the volume V, and the chemical potential μ.

23. Compare the heat capacity $C_{V,N}$ of a system at constant volume and constant number of particles to the heat capacity $C_{V,\mu}$ of the same system at constant volume and constant chemical potential, and discuss them using Le Chatelier-Brown's principle.

24. Show that for a paramagnetic material the relation

$$\chi_S = \chi_T C_M / C_H$$

holds between the isothermal and the adiabatic susceptibilities, where C_M is the heat capacity at constant magnetization and C_H is the heat capacity at constant magnetic field H. Assume that the volume changes of the magnetic material are negligible. Also, given the dependence of the magnetization, M, on T and H, derive a formula for calculating $C_M - C_H$. (Use the Jacobian.)

25. Consider a paramagnetic material which obeys the Curie law $\chi_T = C/T$, and has a heat capacity $C_0 = b/T^2$ for zero magnetization. Derive the heat capacity at constant magnetic field C_H, the heat capacity for constant magnetization C_M, and the adiabatic magnetic susceptibility $\chi_S(H_0) = (\partial M/\partial H)_S$ $(H = H_0)$ when the magnetic field is changed infinitesimally around a given field H_0.

26. Show that the isothermal susceptibility χ_T satisfies the relation $\partial\chi_T/\partial T \to 0$ as $T \to 0$.

27. Show that it is impossible to reach 0 °K by adiabatic demagnetization.

28. The problem of example 8 may also be considered using a free energy F^*, defined by $F^*(T, X) = F(T, x) - Xx$. Following example 1, discuss the physical meaning of this free energy, in particular $\mathrm{d}F^*(T, X)$.

29. A free energy of the form

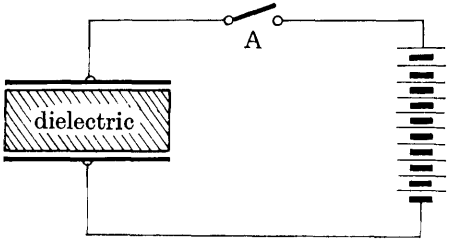
$$F^*(T, H) = F^*(T, 0) - \tfrac{1}{2} V \chi_T H^2 ,$$

is often used for a paramagnetic substance which has an isothermal magnetic susceptibility, χ_T, and is placed in a magnetic field H. Similarly, for a dielectric with a dielectric constant ε in the presence of an electric field E, the function

$$F^*(T, P) = F^*(T, 0) - \frac{V}{8\pi}(\varepsilon - 1) E^2$$

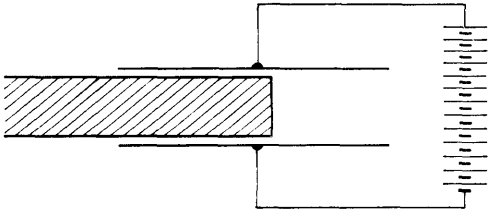
may be used as its free energy. Here, V is the volume. Following the previous problem, compare these free energies with the free energies $F(T, M)$ and $F(T, P)$ where M is the magnetization and P is the polarization. Also obtain the entropy for each case.

30. A dielectric with a temperature-dependent dielectric constant, $\varepsilon(T)$, is placed between the plates of a parallel plate condenser which is connected to a battery of constant electromotive force as shown in the figure. Discuss the heat capacity when the switch is closed and when it is opened after being closed. Assume that the volume of the dielectric is unchanged.



31. Find the amount of heat produced in a condenser such as described in problem 30 when the potential difference is increased quasi-statically from 0 to Φ.

32. Explain the fact that a dielectric is pulled into a condenser when it is inserted between the parallel plates of a condenser, as shown in the figure.



[C]

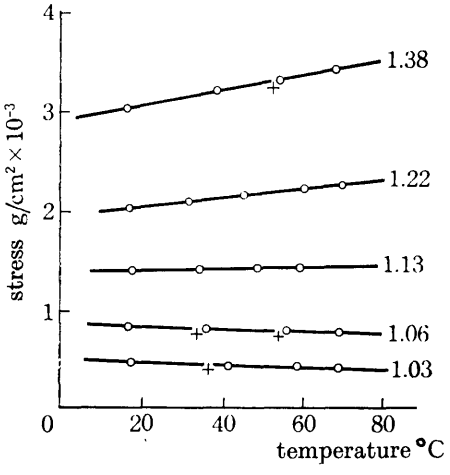
33. The chemical potential of a one-component ideal gas has the form $\mu = \phi(T) + kT \log\{p/p_0(T)\}$. Obtain the functional form of the thermodynamic potential $J(T, V, \mu)$ and prove the relation (3.5).

34. The figure shows the experimental data for the tension of a suitably vulcanized rubber band maintained at a constant length plotted against the temperature. Let l_0 be the natural length of the rubber band at temperature T_0 and l the actual length. The total tension (stress × cross-section) is related

to l as

$$X = AT\left[\frac{l}{l_0} - \{1 + \alpha(T - T_0)\}\left(\frac{l_0}{l}\right)^2\right],$$

where α is the thermal expansion coefficient and is approximately equal to 7×10^{-4} deg^{-1}. Obtain the change in temperature T, when the rubber band at temperature T_0 is stretched suddenly (adiabatically) from its natural length l_0 to L times that. (This is called the Joule effect.) Plot ΔT as a function of L.



Solutions

1. The proof is similar to that of example 1. In this case we only need to consider quasi-static processes, since a uniform temperature is defined. Hence we write the equations for an infinitesimal process.

(i) The heat reservoir does not change its temperature $T^{(e)}$ when it gives a finite amount of heat to the system A. Since the heat reservoir receives no work, it may be assumed that its change is uniquely determined by the heat $d'Q$ it gives off. The changes in the internal energy $U^{(e)}$, and the entropy $S^{(e)}$, of the reservoir are given by the first and the second laws of thermodynamics as

$$dU^{(e)} = -\,d'Q, \qquad \text{and} \qquad dS^{(e)} = -\,d'Q/T^{(e)}. \tag{1}$$

If the internal energy and the entropy of the system A are U and S, the internal energy and the entropy of the combined system become $U^* = U + U^{(e)}$ and $S^* = S + S^{(e)}$. These are functions of state of the combined

system. Since there is no heat supplied to the combined system, we have, by the second law,

$$dS^* = 0, \qquad \text{or} \qquad dS^{(e)} = -\,dS. \tag{2}$$

Considering eq. (1) we have

$$dU^{(e)} = T^{(e)}\,dS^{(e)} = -\,T^{(e)}\,dS.$$

Therefore, the energy change of the combined system,

$$dU^* = dU + dU^{(e)}$$

can be written as

$$dU^* = dU - T^{(e)}\,dS = dU - T\,dS \tag{3}$$

because $T^{(e)}$ is equal to T. The last expression is defined in terms of state variables of the system A and is in fact equal to dF.

(ii) We apply the first law to the combined system. Since the work $d'A$ done on the system is the only work done by the environment on the combined system, we have $dU^* = d'A$. According to (3) we obtain

$$dF = d'A.$$

The name "free energy" comes from this relation.

2. By considering S as a function of p and V, eqs. (3.1) and (3.2) become

$$dU = T\,dS - p\,dV = T\left(\frac{\partial S}{\partial p}\right)_V dp + \left\{T\left(\frac{\partial S}{\partial V}\right)_p - p\right\} dV, \tag{1}$$

$$dH = T\,dS + V\,dp = \left\{T\left(\frac{\partial S}{\partial p}\right)_V + V\right\} dp + T\left(\frac{\partial S}{\partial V}\right)_p dV. \tag{2}$$

Regarding S as $S(T, V) = S(T(p, V), V)$ (T is a function of p and V by the equation of state) we have

$$\left(\frac{\partial S}{\partial p}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V = \frac{C_V}{T}\left(\frac{\partial T}{\partial p}\right)_V. \tag{3}$$

Similarly, from $S(T, p) = S(T(p, V), p)$ we have

$$\left(\frac{\partial S}{\partial V}\right)_p = \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p = \frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p = \frac{C_p}{TV\alpha}. \tag{4}$$

Using an application of eq. (1.23) to eq. (3), we obtain

$$\left(\frac{\partial T}{\partial p}\right)_V = -\left(\frac{\partial V}{\partial p}\right)_T \Big/ \left(\frac{\partial V}{\partial T}\right)_p = \kappa/\alpha$$

or,

$$\left(\frac{\partial S}{\partial p}\right)_V = C_V\kappa/T\alpha. \tag{5}$$

The desired equation is obtained by substituting eqs. (4) and (5) into eqs. (1) and (2).

NOTE: The transformation in eqs. (3), (4) and (5) may be performed using the Jacobian in the following manner:

$$\left(\frac{\partial S}{\partial p}\right)_V = \frac{\partial(S, V)}{\partial(p, V)} = \frac{\partial(S, V)}{\partial(T, V)}\frac{\partial(T, V)}{\partial(p, T)}\Big/\frac{\partial(p, V)}{\partial(p, T)}$$

$$= \left(\frac{\partial S}{\partial T}\right)_V\left\{-\left(\frac{\partial V}{\partial p}\right)_T\right\}\Big/\left(\frac{\partial V}{\partial T}\right)_p = C_V\kappa/\alpha T,$$

$$\left(\frac{\partial S}{\partial V}\right)_p = \frac{\partial(S, p)}{\partial(V, p)} = \frac{\partial(S, p)}{\partial(T, p)}\Big/\frac{\partial(V, p)}{\partial(T, p)} = \left(\frac{\partial S}{\partial T}\right)_p\Big/\left(\frac{\partial V}{\partial T}\right)_p.$$

Note how the partial derivatives are rewritten as Jacobians by inserting extra variables.

3. Since $\alpha=(\partial V/\partial T)_p/V$ and $C_p=T(\partial S/\partial T)_p$, the Jacobian method is used in the following way:

$$\chi_S = \left(\frac{\partial T}{\partial p}\right)_S = \frac{\partial(S, T)}{\partial(S, p)} = \frac{\partial(S, T)}{\partial(p, T)}\Big/\frac{\partial(S, p)}{\partial(p, T)} = -\left(\frac{\partial S}{\partial p}\right)_T\Big/\left(\frac{\partial S}{\partial T}\right)_p$$

$$= \left(\frac{\partial V}{\partial T}\right)_p\Big/\left(\frac{\partial S}{\partial T}\right)_p = TV\alpha/C_p.$$

We have used Maxwell's relation (3.21a), which results from eq. (3.4). The volume dependence of the entropy at constant pressure is $(\partial S/\partial V)_p$. Since this can be rewritten as eq. (4) in the preceding problem, we get $(\partial S/\partial V)_p = 1/\chi_S$. (Or, after the first equation of (4), one may proceed using

$$\left(\frac{\partial S}{\partial V}\right)_p = \left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p = -\left\{\left(\frac{\partial p}{\partial T}\right)_S\Big/\left(\frac{\partial p}{\partial S}\right)_T\right\}\cdot\left(\frac{\partial T}{\partial V}\right)_p = \left(\frac{\partial p}{\partial T}\right)_S = \frac{1}{\chi_S},$$

where Maxwell's relation (3.21a) is used.)

4. Substitute the equation of state in $V=(\partial G/\partial p)_T$:

$$(\partial G/\partial p)_T = A/p + B + Cp + \cdots,$$

which can be integrated to

$$G(T, p) = G(T, p_0) + A \log \frac{p}{p_0} + B(p - p_0) + \tfrac{1}{2}C(p^2 - p_0^2) + \cdots. \tag{1}$$

From this, we obtain

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = S(T, p_0) - A' \log \frac{p}{p_0} - B'(p - p_0) - \tfrac{1}{2}C'(p^2 - p_0^2) + \cdots, \tag{2}$$

and

$$H = G + TS = H(T, p_0) + (A - TA') \log \frac{p}{p_0} + (B - TB')(p - p_0) + \\ + \tfrac{1}{2}(C - TC')(p^2 - p_0^2) + \cdots, \tag{3}$$

where $A' = \mathrm{d}A/\mathrm{d}T$, etc. The heat capacity must be known in order to determine $G(T, p_0)$, $S(T, p_0)$ and $H(T, p_0)$. It is easy to derive U and F, etc. from these equations as functions of p and T.

5. From eq. (3.3) we have $F = U - TS$, $S = -(\partial F/\partial T)_V$, and thus

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V.$$

Differentiate this with respect to V and substitute $(\partial F/\partial V)_T = -p$ to obtain $(\partial U/\partial V)_T = -p + T(\partial p/\partial T)_V$. Similarly, $G = H - TS$, and $S = -(\partial G/\partial T)_p$, and therefore

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p.$$

From $(\partial G/\partial p)_T = V$ we obtain $(\partial H/\partial p)_T = V - T(\partial V/\partial T)_p$.
NOTE: This problem was treated in examples 2 and 4 and problem 15 in Chapter 2, but it is solved more simply using the free energy.

6. This is similar to example 2. The first half is proved in the foregoing problem. The latter half can be shown by substituting Maxwell's relation $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$ (derived from the total differential of (3.4)) into

$$\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial(S, T)}{\partial(p, T)} = \frac{\partial(S, T)}{\partial(S, p)}\frac{\partial(S, p)}{\partial(p, T)} = -\left(\frac{\partial T}{\partial p}\right)_S\left(\frac{\partial S}{\partial T}\right)_p = -\frac{C_p}{T}\left(\frac{\partial T}{\partial p}\right)_S.$$

7. The equation of state of the gas in the problem has the form $p = f(V)T$.

From (3.21a)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = f(V) = \frac{p}{T}.$$

Since $p>0$ and $T>0$, the right side is positive.

8. (i) By eq. (3.2), $T\,\mathrm{d}S + V\,\mathrm{d}p = 0$ when $\mathrm{d}H = 0$. Therefore

$$\left(\frac{\partial S}{\partial p}\right)_H = -\frac{V}{T} < 0.$$

(ii) By (3.1) $T\,\mathrm{d}S - p\,\mathrm{d}V = 0$ when $\mathrm{d}U = 0$. So

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} > 0.$$

NOTE: As was shown in example 2 of Chapter 2, if the equation of state has the form $p = f(V)\,T$ the internal energy is independent of the volume V. Then we may write $(\partial S/\partial V)_U = (\partial S/\partial V)_T$. Thus it is seen that the foregoing problem is a particular case of (ii).

9. The first case is a process where the internal energy $U = \text{const.}$ and the second case one where the enthalpy is constant. But by the results of the foregoing problem $(\partial S/\partial V)_U > 0$ and $(\partial S/\partial p)_H < 0$, and the entropy increases in both cases. Therefore these processes are irreversible.

10. A gas is made to undergo a quasi-static adiabatic expansion by decreasing the external pressure on the gas. Since the gas pressure is equal to the external pressure the drop of temperature can be calculated from $(\partial T/\partial p)_S$, where T and S are the absolute temperature and entropy of the gas. This quantity was called the adiabatic temperature coefficient in problem 3 and can be expressed as $(\partial T/\partial p)_S = TV\alpha/C_p$ in terms of the volume expansion coefficient at constant pressure α, and the heat capacity at constant pressure C_p. Now $(\partial T/\partial p)_S > 0$ if $\alpha > 0$ since T, V and C_p are positive, indicating that the temperature drops with the pressure.

The decrease in temperature in the Joule-Thomson process is given by

$$\left(\frac{\partial T}{\partial p}\right)_H = \left\{T\left(\frac{\partial V}{\partial T}\right)_p - V\right\}\Big/C_p = \frac{(T\alpha - 1)\,V}{C_p}$$

as was shown in problem 24 of Chapter 2. This is not always positive and can be negative (see problem 44, Chapter 2). The temperature decreases as

long as $T\alpha-1>0$. The term -1 in this inequality is not present in the adiabatic quasi-static expansion. Consider the case of a sufficiently small pressure drop, $-\Delta p>0$. The difference in the temperature drop $-(\Delta T)_S>0$, for a adiabatic process and $-(\Delta T)_H>0$, for a Joule-Thomson process is

$$\{-(\Delta T)_S\}-\{-(\Delta T)_H\}=\left[\left(\frac{\partial T}{\partial p}\right)_S-\left(\frac{\partial T}{\partial p}\right)_H\right](-\Delta p)=\frac{V}{C_p}(-\Delta p)>0.$$

NOTE: As can be seen from this problem, for the purpose of cooling a gas (e.g. for liquefaction), quasi-static adiabatic expansion is a better method than the Joule-Thomson process for the following two reasons: firstly, every gas can be cooled down by this method; secondly, the temperature drop is greater.

11. (i)

$$\frac{\kappa_S}{\kappa_T}=\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S\Big/\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T=\frac{\partial(V,S)}{\partial(p,S)}\Big/\frac{\partial(V,T)}{\partial(p,T)}$$
$$=\frac{\partial(V,S)}{\partial(V,T)}\Big/\frac{\partial(p,S)}{\partial(p,T)}=\left(\frac{\partial S}{\partial T}\right)_V\Big/\left(\frac{\partial S}{\partial T}\right)_p=\frac{C_V}{C_p}. \tag{1}$$

(ii)

$$\left(\frac{\partial Y_i}{\partial y_i}\right)_{Y_k}=\frac{\partial(Y_i,Y_k)}{\partial(y_i,Y_k)}=\frac{\partial(Y_i,Y_k)}{\partial(y_i,y_k)}\Big/\frac{\partial(y_i,Y_k)}{\partial(y_i,y_k)}$$
$$=\left\{\left(\frac{\partial Y_i}{\partial y_i}\right)_{y_k}\left(\frac{\partial Y_k}{\partial y_k}\right)_{y_i}-\left(\frac{\partial Y_i}{\partial y_k}\right)_{y_i}\left(\frac{\partial Y_k}{\partial y_i}\right)_{y_k}\right\}\Big/\left(\frac{\partial Y_k}{\partial y_k}\right)_{y_i}. \tag{2}$$

Since $\mathrm{d}U=y_i\,\mathrm{d}Y_i+y_k\,\mathrm{d}Y_k+\cdots$, then if we put $\Phi=U-y_iY_i-y_kY_k$, we have

$$\mathrm{d}\Phi=-Y_i\,\mathrm{d}y_i-Y_k\,\mathrm{d}y_k+\cdots,\qquad\text{or}\qquad\left(\frac{\partial Y_i}{\partial y_k}\right)_{y_i}=\left(\frac{\partial Y_k}{\partial y_i}\right)_{y_k}. \tag{3}$$

Substitute this into (2):

$$\left(\frac{\partial Y_i}{\partial y_i}\right)_{Y_k}=\left(\frac{\partial Y_i}{\partial y_i}\right)_{y_k}-\left(\frac{\partial Y_i}{\partial y_k}\right)^2_{y_i}\Big/\left(\frac{\partial Y_k}{\partial y_k}\right)_{y_i},\qquad\text{or}\qquad\left(\frac{\partial Y_i}{\partial y_i}\right)_{Y_k}<\left(\frac{\partial Y_i}{\partial y_i}\right)_{y_k}. \tag{4}$$

In particular if $Y_i=V$, $y_i=-p$, $Y_k=S$ and $y_k=T$, (4) becomes

$$\kappa_S=\kappa_T-\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)^2_p\Big/C_p. \tag{5}$$

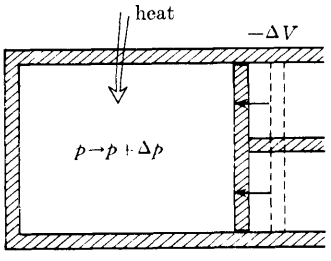
((5) can be derived from (1) above and (6) in example 3.) Therefore

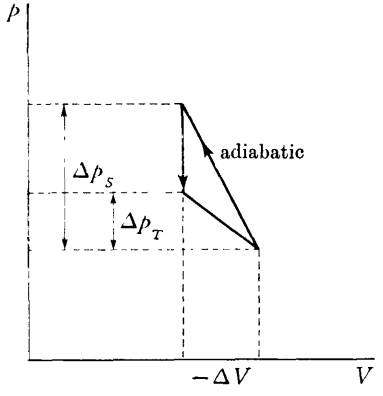
$$\kappa_S<\kappa_T. \tag{6}$$

(iii) Consider matter in a cylinder fitted with a piston. By moving the piston the volume V is changed by an amount $\Delta V<0$. According to (6) the change in the pressure is greater when no heat is allowed to enter the cylinder than when heat can be exchanged:

$$(\Delta p)_S > (\Delta p)_T .$$

Suppose that the matter is first compressed adiabatically and than heat exchange is allowed. The pressure increase will decline from $(\Delta p)_S$ to $(\Delta p)_T$. This shows that the indirect result of the heat transfer caused by the compression (A) is to diminish the direct result of (A) (increased pressure), which is Le Chatelier-Brown's principle.





12. We follow the procedure of example 7. $C_p(T)$ can be integrated with $g_1(p, n)$ as the integration constant:

$$S = \int^T C_p(T') \frac{dT'}{T'} + g_1(p, n) = nC_p^0 \log T + n \int_0^T C_{\text{vib}}(T') \frac{dT'}{T'} + g_1(p, n). \tag{1}$$

Since $(\partial G/\partial T)_p = -S$, this is again integrated to

$$G(p, T, n) = \tag{2}$$

$$= -nC_p^0(T \log T - T) - n \int_0^T dT' \int_0^{T'} C_{\text{vib}}(T'') \frac{dT''}{T''} - Tg_1(p, n) + g_2(p, n).$$

$(\partial G/\partial p)_T = V$ gives

$$-T \frac{\partial g_1}{\partial p} + \frac{\partial g_2}{\partial p} = V = \frac{nRT}{p},$$

or

$$\frac{\partial g_1}{\partial p} = -\frac{nR}{p}, \qquad \text{and} \qquad \frac{\partial g_2}{\partial p} = 0,$$

and thus

$$g_1(p, n) = -nR \log p + \phi_1(n), \qquad g_2 = \phi_2(n). \tag{3}$$

Here ϕ_1 and ϕ_2 are integration constants. Substituting (3) into (2) and remembering that G/n is independent of n, we see that

$$\phi_1(n) = n\alpha \quad (\alpha = \text{const.}) \qquad \text{and} \qquad \phi_2(n) = nU_0 \quad (U_0 = \text{const.}) \tag{4}$$

Therefore, by letting $\alpha - C_p^0 = iR(=\text{const.})$ we get from (2), (3) and (4)

$$G(p, T, n) =$$

$$= n\left[U_0 - C_p^0 T \log T + RT \log p - \int_0^T \mathrm{d}T' \int_0^{T'} C_{\text{vib}}(T'') \frac{\mathrm{d}T''}{T''} - iRT\right] \tag{5}$$

(i is called the chemical constant). From (1) (or differentiating (5)) the entropy is obtained as:

$$S = n\left[C_p^0 \log T - R \log p + \int_0^T C_{\text{vib}}(T') \frac{\mathrm{d}T'}{T'} + iR + C_p^0\right]. \tag{6}$$

NOTE: According to (5) the Gibbs free energy per mole (chemical potential) is written as

$$\bar{G}(T, p) = \bar{G}(T, p_0) + RT \log \frac{p}{p_0}, \tag{7}$$

where $\bar{G}(T, p_0)$ is the value of $\bar{G}$ at some standard pressure p_0.

13. According to example 5 of Chapter 2 the Helmholtz free energy F, of this ideal gas mixture has the form

$$F(T, V, n_1, n_2) = F_1(T, V_1, n_1) + F_2(T, V_2, n_2) - T\Delta S, \tag{1}$$

where V is the volume of the gas mixture, and $V_1 = Vn_1/(n_1+n_2)$ and $V_2 = Vn_2/(n_1+n_2)$ are the volumes occupied by gases 1 and 2 respectively prior to mixing. Now ΔS is the entropy of mixing and is given as

$$\Delta S = -R\left\{n_1 \log \frac{n_1}{n_1+n_2} + n_2 \log \frac{n_2}{n_1+n_2}\right\}. \tag{2}$$

As shown in (9) of the solution to example 7, $F_1(T, V_1, n_1)$ and $F_2(T, V_2, n_2)$

have the forms

$$F_1(T, V_1, n_1) = n_1\Phi_1(T) - n_1RT \log \frac{V_1}{n_1},$$

$$F_2(T, V_2, n_2) = n_2\Phi_2(T) - n_2RT \log \frac{V_2}{n_2}.$$

Therefore

$$F_1(T, V_1, n_1) + n_1RT \log \frac{n_1}{n_1 + n_2} = n_1\Phi_1(T) - n_1RT \log \frac{V}{n_1} = F_1(T, V, n_1),$$

$$F_2(T, V_2, n_2) + n_2RT \log \frac{n_2}{n_1 + n_2} = F_2(T, V, n_2).$$

Hence (1) becomes

$$F(T, V, n_1, n_2) = F_1(T, V, n_1) + F_2(T, V, n_2). \tag{3}$$

By (3.13)

$$G(T, p, n_1, n_2) = n_1 \frac{\partial F}{\partial n_1} + n_2 \frac{\partial F}{\partial n_2} = n_1\bar{G}_1(T, p_1) + n_2\bar{G}_2(T, p_2), \tag{4}$$

where

$$p_1 = \frac{n_1RT}{V} = \frac{pn_1}{n_1 + n_2}, \qquad p_2 = \frac{n_2RT}{V} = \frac{pn_2}{n_1 + n_2} \quad \left(p = \frac{(n_1 + n_2)RT}{V}\right)$$

are the partial pressures and $\bar{G}_1(T, p_1)$ and $\bar{G}_2(T, p_2)$ are the Gibbs free energies per mole of substances 1 and 2 at pressures p_1 and p_2, respectively. These are equal to the chemical potential of the materials in the gas mixture.

NOTE: From the note to the foregoing problem, (4) may be written as

$$G = n_1\bar{G}_1(T, p_0) + n_2\bar{G}_2(T, p_0) + RT\left(n_1 \log \frac{p_1}{p_0} + n_2 \log \frac{p_2}{p_0}\right), \tag{5}$$

where p_0 is a standard pressure. The chemical potential of each component is given by

$$\bar{G}_i = \bar{G}_i(T, p_i) = \bar{G}_i(T, p_0) + RT \log \frac{p_i}{p_0}. \tag{6}$$

14. Let the free energy be $F(T, l)$. Then we have

$$\left(\frac{\partial F}{\partial T}\right)_l = -S, \tag{1}$$

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_l, \tag{2}$$

$$X = \left(\frac{\partial F}{\partial l}\right)_T. \tag{3}$$

(The infinitesimal work $d'A$ with respect to change in length is $d'A = X\,dl$.) Eq. (2) gives

$$\left(\frac{\partial U}{\partial l}\right)_T = \left(\frac{\partial F}{\partial l}\right)_T - T\frac{\partial^2 F}{\partial l \partial T} = X - T\left(\frac{\partial X}{\partial T}\right)_l, \tag{4}$$

and eq. (1) becomes, upon differentiation,

$$\left(\frac{\partial S}{\partial l}\right)_T = -\frac{\partial^2 F}{\partial l \partial T} = -\left(\frac{\partial X}{\partial T}\right)_l. \tag{5}$$

Substituting $X = AT$, we find

$$\left(\frac{\partial U}{\partial l}\right)_T = 0, \qquad \text{and} \qquad \left(\frac{\partial S}{\partial l}\right)_T = -A < 0.$$

Therefore U is independent of l and S decreases with the increase of l. (Note that this is similar to an ideal gas.)

15. For an adiabatic quasistatic elongation (S=const.) we have

$$\left(\frac{\partial T}{\partial l}\right)_S = -\frac{(\partial S/\partial l)_T}{(\partial S/\partial T)_l} = -\frac{T}{C_l}\left(\frac{\partial S}{\partial l}\right)_T = \frac{TA}{C_l} > 0, \tag{1}$$

where C_l is the heat capacity at constant length and A is the constant in the foregoing problem. Also we have

$$\left(\frac{\partial l}{\partial T}\right)_X = -\frac{(\partial X/\partial T)_l}{(\partial X/\partial l)_T} = -A\Big/\left(\frac{\partial X}{\partial l}\right)_T. \tag{2}$$

Thermodynamic stability requires that $(\partial X/\partial l)_T > 0$ (an example of (3.34), similar to (3.35b)). Eqs. (1) and (2) prove the statement of the problem.

16. Being an extensive quantity, the Helmholtz free energy $F(T, V, N_1, N_2, \ldots)$ as a function of the temperature T, the volume V, and the particle numbers must have the form

$$F(T, \alpha V, \alpha N_1, \alpha N_2, \ldots) = \alpha F(T, V, N_1, N_2, \ldots).$$

Differentiate with respect to α and set $\alpha = 1$ to obtain

$$F = V\left(\frac{\partial F}{\partial V}\right)_{T,N} + \sum_j N_j \left(\frac{\partial F}{\partial N_j}\right)_{T,V,N_{j'}},$$

whence

$$F = -pV + \sum N_j \mu_j.$$

Equation (3.12) is obtained by differentiating both sides of this equation and by substituting (3.3).

17. By Maxwell's relation (3.21a) we have

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T, \qquad \text{and} \qquad \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T.$$

According to the third law, the entropy S of a uniform body approaches a constant value independent of the pressure or the density as $T \to 0$, provided that the density is finite. Hence

$$\lim_{T\to 0}\left(\frac{\partial S}{\partial p}\right)_T = 0, \qquad \lim_{T\to 0}\left(\frac{\partial S}{\partial V}\right)_T = 0,$$

and thus

$$\lim_{T\to 0}\left(\frac{\partial V}{\partial T}\right)_p = 0, \qquad \lim_{T\to 0}\left(\frac{\partial p}{\partial T}\right)_V = 0.$$

Alternative solution: From the third law

$$S = \int_0^T \frac{C_p}{T}\,\mathrm{d}T,$$

$$-\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial p}\right)_T = \int_0^T \left(\frac{\partial C_p}{\partial p}\right)_T \frac{\mathrm{d}T}{T}$$

$$= -\int_0^T \left(\frac{\partial^2 V}{\partial T^2}\right)_p \mathrm{d}T = -\left(\frac{\partial V}{\partial T}\right)_p + \lim_{T\to 0}\left(\frac{\partial V}{\partial T}\right)_p,$$

and therefore

$$\lim (\partial V/\partial T)_p = 0,$$

where $(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p$ (see example 3) was used. A similar operation applies to $(\partial p/\partial T)_V$.

18. Since $(\partial U/\partial x)_S = X$, (3.32b) can be written as

$$2\delta_2 U = \delta X\,\delta x = (\partial X/\partial x)_{S,p}\,\delta x^2 \geqq 0,$$

letting $\delta S = \delta p = 0$. Therefore

$$(\partial X/\partial x)_{S,p} > 0. \tag{1}$$

Also, by letting $\delta T = \delta p = 0$, (3.32b) becomes

$$2\delta_2 U = (\partial X/\partial x)_{T,p}\,\delta x^2 \geqq 0,$$

or

$$(\partial X/\partial x)_{T,p} > 0. \tag{2}$$

Alternatively, we may use

$$\left(\frac{\partial X}{\partial x}\right)_S = \frac{\partial(X, S)}{\partial(x, S)} = \frac{\partial(X, S)}{\partial(X, T)}\frac{\partial(X, T)}{\partial(x, T)}\frac{\partial(x, T)}{\partial(x, S)} = \frac{C_X}{C_x}\left(\frac{\partial X}{\partial x}\right)_T$$

(p=const.). Since $C_X>0$, $C_x>0$, we may say that $(\partial X/\partial x)_S$ and $(\partial X/\partial x)_T$ have the same sign.

19. Following (3.32b) we take T, p and N as the independent variables and let $\delta T=\delta p=0$ to obtain

$$2\delta_2 U = \left(\frac{\partial \mu}{\partial N}\right)_{T,p} \delta N^2 \geqq 0, \qquad \text{or} \qquad \left(\frac{\partial \mu}{\partial N}\right)_{T,p} \geqq 0.$$

20. This is similar to problem 39 in Chapter 2, but it is more general. Here we neglect the volume change and consider a unit volume of the material. For the free energy $F(T, M)$

$$\left(\frac{\partial F}{\partial T}\right)_M = -S, \tag{1}$$

$$-T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = U, \tag{2}$$

$$\left(\frac{\partial F}{\partial M}\right)_T = H. \tag{3}$$

According to the problem, the relation between the magnetization M, and the magnetic field H, is given by $M=\chi_T H$. (4)
Substitute (4) into (3) and integrate it to get

$$F(T, M) = F(T, 0) + \tfrac{1}{2}M^2/\chi_T (= F(T, 0) + \tfrac{1}{2}\chi_T H^2). \tag{5}$$

Therefore we have

$$S(T, M) = S(T, 0) - \frac{1}{2}\left(\frac{\mathrm{d}}{\mathrm{d}T}\chi_T^{-1}\right) M^2 \tag{6}$$

$$U(T, M) = U(T, 0) + \frac{1}{2}\left\{\chi_T^{-1} - T\frac{\mathrm{d}}{\mathrm{d}T}\chi_T^{-1}\right\} M^2, \tag{7}$$

where

$$S(T, 0) = -F'(T, 0), \qquad U(T, 0) = F(T, 0) - TF'(T, 0).$$

NOTE: In particular, if we assume the Curie-Weiss law

$$\chi_T^{-1} = (T - \theta)/C, \tag{8}$$

the solution to problem 39 of Chapter 2 is obtained independently from (6) and (7).

21. (i) A convenient thermodynamic function for the independent variables T, V and N is the Helmholtz free energy $F(=U-TS)$, since we have

$$\left(\frac{\partial U}{\partial N}\right)_{T,V} = \mu - T\left(\frac{\partial^2 F}{\partial T\,\partial N}\right)_V = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{V,N}.$$

(ii) To change the independent variables from T, V, $\xi=\mu/T$ to T, V, μ, we note that

$$\left(\frac{\partial \xi}{\partial T}\right)_{\mu,V} = -\frac{\mu}{T^2}, \qquad \left(\frac{\partial \xi}{\partial \mu}\right)_{T,V} = \frac{1}{T}$$

and obtain

$$\begin{aligned}\left(\frac{\partial N}{\partial T}\right)_{V,\xi} &= \frac{\partial(N,\xi,V)}{\partial(T,\xi,V)} = \frac{\partial(N,\xi,V)}{\partial(T,\mu,V)}\bigg/\frac{\partial(T,\xi,V)}{\partial(T,\mu,V)} \\ &= \begin{vmatrix} \left(\frac{\partial N}{\partial T}\right)_{\mu,V} & \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \\ \left(\frac{\partial \xi}{\partial T}\right)_{\mu,V} & \left(\frac{\partial \xi}{\partial \mu}\right)_{T,V} \end{vmatrix} \frac{1}{(\partial\xi/\partial\mu)_{T,V}} = \left(\frac{\partial N}{\partial T}\right)_{\mu,V} - \frac{(\partial\xi/\partial T)_{\mu,V}}{(\partial\xi/\partial\mu)_{T,V}}\left(\frac{\partial N}{\partial \mu}\right)_{T,V} \\ &= \left(\frac{\partial N}{\partial T}\right)_{\mu,V} + \frac{\mu}{T}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}.\end{aligned}$$

The first term can easily be rewritten as

$$\begin{aligned}\left(\frac{\partial N}{\partial T}\right)_{\mu,V} &= \frac{\partial(N,\mu,V)}{\partial(T,\mu,V)} = \frac{\partial(N,\mu,V)}{\partial(N,T,V)}\,\frac{\partial(N,T,V)}{\partial(T,\mu,V)} \\ &= -\left(\frac{\partial \mu}{\partial T}\right)_{N,V}\left(\frac{\partial N}{\partial \mu}\right)_{T,V}.\end{aligned}$$

Hence

$$\left(\frac{\partial N}{\partial T}\right)_{V,\mu/T} = \left(\frac{\partial N}{\partial \mu}\right)_{T,V}\left\{\frac{\mu}{T} - \left(\frac{\partial \mu}{\partial T}\right)_{V,N}\right\}.$$

The desired equation is obtained by substituting the relation derived in (i).

(iii) This problem requires us to find the difference in the heat capacity at constant volume for the case when the particle numbers are constant and for the case when $\xi=$const. If we change the independent variables from T,

V and ξ to T, V and N, we have

$$\left(\frac{\partial U}{\partial T}\right)_{V,\xi} = \frac{\partial(U,\xi,V)}{\partial(T,\xi,V)} = \frac{\partial(U,\xi,V)}{\partial(T,N,V)}\bigg/\frac{\partial(T,\xi,V)}{\partial(T,N,V)}$$
$$= \begin{vmatrix} \left(\frac{\partial U}{\partial T}\right)_{N,V} & \left(\frac{\partial U}{\partial N}\right)_{T,V} \\ \left(\frac{\partial \xi}{\partial T}\right)_{N,V} & \left(\frac{\partial \xi}{\partial N}\right)_{T,V} \end{vmatrix} \frac{1}{(\partial\xi/\partial N)_{T,V}} = \left(\frac{\partial U}{\partial T}\right)_{N,V} - \frac{(\partial\xi/\partial T)_{N,V}}{(\partial\xi/\partial N)_{T,V}}\left(\frac{\partial U}{\partial N}\right)_{T,V}$$
$$= \left(\frac{\partial U}{\partial T}\right)_{V,N} + \left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{\xi,V}.$$

The first equality of (iii) is obtained by substituting the result of (ii). To prove the inequality we use the fact that (3.35c) in this case becomes $(\partial\mu/\partial N)_{T,V} \geqq 0$. Then it is obvious that $(\partial N/\partial\mu)_{T,V} = 1/(\partial\mu/\partial N)_{T,V} \geqq 0$.

22. The heat capacity at constant volume is usually defined for constant particle numbers, i.e., $C_{V,N} = T(\partial S/\partial T)_{V,N}$. We change the independent variables from T, V and N to T, V and μ as follows

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{\partial(S,N,V)}{\partial(T,N,V)} = \frac{\partial(S,N,V)}{\partial(T,\mu,V)}\bigg/\frac{\partial(T,N,V)}{\partial(T,\mu,V)}$$
$$= \begin{vmatrix} \left(\frac{\partial S}{\partial T}\right)_{\mu,V} & \left(\frac{\partial S}{\partial \mu}\right)_{T,V} \\ \left(\frac{\partial N}{\partial T}\right)_{\mu,V} & \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \end{vmatrix} \frac{1}{(\partial N/\partial\mu)_{T,V}} = \left(\frac{\partial S}{\partial T}\right)_{\mu,V} - \frac{(\partial N/\partial T)_{\mu,V}}{(\partial N/\partial\mu)_{T,V}}\left(\frac{\partial S}{\partial \mu}\right)_{T,V}.$$

The first term on the right-hand side corresponds to $C_{V,\mu} = T(\partial S/\partial T)_{V,\mu}$, which is the heat capacity at constant volume and constant chemical potential, μ. To change $(\partial S/\partial\mu)_{T,V}$ in the second term we use one of Maxwell's relations. From (3.5) we have

$$S = -\left(\frac{\partial J}{\partial T}\right)_{V,\mu}, \qquad p = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu}, \qquad N = -\left(\frac{\partial J}{\partial \mu}\right)_{T,V},$$

which give

$$\left(\frac{\partial S}{\partial \mu}\right)_{T,V} = -\frac{\partial^2 J}{\partial\mu\,\partial T} = \left(\frac{\partial N}{\partial T}\right)_{V,\mu},$$
$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial T}\right)_{V,\mu} - \left(\frac{\partial N}{\partial T}\right)^2_{V,\mu}\bigg/\left(\frac{\partial N}{\partial \mu}\right)_{T,V}. \tag{1}$$

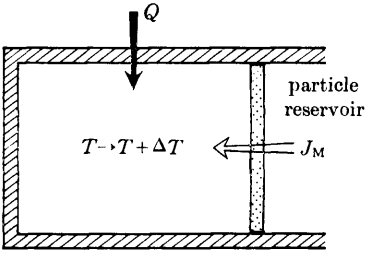
Multiply both sides by T to obtain

$$C_{V,N} = C_{V,\mu} - T\left(\frac{\partial N}{\partial T}\right)^2_{V,\mu} \Big/ \left(\frac{\partial N}{\partial \mu}\right)_{T,V}. \tag{2}$$

23. By (2) of the previous problem we have (analogous to $C_V \leqq C_p$)

$$C_{V,N} \leqq C_{V,\mu}. \tag{1}$$

We follow the example in § 3.9 to interpret this. Consider the temperature rise, ΔT, when the heat Q is supplied (action A) to the system surrounded



by a wall permeable to particles. Besides the flow of heat there is also a flow of particles, J_M (secondary reaction, b). According to Le Chatelier-Brown's principle, the temperature rise $(\Delta T)_N$ when J_M is stopped is greater than the rise $(\Delta T)_\mu$, in the case when the flow is allowed (which means that μ is a constant). Or,

$$(\Delta T)_N > (\Delta T)_\mu. \tag{2}$$

Since $(\Delta T)_N = Q/C_{V,N}$ and $(\Delta T)_\mu = Q/C_{V,\mu}$, (2) and (1) mean the same thing. NOTE: For constant pressure $C_{p,\mu}$ cannot be considered for a single component system because T, p and μ are related through by the Gibbs-Duhem equation (3.12) and are not independent.

24. The problem is similar to problem 19 of Chapter 1 and problem 14 of Chapter 2, but use of the Jacobian method simplifies the solution. We have

$$\chi_S = \left(\frac{\partial M}{\partial H}\right)_S = \frac{\partial(M,S)}{\partial(H,S)} = \frac{\partial(M,S)}{\partial(M,T)}\frac{\partial(M,T)}{\partial(H,T)}\frac{\partial(H,T)}{\partial(H,S)}$$
$$= \left(\frac{\partial S}{\partial T}\right)_M \left(\frac{\partial M}{\partial H}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial M}{\partial H}\right)_T T\left(\frac{\partial S}{\partial T}\right)_M \Big/ T\left(\frac{\partial S}{\partial T}\right)_H = \chi_T \frac{C_M}{C_H}.$$

As in (3.39),

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_M = T\frac{\partial(S, M)}{\partial(T, M)} = T\frac{\partial(S, M)}{\partial(T, H)}\bigg/\frac{\partial(T, M)}{\partial(T, H)}$$

$$= \frac{T}{(\partial M/\partial H)_T}\begin{vmatrix} \left(\frac{\partial S}{\partial T}\right)_H & \left(\frac{\partial S}{\partial H}\right)_T \\ \left(\frac{\partial M}{\partial T}\right)_H & \left(\frac{\partial M}{\partial H}\right)_T \end{vmatrix}$$

$$= \frac{T}{(\partial M/\partial H)_T}\left\{\left(\frac{\partial S}{\partial T}\right)_H\left(\frac{\partial M}{\partial H}\right)_T - \left(\frac{\partial S}{\partial H}\right)_T\left(\frac{\partial M}{\partial T}\right)_H\right\}$$

$$= T\left(\frac{\partial S}{\partial T}\right)_H - T\left(\frac{\partial M}{\partial T}\right)_H^2\bigg/\left(\frac{\partial M}{\partial H}\right)_T = C_H - T\left(\frac{\partial M}{\partial T}\right)_H^2\bigg/\left(\frac{\partial M}{\partial H}\right)_T. \tag{1}$$

We have used Maxwell's relation

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \tag{2}$$

in the next to last equation. This is obtained by transforming $\mathrm{d}F = -S\,\mathrm{d}T + H\,\mathrm{d}M$ to $F^* = F - HM$ or

$$\mathrm{d}F^* = -S\,\mathrm{d}T - M\,\mathrm{d}H. \tag{3}$$

(Here S, M, C_M and C_H are properties per unit mass of the magnetic material.)

25. According to the problem, we have

$$T\frac{\mathrm{d}S(T, 0)}{\mathrm{d}T} = C_{M=0} = \frac{b}{T^2}. \tag{1}$$

By integration,

$$S(T, 0) = -\tfrac{1}{2}b/T^2 + B \qquad (B = \text{const.}). \tag{2}$$

Integrating $\mathrm{d}F(T, 0)/\mathrm{d}T = -S(T, 0)$, we obtain

$$F(T, 0) = A - BT - b/2T \qquad (A = \text{const.}). \tag{3}$$

The equation

$$M = CH/T \qquad (C = \text{const.}) \tag{4}$$

is inserted into (5) of problem 20 to give

$$F(T, M) = A - BT - \frac{b}{2T} + \frac{TM^2}{2C}. \tag{5}$$

Thus

$$S(T, M) = -\frac{\partial F}{\partial T} = B - \frac{b}{2T^2} - \frac{M^2}{2C}, \tag{6}$$

whence

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_M = \frac{b}{T^2}(= C_{M=0}). \tag{7}$$

Since (6) can be written as

$$S(T, H) = B - \frac{b}{2T^2} - \frac{CH^2}{2T^2}, \tag{8}$$

we have

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H = \frac{b + CH^2}{T^2}. \tag{9}$$

As a direct means of obtaining the adiabatic magnetic susceptibility, eliminate T from (6) by (4) to get

$$S(H, M) = B - \tfrac{1}{2}b\left(\frac{M}{CH}\right)^2 - \frac{M^2}{2C}, \tag{10}$$

and thus

$$\chi_S = \left(\frac{\partial M}{\partial H}\right)_{S,H=H_0} = -\left(\frac{\partial S}{\partial H}\right)_M \Big/ \left(\frac{\partial S}{\partial M}\right)_H = \frac{bM^2}{C^2H_0^3} \Big/ \left(\frac{bM}{C^2H_0^2} + \frac{M}{C}\right) \tag{11}$$
$$= \frac{C}{T}\frac{b}{b + CH_0^2}.$$

26. According to the third law, the entropy S has a limiting value independent of H as $T \to 0$. Hence $(\partial S/\partial H)_T \to 0$ $(T \to 0)$. Therefore we have $\lim_{T\to 0}(\partial M/\partial T)_H = 0$ by (2) of problem 24. Substitute $M = \chi_T H$ to obtain

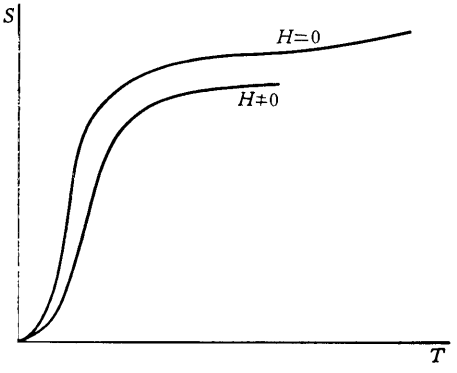
$$\lim_{T\to 0} (\partial \chi_T/\partial T) = 0.$$

NOTE: Therefore, both the Curie law $\chi = C/T$ and the Curie-Weiss law $\chi = C/(T+\theta)$ only hold down to some finite temperature. As $T \to 0$ a deviation must occur from these laws.

27. When the entropy of a paramagnetic substance is plotted as a function of T for constant H, the third law tells us that it approaches a constant (0) independent of H as $T \to 0$. The curves for $H \neq 0$ also approach the same limit as $T \to 0$ as shown in the figure. If H is not too large, (6) of the solution

to problem 20 may be used to give

$$S = S(T, 0) - \frac{1}{2}\left(\frac{\mathrm{d}}{\mathrm{d}T}\chi_T^{-1}\right)M^2$$
$$= S(T, 0) + \frac{1}{2}\left(\frac{\mathrm{d}}{\mathrm{d}T}\chi_T\right)H^2.$$



As $T \to 0$, $\mathrm{d}\chi_T/\mathrm{d}T \to 0$ as was shown in the foregoing problem. Therefore, when the magnetic field is reduced to zero from some finite value at a finite temperature, the temperature stops decreasing at some finite value and it never reaches 0 °K.

28. A plate is attached to the end of the spring and a weight (mass M) is used to balance the spring tension X. Here, z_0 is the height of the plate when $X=0$ and $M=0$, and x is the strain when $X=Mg$ (g=gravitational acceleration). The total potential energy W of the weight on the plate and some stored weights (mass M') kept at the height z_0 is

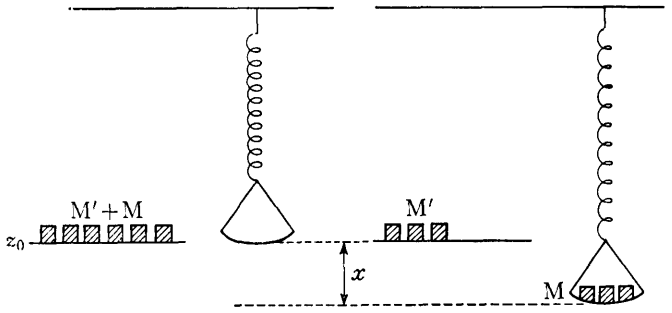
$$W = Mg(z_0 - x) + M'gz_0 = -Mgx + (M + M')gz_0 = -Xx + \text{const.}$$

Now, if $F(T, x)$ is the free energy of the spring at temperature T and at strain x and we put

$$F^* = F(T, x) - Xx = F + W + \text{const.} \tag{1}$$

F^* is the free energy of the total system including the weights. (Since weights are purely mechanical system, their free energy is the potential energy.) If k is the spring constant, we have

$$X = kx \tag{2}$$



and

$$F = F(T, 0) + \tfrac{1}{2}kx^2, \tag{3}$$

so that

$$F^* = \tfrac{1}{2}kx^2 - Xx + F(T, 0) = -X^2/2k + F(T, 0), \tag{4}$$

$$\mathrm{d}F^* = \mathrm{d}F(T, 0) + (kx - X)\,\mathrm{d}x - x\,\mathrm{d}X = \mathrm{d}F(T, 0) - x\,\mathrm{d}X. \tag{5}$$

The last term in (5) is

$$-x\,\mathrm{d}X = \mathrm{d}(\tfrac{1}{2}kx^2) + \mathrm{d}W = \mathrm{d}(\tfrac{1}{2}kx^2) - \mathrm{d}(Xx),$$

i.e. $\mathrm{d}F^*$ gives the sum of the increase in the free energy of the spring and the decrease in the potential energy of the weights when the spring is stretched. NOTE: That $(\partial F^*/\partial T)_X = -S$ properly gives (4) with respect to the entropy, and that $F^* + TS = U$ is the sum of the internal energy of the spring and the potential energy of the weights, should be verified.

29. As was shown in problem 20, the free energy of a paramagnetic body of volume V increases by $\tfrac{1}{2}VM^2/\chi_T$ when it is uniformly magnetized until it acquires a magnetic moment M (per unit volume, the total magnetic moment being MV). Compared with the non-magnetized state,

$$F(T, M) = F(T, 0) + \tfrac{1}{2}VM^2/\chi_T. \tag{1}$$

The interaction energy between the external field H and the magnetic moment is

$$W = -HMV = -\chi_T H^2 V.$$

(This corresponds to the interaction of the weight and the gravitational field in the foregoing problem.) Including this,

$$F^* = F + W = F(T, 0) - \tfrac{1}{2}\chi_T H^2 V \tag{2}$$

may be considered as the free energy of the system plus the interaction of the paramagnetic material and the magnetic field.

In the case of a dielectric with a dielectric constant ε, the electric polarization P (corresponding to M above) in an electric field E is $P=(\varepsilon-1)E/4\pi$ ($(\varepsilon-1)/4\pi$ corresponds to χ above). Therefore, corresponding to (1), we have

$$F(T,P)=F(T,0)+2\pi VP^2/(\varepsilon-1), \tag{3}$$

and to (2),

$$F^*(T,E)=F(T,0)-\frac{\varepsilon-1}{8\pi}VE^2. \tag{4}$$

The entropy S can be obtained either from F or F^*. In the case of a magnetic body, we have

$$\begin{aligned} S=-\left(\frac{\partial F}{\partial T}\right)_M &= S(T,0)-\tfrac{1}{2}V\left(\frac{\partial}{\partial T}\chi_T^{-1}\right)M^2 = S(T,0)+\frac{V}{2\chi_T{}^2}\chi_T'M^2 \\ &= S(T,0)+\tfrac{1}{2}V\chi_T'H^2, \end{aligned} \tag{5}$$

and

$$S=-\left(\frac{\partial F^*}{\partial T}\right)_H = S(T,0)+\tfrac{1}{2}V\chi_T'H^2. \tag{5'}$$

Similarly for a dielectric,

$$S=-\left(\frac{\partial F}{\partial T}\right)_P=-\left(\frac{\partial F^*}{\partial T}\right)_E = S(T,0)+\frac{V}{8\pi}\varepsilon'E^2. \tag{6}$$

30. From (6) of the foregoing problem we have

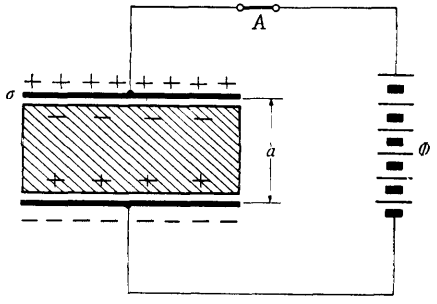
$$S(T,E)=S(T,0)+\frac{V}{8\pi}\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}E^2. \tag{1}$$

(i) When the switch is closed, a constant potential difference Φ is maintained between the condenser plates and a constant field $E_0=\Phi/a$ is established. From (1)

$$C_E=T\left(\frac{\partial S}{\partial T}\right)_E = C_0(T)+\frac{V}{8\pi}T\frac{\mathrm{d}^2\varepsilon}{\mathrm{d}T^2}E_0^2, \tag{2}$$

where $C_0(T)=T\,\mathrm{d}S(T,0)/\mathrm{d}T$.

(ii) If the switch had never been closed, $E=0$ and the heat capacity is $C_0(T)$. If the switch is closed at a temperature T_0, a surface charge of $\sigma=D/4\pi=\varepsilon_0E_0/4\pi$ (D=electric displacement, $\varepsilon_0=\varepsilon(T_0)$) appears on the plates of the condenser. If the switch is then opened, the surface charge remains and the *displacement D in the dielectric remains constant.* The



specific heat under this condition is

$$C_D = T\left(\frac{\partial S}{\partial T}\right)_D = C_0(T) + \frac{V}{8\pi} T \frac{\mathrm{d}^2\varepsilon}{\mathrm{d}T^2} E^2 + \frac{V}{8\pi} T \frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\left(\frac{\partial E^2}{\partial T}\right)_D. \tag{3}$$

Since $D=\varepsilon E$, we have

$$\left(\frac{\partial E^2}{\partial T}\right)_D = -\frac{2E^2}{\varepsilon}\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}.$$

Substitute this and $\varepsilon_0 E_0 = \varepsilon E = D$ into (3) to obtain

$$C_D = C_E - \frac{VT}{4\pi}\frac{D^2}{\varepsilon^3}\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\right)^2. \tag{4}$$

31. The heat absorbed by the dielectric is given by $\mathrm{d}'Q = T\,\mathrm{d}S$ when the potential is isothermally and quasi-statically increased from 0 to Φ. The dependence of the entropy S, on the electric potential is calculated by (6) of the solution of problem 29 and is

$$S(T, E) - S(T, 0) = V\frac{\mathrm{d}\varepsilon(T)}{\mathrm{d}T}\frac{E^2}{8\pi}. \tag{1}$$

If the distance between the plates of the condenser is a and the potential difference is Φ, the electric field is $E=\Phi/a$. Thus the heat given off by the dielectric as the potential difference is raised from 0 to Φ is

$$-Q = -\int_{\Phi=0}^{\Phi} T\,\mathrm{d}S = T\{S(0, T) - S(\Phi/a, T)\} = -VT\frac{\mathrm{d}\varepsilon(T)}{\mathrm{d}T}\frac{\Phi^2}{8\pi a^2}. \tag{2}$$

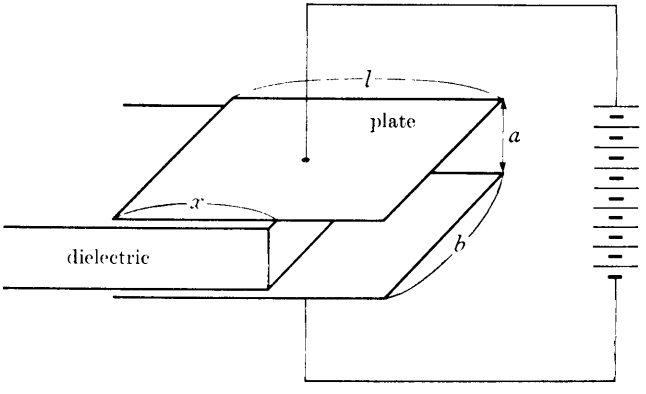
This may be written in another form by using the capacity, $C=\varepsilon A/4\pi a$, of the parallel plate condenser, where A is the area of the plates. Then (2)

becomes

$$-Q = \tfrac{1}{2}C\Phi^2 \frac{\mathrm{d}\log\varepsilon^{-1}(T)}{\mathrm{d}\log T}. \tag{3}$$

$\frac{1}{2}C\Phi^2$ is the static electric energy stored in the condenser.

32. As shown in the figure, a, b and l are, respectively, the distance between the plates, the width of the plate and the length of the parallel plate condenser,



and x is the depth by which the dielectric is inserted into the condenser. The volume V_1 of the dielectric in the field E is $V_1 = abx$. The volume of the condenser which is not occupied by the dielectric is $V_0 = ab(l-x)$. Since the electric field $E = \Phi/a$ is constant, we can use the free energy, F^*, given in problem 29. The total free energy is

$$\begin{aligned} F_{\text{total}} &= F(T,0) - \frac{V_1}{8\pi}(\varepsilon - 1)E^2 + \frac{V_0}{8\pi}E^2 \\ &= F(T,0) - \frac{abx}{8\pi}\varepsilon E^2 + \frac{abl}{8\pi}E^2. \end{aligned}$$

$F(T, 0)$ is the free energy of the entire dielectric when it has no electric field. The second term is the sum of the change in the free energy of the dielectric when it has been polarized by the electric field and its energy of interaction with the field, and the third term is the energy of the electric field. If x is increased, the free energy is decreased, so that the dielectric is pulled into the condenser with a force

$$X = -\frac{\partial F_{\text{total}}}{\partial x} = \frac{ab\varepsilon}{8\pi}E^2.$$

33.

$$J = -pV = -NkT, \tag{1}$$

$$\mu = \phi + kT \log \frac{p}{p_0}. \tag{2}$$

From (2),

$$p = p_0 \, e^{(\mu-\phi)/kT} = NkT/V, \tag{3}$$

or

$$J(T, V, \mu) = -p_0 V \, e^{(\mu-\phi)/kT}. \tag{4}$$

By differentiating (4) with respect to μ and V and using (3) we see that

$$\left(\frac{\partial J}{\partial \mu}\right)_{T,V} = -\frac{p_0 V}{kT} e^{(\mu-\phi)/kT} = -N, \tag{5}$$

and

$$\left(\frac{\partial J}{\partial V}\right)_{T,\mu} = -p_0 \, e^{(\mu-\phi)/kT} = -p. \tag{6}$$

Also we have

$$\begin{aligned}\left(\frac{\partial J}{\partial T}\right)_{V,\mu} &= -p_0 V \, e^{(\mu-\phi)/kT} \left\{\frac{\partial \log p_0}{\partial T} + \left(\frac{\partial}{\partial T} \frac{\mu-\phi}{kT}\right)_\mu\right\} \\ &= -N\left\{kT \frac{\partial \log p_0}{\partial T} - \frac{\partial \phi}{\partial T} - \frac{\mu-\phi}{T}\right\}.\end{aligned}$$

As can be confirmed by (2), this satisfies

$$\left(\frac{\partial J}{\partial T}\right)_{V,\mu} = N\left(\frac{\partial \mu}{\partial T}\right)_p = -S. \tag{7}$$

34. The rate of temperature change due to the adiabatic elongation of a rubber band is given as

$$\left(\frac{\partial T}{\partial l}\right)_S = -\left(\frac{\partial S}{\partial l}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_l = \frac{T}{C_l}\left(\frac{\partial X}{\partial T}\right)_l, \tag{1}$$

where C_l is the heat capacity at constant length. Here the Maxwell relation, $(\partial S/\partial l)_T = -(\partial X/\partial T)_l$ obtained from $dF = -S dT + X dl$, was used. For $T = T_0$ the given equation becomes

$$\left(\frac{\partial X}{\partial T}\right)_l = A(L - L^{-2}) - \alpha A T_0 L^{-2},$$

or

$$\left(\frac{\partial T}{\partial l}\right)_S = \frac{T_0}{C_l} A \{L - (1 + \alpha T_0) L^{-2}\}.$$

The temperature change due to an adiabatic elongation from $L=1$ to L is

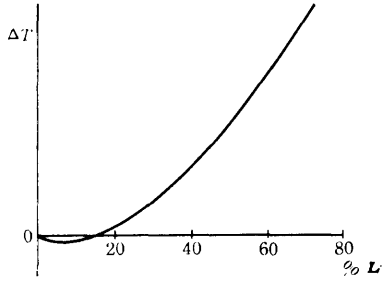
$$\Delta T = \int_{l_0}^{Ll_0} \left(\frac{\partial T}{\partial l}\right)_S \mathrm{d}l = \frac{T_0 A l_0}{C_l} \int_1^L \{L - (1+\alpha T_0)\, L^{-2}\}\, \mathrm{d}L$$

$$= \frac{A l_0}{2C_l} T_0 \frac{L-1}{L} \{L^2 + L - 2(1+\alpha T_0)\}. \tag{2}$$

If $T_0 = 300$ °K, $\delta = \alpha T_0 = 0.21$. The expression in parentheses in (2) vanishes when $L = 1+\varepsilon$, where ε is determined by $3\varepsilon + \varepsilon^2 = 2\delta$, or

$$\varepsilon = \tfrac{2}{3}\delta - \tfrac{1}{3}\varepsilon^2 \doteqdot 0.14 - \tfrac{1}{3}\cdot 0.020 \doteqdot 0.13.$$

Equation (2) is plotted against L in the figure.



NOTE: The relation given in this problem between the tension and the strain can be derived from the statistical mechanical theory of rubber elasticity and actually applies quite well to moderately vulcanized rubber and also to some other kinds of rubber-like materials. The thermal effect that is considered here is called the Joule effect. As seen in the figure, the fact that $\Delta T < 0$ for small strains is due to thermal expansion. Ignoring this, such rubber-like materials are heated up ($\Delta T > 0$) when they are elongated adiabatically. This is a characteristic of rubber-like elasticity. One can easily verify this with a rubber band.

CHAPTER 4

PHASE EQUILIBRIUM AND CHEMICAL EQUILIBRIUM

There are no new principles in this chapter. Here we deal with the most important applications of thermodynamics to physics and physical chemistry such as the equilibrium between different phases of a single component, the equilibrium between different phases of a system with two or more components and the general problems of chemical equilibrium concerning dissociation or recombination of component particles. In the section on fundamental topics, we will discuss a few theorems and concepts useful for treating these problems.

Fundamental topics

§ 4.1. PHASE

A substance which is physically and chemically homogeneous is considered a single phase. Different states of aggregation such as gas, liquid, or different crystalline states are different phases.

§ 4.2. EQUILIBRIUM BETWEEN DIFFERENT PHASES OF A PURE SUBSTANCE

When two phases, 1 and 2 (indicated by single and double primes), are in contact with each other and are in equilibrium, the pressure on both sides of the interface is equal or different depending on the nature of the interface.

(1) *Plane interface which transmits pressure.* By (3.26a-c) we must have

$$p' = p'' = p\,, \tag{4.1}$$

$$T' = T'' = T\,, \tag{4.2}$$

and

$$\mu'(p, T) = \mu''(p, T) \qquad \text{or} \qquad \tilde{G}' = \tilde{G}''\,. \tag{4.3}$$

Equation (4.3) is the condition for phase equilibrium. When the surfaces $\mu = \mu'$ and $\mu = \mu''$ are constructed in the space (μ, P, T), the intersection line forms the *coexistence line of the two phases.* A *phase transition* occurs when this line is crossed. The phase with the lower chemical potential is always realized as the more *stable phase.* The order of the phase transition is

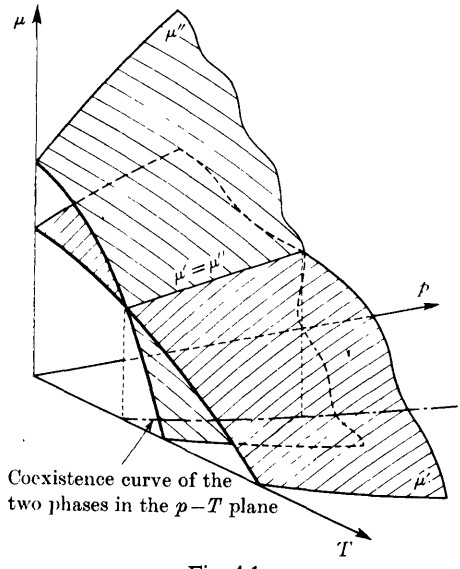


Fig. 4.1.

determined by the order of contact between the surfaces $\mu=\mu'$ and $\mu=\mu''$. Fig. 4.1 represents a first order phase transition.

a) *First-order phase transition*: The conditions for this are $\Delta\mu=\mu'-\mu''=0$, $\partial\Delta\mu/\partial T\neq 0$ and $\partial\Delta\mu/\partial p\neq 0$. From (4.3) we have

$$\Delta\frac{\partial\bar{G}}{\partial p}\,\mathrm{d}p+\Delta\frac{\partial\bar{G}}{\partial T}\,\mathrm{d}T=0,$$

or

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta\bar{S}}{\Delta\bar{V}}=\frac{q}{T\Delta\bar{V}}\qquad\text{(Clausius-Clapeyron equation)},\tag{4.4}$$

where

$$q=T\,\Delta\bar{S}=T(\bar{S}'-\bar{S}'')$$

is the heat of transition per mole and $\Delta\bar{V}$ is the volume change per mole in the transition.

b) *Second-order phase transition*: The conditions for this are $\Delta\mu=0$, $\partial\Delta\mu/\partial T=0$, $\partial\Delta\mu/\partial p=0$, while the second order derivatives be, in general, not equal to zero. Therefore, along the coexistence line it follows that

$$\left.\begin{aligned}&\Delta\frac{\partial\bar{V}}{\partial p}\,\mathrm{d}p+\Delta\frac{\partial\bar{V}}{\partial T}\,\mathrm{d}T=0 &&\left(\frac{\partial\Delta\bar{G}}{\partial p}=0\right),\\&\Delta\frac{\partial\bar{V}}{\partial T}\,\mathrm{d}p-\frac{\Delta C_p}{T}\,\mathrm{d}T=0 &&\left(\frac{\partial\Delta\bar{G}}{\partial T}=0\right).\end{aligned}\right\}\tag{4.5}$$

In order that $\mathrm{d}p/\mathrm{d}T$ have a finite value, it is necessary that

$$\begin{vmatrix} \Delta \dfrac{\partial \bar{V}}{\partial p} & \Delta \dfrac{\partial \bar{V}}{\partial T} \\ \Delta \dfrac{\partial \bar{V}}{\partial T} & -\Delta \dfrac{C_p}{T} \end{vmatrix} = 0, \quad \text{or} \quad \Delta \frac{\partial \bar{V}}{\partial p} \Delta C_p + T\left(\Delta \frac{\partial \bar{V}}{\partial T}\right)^2 = 0. \tag{4.6}$$

There is no latent heat in this type of transition, but there may be discontinuities or singularities in the specific heat at the transition point.

Second order transitions may be less familiar to the reader. There are, however, a number of examples in alloys and magnetic materials. A particularly interesting case is the phase transition of a gas through the critical point $T = T_c$ keeping the density at the critical density.

c) *Higher-order phase transitions*: When the partial derivatives of μ up to $n-1$-th order are all continuous and the lowest order discontinuity appears in the n-th order partial derivatives, the phase transition is said to be of the n-th order.

(2) When the interface is not a plane, and so there generally exists some effect due to *surface tension*, or when the wall between the two phases is permeable to matter but does not transmit pressure, the pressure in the different phases is not equal: i.e.,

$$p' \neq p''.$$

On the other hand (4.2) and (4.3) must hold. Therefore we have

$$\bar{G}'(p', T) = \bar{G}''(p'', T).$$

Then the relation between p' and p'' is determined by

$$\bar{V}' \, \mathrm{d}p' = \bar{V}'' \, \mathrm{d}p'' \qquad \text{(Gibbs-Poynting equation)}. \tag{4.7}$$

§ 4.3. SURFACE TENSION

Definition of surface tension: The work necessary in order to change the area of the interface between two phases is the work done against the surface tension. If this is included, the equation for the energy change (2.14) for a quasi-static process becomes

$$\mathrm{d}U = T\,\mathrm{d}S - p'\,\mathrm{d}V' - p''\,\mathrm{d}V'' + \gamma\,\mathrm{d}\sigma + \mu'\,\mathrm{d}N' + \mu''\,\mathrm{d}N'', \tag{4.8}$$

where p' and p'' are the internal pressure of phases 1 and 2, $\mu'(T, p')$, $\mu''(T, p'')$ are the chemical potentials of the phases, and σ is the area of the interface.

The *surface tension*, γ, is defined by this equation, i.e.,

$$\gamma = \left(\frac{\partial U}{\partial \sigma}\right)_{S,V',V'',N',N''}. \tag{4.8'}$$

Pressure difference due to the surface tension: When the interface between the two phases is a sphere of radius r, the pressure difference is given by

$$p' - p'' = \frac{2\gamma}{r}. \tag{4.9}$$

This is obtained from the equilibrium condition $\mathrm{d}U=0$ (3.30a) by letting $\mathrm{d}S=\mathrm{d}N'=\mathrm{d}N''=0$, $\mathrm{d}V''=-\mathrm{d}V'$ and considering that $\mathrm{d}V'/\mathrm{d}\sigma=\frac{1}{2}r$ in (4.8).

Equilibrium condition for mass action is given by

$$\mu'(T, p') = \mu''(T, p''). \tag{4.10}$$

For example, the relation between the radius, r, of a spherical drop of a liquid and its vapor pressure is given by

$$\mu_l\left(T, p_r + \frac{2\gamma}{r}\right) = \mu_g(T, p_r) \tag{4.10'}$$

(see problem 34).

§ 4.4. EQUILIBRIUM OF A MANY-COMPONENT SYSTEM IN DIFFERENT PHASES

For simplicity, we assume that mechanical equilibrium is established at the interfaces of the different phases, so that the pressure is uniform. The different components are denoted by the subscripts $1, 2, \ldots, c$, and the phases by superscripts $1, 2, \ldots, r$. The equilibrium conditions are:

$$p' = p'' = \cdots = p^{(r)} = p, \tag{4.11a}$$

$$T' = T'' = \cdots = T^{(r)} = T, \tag{4.11b}$$

$$\left.\begin{array}{l} \mu_1' = \mu_1'' = \cdots = \mu_1^{(r)}, \\ \cdots\cdots\cdots \\ \mu_c' = \mu_c'' = \cdots = \mu_c^{(r)}, \end{array}\right\} \tag{4.12}$$

or

$$\bar{G}_j' = \bar{G}_j'' = \cdots = \bar{G}_j^{(r)}, \qquad j = 1, 2, \ldots, c. \tag{4.12'}$$

PROOF: We generalize the treatment of § 3.6. Let the entropy of each phase be $S^{(k)}$, the energy $U^{(k)}$, the volume $V^{(k)}$ and the mole number of each

component $N_j^{(k)}$. Then the equilibrium conditions are:

$$\delta S = \delta S' + \delta S'' + \cdots + \delta S^{(r)}$$
$$= \sum_{k=1}^{r} \left(\frac{\partial S^{(k)}}{\partial U^{(k)}} \delta U^{(k)} + \frac{\partial S^{(k)}}{\partial V^{(k)}} \delta V^{(k)} + \sum_j \frac{\partial S^{(k)}}{\partial N_j^{(k)}} \delta N_j^{(k)} \right) = 0, \tag{a}$$

$$\delta U = \sum_{k=1}^{r} \delta U^{(k)} = 0, \tag{b}$$

$$\delta V = \sum_{k=1}^{r} \delta V^{(k)} = 0, \tag{c}$$

$$\delta N_j = \sum_{k=1}^{r} \delta N_j^{(k)} = 0, \qquad j = 1, 2, \ldots, c. \tag{d}$$

The conditions (b–d) are obtained by use of the conditions that U, V and N_j are constant. Using Lagrange's undetermined multipliers, multiply (b) by $-1/T$, (c) by p/T and (d) by $-\mu_j/T$ and add to (a) to obtain

$$\delta S - \frac{1}{T} \delta U + \frac{p}{T} \delta V - \sum_{j=1}^{c} \frac{\mu_j}{T} \delta N_j =$$
$$= \sum_{k=1}^{r} \left\{ \left(\frac{\partial S^{(k)}}{\partial U^{(k)}} - \frac{1}{T} \right) \delta U^{(k)} + \left(\frac{\partial S^{(k)}}{\partial V^{(k)}} + \frac{p}{T} \right) \delta V^{(k)} + \sum_j \left(\frac{\partial S^{(k)}}{\partial N_j^{(k)}} - \frac{\mu_j}{T} \right) \delta N_j^{(k)} \right\}$$
$$= 0.$$

Since the variations may be regarded as independent, their coefficients are zero. Thus we get (4.11a, b) and (4.12).

DIVERTISSEMENT 10

Equilibrium of heterogeneous substances.

Die Energie der Welt ist constant.

Die Entropie der Welt strebt einem Maximum zu.

By these simple statements R. Clausius (1822–1888) summarized his work "Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie" which was published in 1865, fifteen years after his discovery of the second law in the Poggendorf Annalen (Annalen der Physik und Chemie) Bd. CXXV, pp. 351–400. In this very important work he established basic expressions of the first and the second laws of thermodynamics which are now familiar to us.

Ten years later, in 1875, J. Willard Gibbs (1839–1903) put these statements at the head of his celebrated paper "On the equilibrium of heterogenous substances" (The Scientific Papers of J. Willard Gibbs, Vol. i

(Dover Publication Inc., New York)). In this work Gibbs used these principles to establish the most general formulation of equilibrium conditions for heterogenous systems, introducing for the first time the concept of chemical potential. The phase rule was one of the beautiful theorems resulted from this formulation. This paper remained almost entirely unknown to European scientists for fifteen years until 1891, when it was translated into German by W. Ostwald (later in 1899 into French by Le Chatelier). One reason for this was that Gibbs' paper was published in Transactions of the Connecticut Academy (Vol. III, pp. 108–248) – a journal with very limited circulation. Another reason was that the paper was difficult to understand. Ostwald wrote – "Von dem Bedürfniss nach grösstmöglicher Allgemeinheit der Untersuchung grösstmöglicher Unzweideutigkeit des Ausdruckes geleitet, hat der Verfasser eine Form der Darstellung gewählt, welche durch ihre abstrakte Gestalt und ihre oft schwer übersehbare Darstellungsweise vom Leser eine nicht gewöhnliche Aufmerksamkeit und Hingabe fordert."

When it was introduced to Europe so many years after it was first written, Gibbs' work was still completely fresh. "Der Inhalt des Werkes ist noch heute von unmittelbarer Wichtigkeit und das Interesse an demselben ist keinesweges ein bloss historisches. Denn von der fast unabsehbaren Fülle der Ergebnisse, die es enthält oder anbahnt, ist bisher nur ein geringer Antheil fruchtbar gemacht worden. Noch liegen ungehobene Schätze für den theoretischen wie namentlich den experimentellen Forscher von grösster Mannigfaltigkeit und Bedeutung in den Kapiteln desselben zu Tage. Seitdem wir für das ausgedehnte Gebiet der verdünnten Lösungen die Werthe der Energie und Entropie ebenso wie für Gase kennen, ist es möglich geworden, die allgemeinen Functionen der Gibbs'schen Gleichungen durch experimentell messbare Grössen darzustellen, wie das zum Theil schon geschehen ist, zum grössten Theil aber noch der Ausführung harrt."

§ 4.5. GIBBS' PHASE RULE

THEOREM: When a system consisting of c different components in different phases is in equilibrium, the *degrees of freedom, f*, of the equilibrium state is given by

$$f = c - r + 2. \tag{4.13}$$

By degrees of freedom, we mean the number of internal variables that can be freely changed under the condition of equilibrium.

PROOF: The *internal condition* of a single phase consisting of c components is determined by the composition ratio of the components. This means that there are $c-1$ internal variables as far as the composition is concerned. Besides these variables, p and T are common for the different phases. Thus, altogether we should have $(c-1)\,r+2$ variables for r phases. Being intensive

quantities, the chemical potentials, $\mu_j^{(k)}$ $(k=1,\ldots,r; j=1,\ldots,c)$, are determined by these internal variables only. Since the equilibrium condition (4.12) consists of $(r-1)c$ equations, the number of variables that can be freely changed after satisfying the conditions of equilibrium is given by

$$f = (c-1)\,r + 2 - (r-1)\,c = c - r + 2\,.$$

EXAMPLE: Equilibrium of two phases of a pure substance (1 component, 2 phase system): $c=1$, $r=2$, $f=1$. Equilibrium of three phases of a pure substance: $c=1$, $r=3$, $f=0$ (triple point). Equilibrium of two phases of a two-component system: $c=2$, $r=2$, $f=2$.

DIVERTISSEMENT 11

Classification of phase transitions described in § 4.1 is one given by P. Ehrenfest (Leiden Commen. 75f, 1933), who was the first to make such a classification. His idea of the order of a phase change is based on the Taylor expansion of $\Delta\mu(T + \mathrm{d}T, p + \mathrm{d}p)$ in powers of $\mathrm{d}T$ and $\mathrm{d}p$. If we keep terms of the first order only, we obtain a transition of the first order. If terms of the first order vanish *along* the equilibrium curve, and if we retain terms of the second order alone, we have a change of the second order, which generally exhibits *finite* discontinuity in specific heats.

We know many first-order transitions, e.g. the liquid-vapor transition of pure substance, except at the critical point, at which C_p becomes infinite (see Fig. 3.7). For second-order changes, however, we know only a few examples which show some deviations from Ehrenfest's scheme. In the case of the transition of a superconductor to the normal state, for instance, the equilibrium curve is drawn in the H–T plane, where H is the applied magnetic field. The transition occurs without latent heat only at one point $H=0$ on the equilibrium curve, where $C_H(=C_V)$ makes a jump. L. Onsager (Phys. Rev. **65** (1944) 117) proved that $C_H(=C_V)$ becomes logarithmically infinite at the transition point but is continuous everywhere else for a two-dimensional Ising ferromagnet, in the case $H=0$. L. Tisza (M. I. T. Laboratory of Electronics Technical Report, No. 127, 1949; *Phase Transitions in Solids* (Wiley, New York, 1951)) pointed out that the Taylor expansion is invalidated by the possibility of infinite differential coefficients of μ of the second or higher order for one or both phases. Thus Ehrenfest's original classification is certainly incomplete.

C. N. Yang and T. D. Lee (Phys. Rev. **87** (1952) 404, 410) proved the mathematical equivalence between the theory of vapor-liquid transition and that of the ferromagnetic problem for simple models. Both theories have the same structure, and the magnetization curve can be obtained from the isotherm in the p–V plane, and vice versa: the magnetic field corresponds to the chemical potential, and the magnetization to the den-

sity. This means that the vapor-liquid transition will appear as a second order change, if the evaporation of a substance is observed under its vapor pressure.

The specific heat C_p is considered to be less fundamental than C_V, in the sense that the anomaly in C_V is linked with ordering mechanisms: long-range molecular interactions seem to cause a jump in C_V, while short-range interactions seem to result in an infinite C_V at the transition point. O. K. Rice (J. Chem. Phys. **22** (1954) 1535) showed that, if such short-range interaction is independent of volume, the transition remains of the second order, but that, if it depends on the volume, a system with $C_V = \infty$ becomes unstable against the change in volume and the transition changes into a first-order transition. He stated that we should never expect to find any infinite specific heats, apart from a first-order transition.

§ 4.6. THE CHEMICAL POTENTIAL OF A GAS

The chemical potential per mole (Gibbs free energy), $\bar{G}(T, p)$, of a pure ideal gas is

$$\bar{G}(T, p) = \bar{G}(T, p_0) + RT \log (p/p_0) \tag{4.14}$$

$$\equiv \bar{\bar{G}}(T) + RT \log p, \tag{4.14'}$$

where

$$\bar{\bar{G}}(T) = U_0 - C_p^0 T \log T - T \int_0^T \frac{\mathrm{d}T_1}{T_1^2} \int_0^{T_1} C'(T_2)\, \mathrm{d}T_2 - RTi(+ RT \log p_0) \tag{4.15a}$$

is the chemical potential at the temperature T and the standard pressure* p_0 (if this is taken as 1, the last term is 0).

Also,

$$\bar{U}(T) = U_0 + (C_p^0 - R)\, T + \int_0^T C'(T_1)\, \mathrm{d}T_1 \tag{4.15b}$$

is the internal energy per mole. U_0 is the molar internal energy at $T=0$, and C_p^0 is the molar specific heat at constant pressure due to the translational motion and the rotational motion of the molecule. For a monatonic gas, $C_p^0 = \frac{5}{2}R$, for a diatomic gas $C_p^0 = \frac{7}{2}R$, and for a polyatomic gas, $C_p^0 = 4R$. Also $C'(T)$ is the specific heat due to the internal vibrations of the molecules, which is normally small at room temperature and i is the chemical constant. NOTE: (4.15a) is a good approximation for normal gases except at very low temperatures. However, for light gases such as hydrogen, the specific heat

* Henceforth, the double bar on G ($\bar{\bar{G}}$) indicates a quantity per mole at standard pressure.

due to rotation is not constant below 100 °K, and (4.15a) requires some correction (see example 1 and problem 6 in Chapter 3 of Statistical Mechanics).

The molar chemical potential $\bar{G}_j$ of the j-th component in an *ideal gas mixture* is

$$\bar{G}_j(T,p) = \bar{G}_j^0(T,p_0) + RT\log(p_j/p_0) \tag{4.16}$$

$$\equiv \bar{G}_j^0(T) + RT\log p_j = \bar{G}_j^0(T) + RT\log p + RT\log y_j\,. \tag{4.16'}$$

Here, $\bar{G}_j^0(T,p_0)$ is the chemical potential of the pure* gas of the j-th component at the pressure p_0, $\bar{G}_j^0(T)$ is that at the standard pressure $p_0=1$, p is the total pressure, and

$$\left.\begin{array}{ll} p_j = y_j p & \text{is the partial pressure,} \\ \text{where } y_j = n_j/\sum n_j & \text{is molar fraction of the } j\text{-th component.} \end{array}\right\} \tag{4.17}$$

The Gibbs free energy of an ideal gas mixture is

$$\begin{aligned} G(T,p,n_1,\ldots,n_c) &= \sum_{j=1}^{c} n_j\bar{G}_j(T,p) \\ &= \sum_{j=1}^{c} n_j G_j^0(T,p) - T\,\Delta S\,, \end{aligned} \tag{4.18}$$

where

$$\Delta S = -R\sum n_j \log y_j = -Rn\sum y_j \log y_j \tag{4.19}$$

is the entropy of mixing (see example 5 in Chapter 2 and problem 13 in Chapter 3).

Real gases: Equations (4.14) and (4.16) are modified in the following manner to include deviations from ideal gases:

$$\text{Pure gas:}\quad \bar{G}(T,p) = \bar{G}(T) + RT\log pv\,, \tag{4.20}$$

$$\begin{aligned} \text{Mixture:}\quad \bar{G}_j(T,p) &= \bar{G}_j^0(T) + RT\log p_j v_j \\ &= \bar{G}_j^0(T) + RT\log p + RT\log y_j v_j\,, \end{aligned} \tag{4.21}$$

where $\bar{G}$ or $\bar{G}_j^0$ is the chemical potential of the pure gas at temperature T and the standard pressure p_0. Here, v or v_j is the *fugacity* which has the property

$$\lim_{p\to 0} v = 1\,, \qquad \lim_{p\to 0} v_j = 1\,. \tag{4.22}$$

NOTE: For real gases, $\bar{G}$ and $\bar{G}_j^0$ are not accurately expressed by (4.15). Also $p_j = py_j$ in (4.21) is only the partial pressure defined in a formal way and does

* Henceforth, the superscript 0 indicates pure matter.

not have such a direct physical meaning as in the case of ideal gases. Since any real gas approaches an ideal gas as p goes to zero, the fugacity v must approach 1 as $p \to 0$.

§ 4.7. CHEMICAL POTENTIAL AND SATURATION VAPOR PRESSURE OF LIQUIDS AND SOLIDS

According to (4.3) the *molar chemical potential of a pure liquid* (*solid*), $\bar{G}_{\text{liq}}(T, p)$, $(\bar{G}_{\text{sol}}(T, p))$ must be equal to the chemical potential of the saturated vapor (pressure p):

$$\bar{G}_{\text{liq}}(T, p) = \bar{G}_{\text{gas}}(T, p) = \bar{\bar{G}}_{\text{gas}}(T) + RT \log p, \tag{4.23}$$

where $\bar{G}_{\text{gas}}$ is the chemical potential of the saturated vapor. (Here we have used the ideal gas equation (4.14). This is permissible since the saturation vapor pressure of liquids and solids is usually low.)

The molar chemical potential of the j-th component in a solution (or a *solid solution*) $\bar{G}_{j,\,\text{liq}}(T, p)$ is given by

$$\bar{G}_{j,\,\text{liq}}(T, p) = \bar{G}_{j,\,\text{gas}}(T, p) = \bar{\bar{G}}^0_{j,\text{gas}}(T) + RT \log p_j, \tag{4.24}$$

where $\bar{G}_{j,\,\text{gas}}$ is the chemical potential of the j-th component in the gas phase (considered as an ideal gas mixture), $\bar{\bar{G}}^0_{j,\,\text{gas}}$ the chemical potential of the j-th component at the standard pressure p_0 and the temperature T, and p_j is the saturation vapor pressure of the j-th component in the solution (solid solution) (see (4.16)). Equation (4.24) can be rewritten in the following way by comparing it with a pure liquid of the j-th component:

$$\bar{G}_{j,\,\text{liq}}(T, p) = \bar{G}^0_{j,\,\text{liq}}(T, p^0_j) + RT \log \frac{p_j}{p^0_j}, \tag{4.25}$$

where $\bar{G}^0_{j,\,\text{liq}}$, the chemical potential of the j-th pure liquid, is given by

$$\bar{G}^0_{j,\,\text{liq}} = \bar{\bar{G}}^0_{j,\,\text{gas}} + RT \log \frac{p^0_j}{p_0}, \tag{4.26}$$

in which p^0_j is the saturation vapor pressure at the temperature T, of the pure j-th liquid. Equation (4.25) is obtained by eliminating $\bar{\bar{G}}^0_{j,\,\text{gas}}$ from (4.26) and (4.24).

In the normal range of pressures (say, 1 atm) the pressure dependence of the chemical potential of a liquid (solid) is small so that p^0_j in $\bar{G}^0_{j,\,\text{liq}}(T, p^0_j)$ in (4.25) may be replaced by p, which simplifies (4.25) to

$$\bar{G}_{j,\,\text{liq}}(T, p) = \bar{G}^0_{j,\,\text{liq}}(T, p) + RT \log \frac{p_j}{p^0_j}. \tag{4.27}$$

This equation expresses the chemical potential in a solution in terms of the chemical potential of the pure liquid and the saturation vapor pressure of each component. If the pressure change neglected in (4.27) is taken into consideration, (4.27) is modified to

$$\bar{G}_{j,\,\mathrm{liq}}(T, p) = \bar{G}^0_{j,\,\mathrm{liq}}(T, p) + RT \log \frac{p_j}{p_j^0} + \int_p^{p_j^0} \bar{V}_j^0 \, \mathrm{d}p. \tag{4.27'}$$

The last term is usually small.

§ 4.8. DILUTE SOLUTIONS

Two component solutions: The solvent is denoted by 1 and the solute by 2. The molar concentration is $x_1 : x_2 \, (x_1 + x_2 = 1)$. For sufficiently small concentration, the saturation vapor pressure of the solvent p_1 follows the equation

$$p_1 = x_1 p_1^0 \qquad (T = \text{const.}, \, x_1 \to 1, \, x_2 \to 0), \tag{4.28}$$

which is *an empirical limiting law* (p_1^0 is the saturation vapor pressure of the pure solvent). This is called *Raoult's law*. Corresponding to this, the saturation vapor pressure of the solute p_2 follows *Henry's law*,

$$p_2 = k_2 x_2 \qquad (T = \text{const.}, \, x_2 \sim 0), \tag{4.29}$$

where k_2 is a constant characteristic of the solution. The chemical potential for each component becomes

$$\bar{G}_1(T, p) = \bar{G}_1^0(T, p) + RT \log x_1 \qquad (x_1 \sim 1) \tag{4.30a}$$

$$\begin{aligned} \bar{G}_2(T, p) &= \bar{G}_2^0(T, p) + RT \log \frac{k_2 x_2}{p_2^0} \qquad (x_2 \sim 0) \\ &= \phi_2^0(T) + RT \log x_2 . \end{aligned} \tag{4.30b}$$

Equations (4.29) and (4.30b) are derived from the Gibbs-Duhem relation (see problem 13).

Many component solution: The solvent is denoted by 1 and the solutes by 2, 3, ... The molar concentrations are $x_1 : x_2 : x_3 : \ldots$. By analogy with (4.28), we have in the limit as $x_1 \sim 1, x_2 \to 0, x_3 \to 0, \ldots$ (Raoult's law for a *dilute solution*)

$$p_1 = x_1 p_1^0, \qquad \text{or} \qquad \frac{p_1^0 - p_1}{p_1^0} = x_2 + x_3 + \cdots . \tag{4.31}$$

In this case, it is not possible to determine $\bar{G}_2, \bar{G}_3, \ldots, p_2, p_3, \ldots$ from the Gibbs-Duhem relations alone. However, if we assume that interaction between the solutes can be ignored in the limit of a dilute solution, we may

assume that

$$p_j = k_j x_j \qquad (j = 2, 3, \ldots; x_j \sim 0), \tag{4.32}$$

$$\bar{G}_j = \bar{G}_j^0 + RT \log \frac{k_j x_j}{p_j^0} = \phi_j^0 + RT \log x_j, \tag{4.33}$$

which equations are analogous to the two-component case.

§ 4.9. IDEAL SOLUTION (IDEAL SOLID-SOLUTION) AND REGULAR SOLUTION

If the relations

$$\left.\begin{aligned} \bar{G}_1 &= \bar{G}_1^0(T, p) + RT \log x_1, \\ \bar{G}_2 &= \bar{G}_2^0(T, p) + RT \log x_2 \end{aligned}\right\} \tag{4.34}$$

are valid over all possible ranges of temperature, pressure and concentration ratio, the system is said to be an *ideal solution* (ideal solid-solutions in the case of a solid). Although this is an idealization, there are real systems which are not very far from this.

The change in the Gibbs free energy when an ideal solution is made from pure substances is given by

$$\Delta\bar{G} = x_1\bar{G}_1 + x_2\bar{G}_2 - x_1\bar{G}_1^0 - x_2\bar{G}_2^0 = RT(x_1 \log x_1 + x_2 \log x_2),$$

or

$$\Delta\bar{H} = 0, \qquad \Delta\bar{S} = -R(x_1 \log x_1 + x_2 \log x_2), \tag{4.35}$$

which gives us the entropy of mixing, $\Delta\bar{S}_{\text{ideal}}$.

The saturation vapor pressures are:

$$p_1 = x_1 p_1^0, \qquad p_2 = x_2 p_2^0. \tag{4.36}$$

Regular solution: Hildebrand considered a solution such that

$$\Delta\bar{H} \neq 0 \qquad \text{and} \qquad \Delta\bar{S} = \Delta\bar{S}_{\text{ideal}} \tag{4.37}$$

and called it a regular solution. There are real systems which approximate this. Let $\Delta\bar{H}$ be a function of x_2. Then we have

$$\left.\begin{aligned} \bar{G}_1 &= \bar{G}_1^0 + \Delta\bar{H} - x_1 \frac{\partial \Delta\bar{H}}{\partial x_2} + RT \log x_1 \\ &\qquad = \phi_1^0(T, p, x_2) + RT \log x_1, \\ \bar{G}_2 &= \bar{G}_2^0 + \Delta\bar{H} + x_2 \frac{\partial \Delta\bar{H}}{\partial x_2} + RT \log x_2 \\ &\qquad = \phi_2^0(T, p, x_2) + RT \log x_2. \end{aligned}\right\} \tag{4.38}$$

§ 4.10. EXPRESSIONS FOR CONCENTRATION OF SOLUTIONS

There are various ways to express the concentration of a solution. The following are some of those commonly used:

1) mole fraction, x_2

$$= \frac{\text{mole number of solute}}{\text{mole number of solvent} + \text{mole number of solute}} = \frac{n_2}{n_1 + n_2};$$

2) molality, m_2

$$= \text{mole number of solute in 1kg of solvent};$$

3) molarity or molar concentration, c_2

$$= \text{mole number of solute in 1 litre of solution}.$$

Let the molecular weight of the solvent be $\bar{M}_1$, that of the solute $\bar{M}_2$, the density of the solution ρ and the density of the solvent ρ_1. The above mentioned parameters are related to one another in the following way:

$$m_2 = \frac{1000}{\bar{M}_1}\frac{x_2}{x_1}, \qquad x_2 = \frac{m_2}{m_2 + (1000/\bar{M}_1)}, \tag{4.39}$$

$$C_2 = \frac{m_2\rho}{1000 + \bar{M}_2 m_2} \times 1000, \qquad m_2 = \frac{C_2}{\rho - (C_2\bar{M}_2/1000)}. \tag{4.40}$$

When $x_2 \sim 0$, they can be approximated by

$$m_2 \sim \frac{1000}{\bar{M}_1} x_2, \qquad C_2 \sim \rho_1 m_2. \tag{4.41}$$

§ 4.11+. ACTIVITY AND ACTIVITY COEFFICIENT

Write the chemical potential of the j-th component in a solution as

$$\bar{G}_j(T, p) = \bar{G}_j^0(T, p) + RT \log a_j(T, p) \tag{4.42}$$

$$\fallingdotseq \bar{G}_j^0(T) + RT \log a_j(T), \tag{4.42'}$$

which are analogous to (4.34). $\bar{G}_j^0$ and $\bar{G}_j^0$ were defined before (§ 4.7). Equation (4.42) or (4.42′) defines the activity $a_j(T, p)$ of the j-th component in the solution. Usually the pressure dependence of $\bar{G}_j^0(T, p)$ and $a_j(T, p)$ can be ignored, so that eq. (4.42′) is a good approximation. In eq. (4.42′), we put

$$a_j = \gamma_j x_j, \qquad \text{or} \qquad \gamma_j = \frac{a_j}{x_j}, \tag{4.43}$$

which defines the *activity coefficient* γ_j. Let the saturation vapor pressure be p, the concentration of the j-th component y_j, the fugacity v_j and the

saturation vapor pressure and the fugacity of the j-th pure liquid be p_j^0 and v_j^0. Then we have

$$a_j = \frac{y_j p}{p_j^0}\frac{v_j}{v_j^0} \xrightarrow[\text{(sat. vapor} \downarrow \text{ideal gas)}]{} \frac{y_j p}{p_j^0}, \tag{4.44a}$$

$$\gamma_j = \frac{y_j p}{x_j p_j^0}\frac{v_j}{v_j^0} \xrightarrow[\text{(sat. vapor} \downarrow \text{ideal gas)}]{} \frac{y_j p}{x_j p_j^0}. \tag{4.44b}$$

For an ideal dilute solution ($x_1 \sim 1$, $x_2 \sim 0$) we have by (4.33)

$$a_1 \sim x_1, \qquad \gamma_1 \sim 1, \qquad a_2 \sim \frac{k_2 x_2}{p_2^0}, \qquad \gamma_2 \sim \frac{k_2}{p_2^0}. \tag{4.45}$$

Other definitions of the activity of solutes in general dilute solutions: The chemical potential of solutes in an ideal dilute solutions can be written in various forms depending on the way we express the concentration:

$$\bar{G}_2 = \phi_2^0 + RT \log x_2 \tag{4.46a}$$

$$= \phi_2' + RT \log m_2 \tag{4.46b}$$

$$= \phi_2'' + RT \log C_2, \tag{4.46c}$$

where

$$\phi_2' = \phi_2^0 - RT \log(1000/\bar{M}_1), \qquad \text{and} \qquad \phi_2'' = \phi_2' - RT \log \rho_1.$$

In order to write the chemical potential of a general dilute solution in a form analogous to (4.46a-c), the activities a_2^0, a_2', a_2'' and the activity coefficients γ_2^0, γ_2', γ_2'' are introduced by the following equations:

$$\bar{G}_2 = \phi_2^0 + RT \log a_2^0 \equiv \phi_2^0 + RT \log(\gamma_2^0 x_2) \qquad (a_2^0 = \gamma_2^0 x_2) \tag{4.47a}$$

$$= \phi_2' + RT \log a_2' \equiv \phi_2' + RT \log(\gamma_2' m_2) \qquad (a_2' = \gamma_2' m_2) \tag{4.47b}$$

$$= \phi_2'' + RT \log a_2'' \equiv \phi_2'' + RT \log(\gamma_2'' C_2) \qquad (a_2'' = \gamma_2'' C_2). \tag{4.47c}$$

In the limit of an ideal dilute solution, γ_2^0, γ_2' and γ_2'' all become 1.

§ 4.12+. SOLUTION OF STRONG ELECTROLYTES

A solution in which the solute molecules are completely dissociated into positive and negative ions is called a strong electrolyte. Consider a solute molecule $A_{\nu_+}B_{\nu_-}$ which dissociates in the solution:

$$A_{\nu_+}B_{\nu_-} \rightarrow \nu_+ A^{z_+} + \nu_- B^{z_-} \qquad (z_+ > 0, z_- < 0) \tag{4.48}$$

into ν_+ positive ions A^{z^+} of valence z_+ and ν_- negative ions, B^{z^-}, of valence $|z_-|$. From the condition of electrical neutrality, we have

$$\nu_+ z_+ + \nu_- z_- = 0. \tag{4.49}$$

Let x_2 be the concentration of the solute, x_+ the concentration of positive ions and x_- the concentration of negative ions (in mole fractions), then

$$x_+ = \nu_+ x_2, \qquad x_- = \nu_- x_2. \tag{4.50}$$

Let γ_+ be the activity coefficient of positive ions, γ_- that of negative ions and $\bar{\gamma}$ the mean activity coefficient. $\bar{\gamma}$ is defined by

$$\bar{\gamma}^{\nu} = \gamma_+^{\nu_+}\gamma_-^{\nu_-}, \qquad \nu_+ + \nu_- = \nu. \tag{4.51}$$

The molar chemical potential of the solute in solution, $\bar{G}_2 \equiv \bar{G}_{A_{\nu_+}B_{\nu_-}}$ is

$$\begin{aligned}\bar{G}_2 \equiv \bar{G}_{A_{\nu_+}B_{\nu_-}} &= \phi^0_{A_{\nu_+}B_{\nu_-}}(T, p) + \nu_+ RT \log(\gamma_+ x_+) + \nu_- RT \log(\gamma_- x_-) \\ &= \phi^0_{A_{\nu_+}B_{\nu_-}} + \nu RT \log x_2 + RT \log(\nu_+^{\nu_+}\nu_-^{\nu_-}) + \nu RT \log \bar{\gamma}.\end{aligned} \tag{4.52}$$

Debye-Hückel equation:

$$\log \bar{\gamma} = -\frac{z_+ |z_-| e^2}{2DkT} \frac{\kappa}{1 + \kappa a}, \tag{4.53a}$$

where

$$\kappa^2 = \frac{4\pi e^2 N_0 (\nu_+ z_+^2 + \nu_- z_-^2) C_2}{1000 DkT}. \tag{4.53b}$$

Here, D is the dielectric constant, N_0 is Avogadro's number (6.024×10^{23} mol^{-1}), e is the elementary electric charge (charge of an electron), a is the average diameter of the ions and C_2 is the molarity of the solute.
Ionic strength is defined by

$$I = \tfrac{1}{2}\sum z_i^2 C_i = \tfrac{1}{2}(\nu_+ z_+^2 + \nu_- z_-^2) C_2. \tag{4.54}$$

Eq. (4.53a) then becomes

$$\log \bar{\gamma} = -z_+ |z_-| A \sqrt{I}/(1 + Ba\sqrt{I}), \tag{4.55a}$$

where

$$A = \frac{e^3 N_0^2}{(DRT)^{\frac{3}{2}}}\left(\frac{2\pi}{1000}\right)^{\frac{1}{2}}, \qquad B = \left(\frac{8\pi e^2 N_0^2}{1000 DRT}\right)^{\frac{1}{2}}. \tag{4.55b}$$

In a dilute solution, κa in the denominator of eq. (4.53a) may be ignored compared to 1. Correspondingly, eq. (4.55a) can be approximated by

$$\log \bar{\gamma} = -z_+ |z_-| A \sqrt{I}. \tag{4.56}$$

Additivity for ions: The value of $\phi^0_{A_{\nu_+}B_{\nu_-}}$ depends on how the standard state is chosen. Once definite states of the pure substances A and B are chosen as the standards, it is possible to put

$$\phi^0_{A_{\nu_+}B_{\nu_-}} = \nu_+ \phi_{A^{z_+}} + \nu_- \phi_{B^{z_-}}. \tag{4.57}$$

$\phi^{A^{z+}}$ and $\phi^{B^{z-}}$ are the standard free energies of formation of 1 mole of ions of A^{z+} and B^{z-} in the solution from the pure substances and are determined experimentally. This additivity is the basis of Arrhenius' theory of electrolytic dissociation. However, since the ions always appear in pairs of positive and negative ions, the common additive constant may be chosen arbitrarily. For convenience, the usual agreement is to put

$$\phi_{H^+}(\mathrm{aq}) = 0. \tag{4.58}$$

§ 4.13. CHEMICAL EQUILIBRIUM

We consider now the equilibrium of the chemical reaction expressed by

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightleftarrows l\mathrm{L} + m\mathrm{M} + \cdots \tag{4.59}$$

or

$$\nu_A\mathrm{A} + \nu_B\mathrm{B} + \cdots + \nu_L\mathrm{L} + \nu_M\mathrm{M} + \cdots = 0 \tag{4.59'}$$
$$(\nu_A = -a,\ \nu_B = -b, \ldots, \nu_L = l,\ \nu_M = m, \ldots).$$

Since p and T are usually constant in chemical reactions we assume this in the following.

Free energy, enthalpy and entropy of reaction: Let the Gibbs free energy be $G(n_A, n_B, \ldots, p, T)$. Consider the changes in the mole number of each component

$$\delta n_A = \nu_A\,\delta\lambda, \quad \delta n_B = \nu_B\,\delta\lambda, \ldots, \delta n_L = \nu_L\,\delta\lambda, \ldots. \tag{4.60}$$

Then the corresponding change δG becomes

$$\delta G = \sum_A \frac{\partial G}{\partial n_A}\delta n_A = \delta\lambda \sum_A \nu_A \bar{G}_A,$$

therefore

$$\frac{\delta G}{\delta\lambda} = \Delta\bar{G}, \quad \Delta\bar{G} = \sum_A \nu_A\bar{G}_A = -a\bar{G}_A - b\bar{G}_B \cdots + l\bar{G}_L + m\bar{G}_M + \cdots. \tag{4.61}$$

Here $\Delta\bar{G}$ is the free energy of reaction, and λ is the *degree of advancement of the reaction*. The enthalpy of reaction, $\Delta\bar{H}$, and the entropy of reaction, $\Delta\bar{S}$, are derived from $\Delta\bar{G}$ by means of the equations

$$\Delta\bar{G} = \Delta\bar{H} - T\,\Delta\bar{S}, \tag{4.62a}$$

$$\Delta\bar{H} = -T^2\frac{\partial}{\partial T}\frac{\Delta\bar{G}}{T}, \quad \Delta\bar{S} = -\frac{\partial}{\partial T}\Delta\bar{G}. \tag{4.62b}$$

If $\Delta\bar{G} < 0$ the reaction (4.59) advances *spontaneously* from the left to the right (as long as there is no inhibition).

The equilibrium condition is $\delta G = 0$ or

$$\Delta \bar{G} = \sum \nu_A \bar{G}_A = 0. \tag{4.63}$$

Standard free energy of reaction: If $\bar{G}_A^0$, $\bar{G}_B^0, \ldots$ are the chemical potentials of the pure substances A, B,... respectively, at temperature T and standard pressure (normally 1 atm), the following quantities can be defined:

standard free energy of reaction $\Delta \bar{G} = \sum \nu_A \bar{G}_A^0$, (4.64a)

standard enthalpy of reaction $\Delta \bar{H} = \sum \nu_A \bar{H}_A^0 = -T^2 \dfrac{\partial(\Delta \bar{G}/T)}{\partial T}$, (4.64b)

standard entropy of reaction $\Delta \bar{S} = \sum \nu_A \bar{S}_A^0 = -\dfrac{\partial \Delta \bar{G}}{\partial T}$. (4.64c)

Law of mass action: If the reaction (4.59) is a gaseous reaction, we have

$$\Delta \bar{G} = \sum \nu_A \{\bar{G}_A + RT \log(p_A f_A)\} \qquad (f_A = \text{fugacity}^*).$$

Therefore eq. (4.63) can be written as

$$K \equiv \prod (p_A f_A)^{\nu_A} \equiv \frac{p_L^l p_M^m \cdots}{p_A^a p_B^b \cdots} \frac{f_L^l f_M^m \cdots}{f_A^a f_B^b \cdots}$$
$$= \exp(-\Delta \bar{G}/RT); \tag{4.65}$$

K is the *equilibrium constant*. If the gases can be considered as ideal, we have simply $f_A = f_B = \ldots = 1$.

Similarly for a reaction in a solution, (4.63) can be written as

$$K \equiv \prod a_A^{\nu_A} \equiv \frac{a_L^l a_M^m \cdots}{a_A^a a_B^b \cdots} = \exp\left(-\frac{\Delta \bar{G}}{RT}\right). \tag{4.66}$$

EXAMPLE: $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g)$.
If the gases are assumed to be ideal, eq. (4.65) applies:

$$K_p = \frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} p_{H_2}^{\frac{3}{2}}} = \exp\left[-\frac{1}{RT}(\bar{G}_{NH_3} - \tfrac{1}{2}\bar{G}_{N_2} - \tfrac{3}{2}\bar{G}_{H_2})\right].$$

§ 4.14. THERMODYNAMICS OF ELECTROCHEMICAL CELLS

Electrochemical cell: An electrostatic potential difference develops between two metallic electrodes which sandwich several electrolytes (usually solutions or sometimes solids).

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* f_A is a dimensionless quantity (expressed as ν_A in (4.21)). In this equation p_A is in units of the standard pressure p_0. More explicitly,

$$\Delta \bar{G} = \Sigma\, \nu_A (\bar{G}_A{}^0 + RT \log p_A f_A / p_0).$$

EXAMPLE: 1. $Cu|CuSO_4(aq)|ZnSO_4(aq)|Zn$ (Daniell cell) (4.67a)

2. $Ag(c), AgCl_2(c)|M^+Cl^-(aq)|Hg_2Cl_2(c), Hg(l)$. (4.67b)

When the external circuit of the cell is closed the electrons (e) flow from the anode to the cathode through the wire and in general *reduction* and *oxidation* take place at the cathode and anode, respectively. For example,

$$Cu^{++} + 2e \rightarrow Cu\,(\text{reduction}), \quad Zn \rightarrow Zn^{++} + 2e\,(\text{oxidation}). \tag{4.68}$$

As a result of such electrode reactions a certain net reaction takes place in the cell corresponding to the amount of charge, q, transferred through the

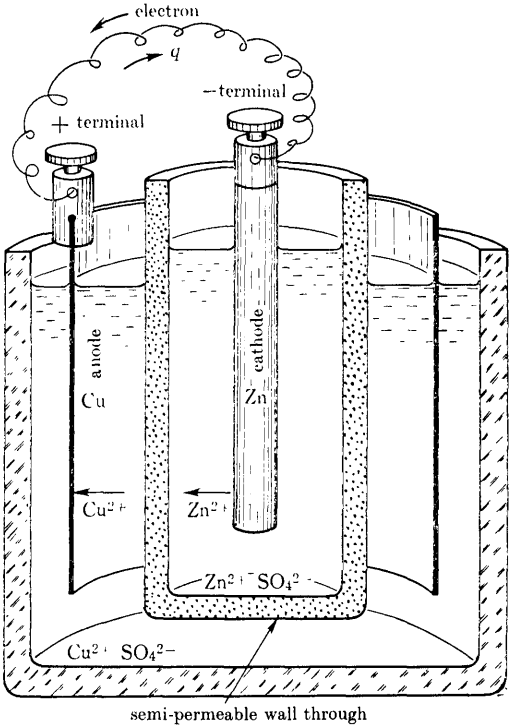


Fig. 4.2. Daniell cell.

external circuit. In a Daniell cell, by (4.68), the reaction is

$$Zn + Cu^{++} \rightarrow Cu + Zn^{++} \quad \text{or} \quad Zn + CuSO_4 \rightarrow Cu + ZnSO_4. \tag{4.69}$$

Generally, (2.25) requires that

$$-W \leqq -\delta G, \tag{4.70}$$

where $-W$ is the work done to the environment and $-\delta G$ is the decrease of the free energy.

Reversible cell: Consider the circuit shown in Fig. 4.3. When a potential difference, E_e, is applied to the terminals of the cell, g, by a potentiometer, the current flowing through the cell becomes zero and the reaction in the cell is balanced

$$E_e = E \qquad \text{(e.m.f. of the cell g)}.$$

If, however, E_e is made slightly smaller than E ($E_e < E$), then the reaction advances, while if E_e is made slightly larger than E, the reaction will proceed in the opposite direction. If all the physical and chemical phenomena

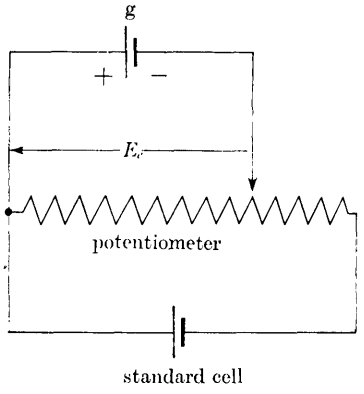


Fig. 4.3.

in the cell g are reversible, then by maintaining $E_e = E$ it is possible to cause *quasi-static changes* in the cell. A cell in which this is possible is called a reversible cell. Cells in which there are contacts between electrolytic solutions are generally irreversible, but in some cases they may be considered as approximately a reversible cell. (Example: Daniell cell.)

Electromotive force of a reversible cell: We write the internal reaction of the cell in the form (4.59). The electric change δq transferred during the advancement, $\delta\lambda$, of the reaction is then given by

$$\delta q = z\mathfrak{F}\,\delta\lambda$$

($z = 2$ in the example of (4.69)), where $\mathfrak{F}$ is the Faraday constant:

$$\mathfrak{F} = 96485.3 \text{ coulomb/g-equiv.}$$

Here the work is $-W = E\,\delta q$. Since the equal sign applies in (4.70) (reversible

change), the electromotive force, E, is given by

$$E = -\Delta\bar{G}/z\mathfrak{F}, \tag{4.71}$$

where $\Delta\bar{G}$ is the *free energy of reaction.*

Electrochemical potential: If, in a system under consideration, a particle, j, has a charge $z_j e$ and this system is at a potential Φ with respect to the environment at zero potential, considered as earthed, (1.7b) must be changed to

$$\mathrm{d}'Z = \sum_j (\mu_j + z_j e\Phi)\,\mathrm{d}N_j = \sum \eta_j\,\mathrm{d}N_j. \tag{4.72}$$

Here, $\eta_j = \mu_j + z_j e\Phi$ is called the electrochemical potential of the j-th component of the system (e is replaced by $\mathfrak{F}$ if we consider a mole).

Instead of (4.3), if the potentials of the phases are Φ' and Φ'' respectively, the equilibrium condition in the mass action of the j-th component with respect to phases 1 and 2 becomes

$$\eta_j' = \eta_j''. \tag{4.73}$$

NOTE: Equation (4.71) for the electromotive force can be derived by considering the equilibrium between the various phases in contact within the cell (see problem 10).

§ 4.15. APPLICATION OF THE THIRD LAW OF THERMODYNAMICS

According to the third law of thermodynamics, the free energy, or the standard free energy of a reaction,

$$\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S}$$

can be obtained from thermal data. $\Delta\bar{H}$ can be measured as the *reaction heat.* $\Delta\bar{S}$ is obtained by knowing the specific heat, the heat of fusion and the heat of vaporization for each of the substances involved in the reaction over the range from 0 °K to the temperature of reaction. For instance, it can be calculated from the formula

$$S_{\mathrm{gas}}(T, p) = \int_0^{T_f} C_{p,\,\mathrm{solid}} \frac{\mathrm{d}T}{T} + \frac{L_f}{T_f} + \int_{T_f}^{T_b} C_{p,\,\mathrm{liq}} \frac{\mathrm{d}T}{T} + \frac{L_v}{T_b} + \int_{T_b}^{T} C_{p,\,\mathrm{gas}} \frac{\mathrm{d}T}{T}, \tag{4.74}$$

where T_f is the melting point at the pressure p, L_f the heat of fusion, T_b the boiling point at pressure p, L_v the latent heat of vaporization, $C_{p,\mathrm{solid}}$, $C_{p,\mathrm{liq}}$, $C_{p,\mathrm{gas}}$ are the specific heats at constant pressure in the respective states indicated by the subscript. The values, $\Delta\bar{S}$ or $\Delta\bar{S}^0$, obtained in this manner

agree with those obtained from the temperature dependence of the equilibrium constant or from the electromotive force of the cell. The existence of a great number of such experimental results led Nernst to his discovery of the third law. It is thus possible to calculate the constants of chemical equilibrium and the electromotive force of the cell, etc. from thermal data.

Chemical constant: The constant, i, which appears in (4.15a) gives the absolute value of the entropy of an ideal gas. It is sometimes called the vapor pressure constant since it also gives the absolute value of the vapor pressure of the liquid or solid phase. It can be derived from the molecular structure of the gas by statistical mechanics. But in the frame work of thermodynamics, it is strictly a constant characteristic of a substance and is to be determined empirically. Since this determines the equilibrium constants of gas reactions it is also called the chemical constant.

Examples

1. The isotherms of a van der Waals gas plotted in the (V, p) plane have minima and maxima if the temperature is below the critical temperature. Between the minimum and the maximum of an isotherm, the pressure decreases with decrease of volume so that the states must be unstable and cannot be realized. In this region the system will separate into two phases, the liquid phase and the gas phase. How is the equilibrium pressure for coexistence of the two phases determined from a given isotherm of the van der Waals type? How is the whole mass of the system distributed among the two phases? Express the answer geometrically.

SOLUTION

In Fig. 4.4, ABCDEFG is an isotherm for one mole of a van der Waals gas. The states on AB are liquid, and those on FG are gaseous. Two phases in equilibrium must have equal pressures (condition (4.1)) and equal chemical potentials (4.3). Thus if B and F are in equilibrium, they must lie on the same horizontal line. The chemical potentials (Gibbs free energy per mole) of the states B, D and F can be compared by considering the change in the chemical potential along the isotherm. From the equation

$$\mathrm{d}\bar{G} = \bar{V}\,\mathrm{d}p$$

we find

$$\bar{G}(\mathrm{D}) - \bar{G}(\mathrm{F}) = \int_{\mathrm{FED}} \bar{V}\,\mathrm{d}p = \text{area (FEDF)}$$

and

$$\bar{G}(\mathrm{D}) - \bar{G}(\mathrm{B}) = \text{area}\,(\mathrm{DCBD}).$$

Therefore the state corresponding to D has a higher free energy than B or F and so it is unstable. According to the above equations, we have

$$\bar{G}(\mathrm{B}) - \bar{G}(\mathrm{F}) = \text{area}\,(\mathrm{FEDF}) - \text{area}\,(\mathrm{DCBD}).$$

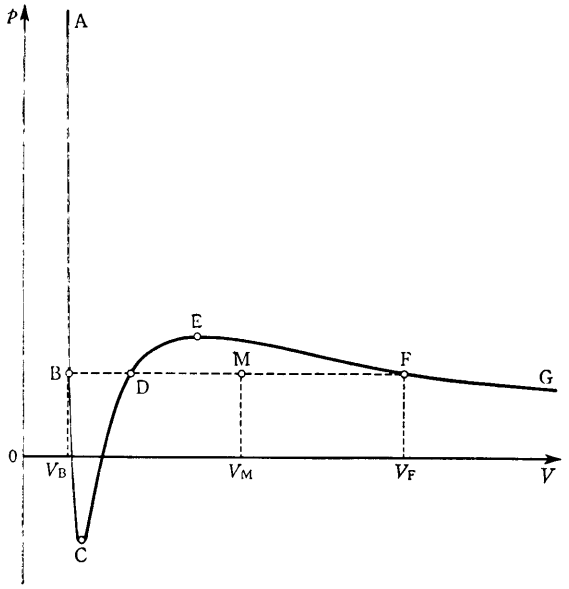


Fig. 4.4.

Thus, if the horizontal line is drawn in such a way that the two areas are equal, then $\bar{G}(\mathrm{B})=\bar{G}(\mathrm{F})$, which is the equilibrium condition of the two phases. If the horizontal line is drawn higher or lower, $\bar{G}(\mathrm{B})<\bar{G}(\mathrm{F})$ or $\bar{G}(\mathrm{B})>\bar{G}(\mathrm{F})$ and either the liquid phase or the gaseous phase becomes the stable phase. In other words, when the horizontal line BDF cuts off equal areas the curves AB (liquid phase) and GF (gaseous phase) become a stable isotherm. The coexistence of two phases occurs at this pressure $p_{\mathrm{F}}(=p_{\mathrm{B}})$ (saturated vapor pressure) for a given temperature.

When two phases coexist, part of the whole system is liquid and the rest is gaseous. Under these circumstances the state of the system is represented by a point on BF. Thus a quasi-static isothermal compression proceeds along GFDBA. The ratio of two phases at some intermediate point M, is determined in the following way. Of the total n moles of the substance, let us

suppose that nx moles are in the liquid phase. The total volume, nV_M, is the sum of nxV_B and $n(1-x)\,V_F$, or

$$xV_B + (1-x)\,V_F = V_M.$$

Thus

$$\frac{x}{1-x} = \frac{V_F - V_M}{V_M - V_B},$$

i.e. the ratio $\overline{MF}:\overline{MB}$ gives the mole ratio of the liquid and gas phases. NOTE: The condition of equal area to determine the stable equilibrium curve is called *Maxwell's rule.*

Strictly speaking, the states corresponding to the curve CDE cannot be realized as thermodynamic states since the stability condition is not satisfied. Therefore, the quasi-static processes involving these states are merely hypothetical. In the solution given here, we have applied the equation $d\bar{G} = \bar{V}\,dp$ to these nonequilibrium states. The proof is therefore not completely satisfactory. One can, however, remedy this defect by an alternative proof for a van der Waals gas (see problem 47).

2. The Gibbs free energy per mole of a two component system is given by $\bar{G}(x) = x_1\bar{G}_1 + x_2\bar{G}_2$. Here x_1 and x_2 are the molar ratios of the components 1 and 2, and $\bar{G}_1$ and $\bar{G}_2$ are chemical potentials per mole, respectively. Show that, if the plot of $\bar{G}(x)$ ($x = x_1$ or x_2) as a function of x_1 has a common tangent $Q'Q''$, the states between $Q'Q''$ separate into two phases, Q' and Q''.

SOLUTION

Set $x = x_1$. From the Gibbs-Duhem relation, $x_1\,\partial\bar{G}_1/\partial x_1 + x_2\,\partial\bar{G}_2/\partial x_1 = 0$, we have

$$\frac{\partial\bar{G}}{\partial x_1} = \bar{G}_1 + \left(\frac{dx_2}{dx_1}\right)\bar{G}_2 + x_1\frac{\partial\bar{G}_1}{\partial x_1} + x_2\frac{\partial\bar{G}_2}{\partial x_1} = \bar{G}_1 - \bar{G}_2. \tag{1}$$

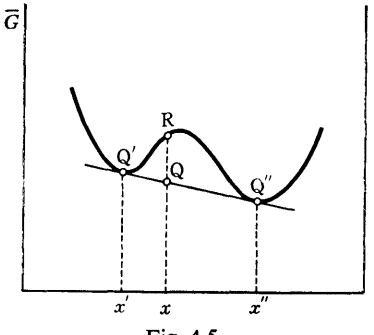


Fig. 4.5.

If the values of the functions at x_1' and x_1'' are denoted by $'$ and $''$, the condition that a common tangent $Q'Q''$ can be drawn is

$$\bar{G}_1' - \bar{G}_2' = \bar{G}_1'' - \bar{G}_2'' = \frac{\bar{G}'' - \bar{G}'}{x_1'' - x_1'}. \tag{2}$$

Using $\bar{G} = x_1\bar{G}_1 + x_2\bar{G}_2$, we get from (2)

$$\bar{G}_1' - \bar{G}_2' = \bar{G}_1'' - \bar{G}_2'' = \frac{x_1''\bar{G}_1'' + x_2''\bar{G}_2'' - x_1'\bar{G}_1' - x_2'\bar{G}_2'}{x_1'' - x_1'},$$

from which we get

$$\frac{x_1'\bar{G}_1' - x_1'\bar{G}_2'}{x_1'} = \frac{-x_1''\bar{G}_1'' + x_1''\bar{G}_2''}{-x_1''} = \frac{x_1''\bar{G}_1'' + x_2''\bar{G}_2'' - x_1'\bar{G}_1' - x_2'\bar{G}_2'}{x_1'' - x_1'}$$
$$= \frac{\bar{G}_2'' - \bar{G}_2'}{0},$$

and

$$\frac{-x_2'\bar{G}_1' + x_2'\bar{G}_2'}{-x_2'} = \frac{x_2''\bar{G}_1'' - x_2''\bar{G}_2''}{x_2''} = \frac{x_1''\bar{G}_1'' + x_2''\bar{G}_2'' - x_1'\bar{G}_1' - x_2'\bar{G}_2'}{x_1'' - x_1'}$$
$$= \frac{\bar{G}_1'' - \bar{G}_1'}{0}.$$

This means that

$$\bar{G}_1' = \bar{G}_1'' \quad \text{and} \quad \bar{G}_2' = \bar{G}_2'', \tag{3}$$

which is equivalent to (2). (If (3) is valid, (2) is obviously valid.) Eq. (3) is the condition that two phases with different molar concentrations (denoted by single and double primes) can coexist. Thus a system that has a density x_1 between Q' and Q'' separates into two phases with the ratio of

$$C' = \frac{x_1'' - x_1}{x_1'' - x_1'}, \qquad C'' = \frac{x_1 - x_1'}{x_1'' - x_1'}, \tag{4}$$

and its free energy (point Q in Fig. 4.5) is lower than $\bar{G}(x)$ (point R in Fig. 4.5). In other words,

$$C'\bar{G}' + C''\bar{G}'' < \bar{G}(x). \tag{5}$$

3. Based on the definition (4.8), show that the Helmholtz free energy per unit area of an interface is equal to the surface tension γ. Also show that the internal energy per unit area at the interface is equal to $\gamma - T\,\mathrm{d}\gamma/\mathrm{d}T$.

SOLUTION

First note that surface tension has a meaning when two phases in thermal

equilibrium have a clear interface between them. In order to define the interface clearly, the total volume under consideration must be divided into two parts, one for each phase, such that $V=V'+V''$ and $N=n'V'+n''V''$.* N is the total number of particles in the volume, n' and n'' are the density of particles in each phase measured at a sufficiently large distance from the interface. Then the extensive variables, e.g. the Helmholz free energy of the combined system, $F(T, V', V'', \sigma, N', N'')\equiv U-TS$, differs from the sum $F'(T, V', N')+F''(T, V'', N'')$ of the free energies of the volumes divided in the above manner. Since this is the effect of the surface, the free energy of the surface F_σ is defined as

$$F_\sigma = F - (F' + F''). \tag{1}$$

The equations obtained from (4.8)

$$\mathrm{d}F = \mathrm{d}(U - TS) = - S\,\mathrm{d}T - p'\,\mathrm{d}V - p''\,\mathrm{d}V'' + \gamma\,\mathrm{d}\sigma + \mu'\,\mathrm{d}N' + \mu''\,\mathrm{d}N'',$$
$$\mathrm{d}F' = - S'\,\mathrm{d}T - p'\,\mathrm{d}V' + \mu'\,\mathrm{d}N',$$

and a similar one for $\mathrm{d}F''$ combine to give

$$\mathrm{d}F_\sigma = - S_\sigma\,\mathrm{d}T + \gamma\,\mathrm{d}\sigma. \tag{2}$$

Here $S_\sigma\equiv S-(S'+S'')$ is the entropy of the surface. Hence F_σ is a function of T and σ. If at constant temperature, the linear dimension of the system is increased by the factor $\alpha^{\frac{1}{2}}$, the area of the surface increases α times and we have $F_\sigma(T, \alpha\sigma)=\alpha F_\sigma(T, \sigma)$. We can differentiate this with respect to α and set $\alpha=1$ to obtain

$$F_\sigma = \sigma\,\partial F_\sigma/\partial\sigma = \sigma\gamma.$$

This means that γ is the surface Helmholtz free energy per unit area. Also, since γ is a function only of the intensive variable T, the surface entropy is

$$S_\sigma = - \partial F_\sigma/\partial T = - \sigma\,\mathrm{d}\gamma/\mathrm{d}T.$$

Hence the internal energy is given by

$$U_\sigma = F_\sigma + TS_\sigma = \left(\gamma - T\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right)\sigma, \qquad \text{or} \qquad \frac{U_\sigma}{\sigma} = \gamma - T\frac{\mathrm{d}\gamma}{\mathrm{d}T}.$$

4. Show that the vapor pressure $p_s(T)$ in a condensed phase (liquid or solid phase) is determined by the formula

$$\log p_s = -\frac{L_0}{RT} + \frac{C_p^0}{R}\log T + \int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T \frac{C'(T) - C_p''(T)}{R}\,\mathrm{d}T + i,$$

* More specifically the interface is so chosen that it will be perpendicular to the gradient of n'.

where L_0 is the latent heat of vaporization at 0 °K and C_p'' is the molar specific heat at constant pressure of the condensed phase (C_p^0, $C'(T)$ and i are explained in (4.15) and below).

SOLUTION

Obtain the entropy of a mole of the gas from (4.14) and (4.15) as

$$\begin{aligned}\bar{S}(T, p) &= -\,\partial\bar{G}(T, p)/\partial T \\ &= C_p^0 \log T + \int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T C'(T)\,\mathrm{d}T + \frac{1}{T}\int_0^T C'(T)\,\mathrm{d}T + \\ &\qquad + Ri + C_p^0 - R\log p. \qquad (1)\end{aligned}$$

According to the third law, this is equal to the entropy increase resulting from quasi-statically heating a mole of the substance in the condensed phase at pressure p from 0 °K to T °K and then quasi-statically changing it to a gas at T °K by adding the latent heat, L, or

$$\int_0^T \frac{C_p''(T)\,\mathrm{d}T}{T} + \frac{L}{T}. \qquad (2)$$

Now we know that $L = \bar{H}' - \bar{H}''$ and $(\partial\bar{H}/\partial T)_p = C_p$, so that

$$L = L_0 + \int_0^T (C_p' - C_p'')\,\mathrm{d}T = L_0 + C_p^0 T + \int_0^T (C' - C_p'')\,\mathrm{d}T \qquad (3)$$

(where $L_0 = \bar{H}'(0, p) - \bar{H}''(0, p)$ is the latent heat at 0 °K). Putting (1) = (2) and using (3) we have

$$\begin{aligned}&\int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T C'(T)\,\mathrm{d}T + \frac{1}{T}\int_0^T C'(T)\,\mathrm{d}T + C_p^0\log T + C_p^0 + Ri - R\log p = \\ &\qquad = \int_0^T \frac{C_p''(T)\,\mathrm{d}T}{T} + \frac{L_0}{T} + C_p^0 + \frac{1}{T}\int_0^T (C' - C_p'')\,\mathrm{d}T.\end{aligned}$$

Integrating this by parts, we get

$$\int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T C_p''(T)\,\mathrm{d}T = -\frac{1}{T}\int_0^T C_p''(T) + \int_0^T \frac{C_p''\,\mathrm{d}T}{T}, \qquad (4)$$

from which we obtain the desired equation. Note that $\lim_{T\to 0} C_p''(T)=0$ (third law) is necessary to obtain (4).

NOTE: If the molar specific heat of the gas phase with respect to the rotation and oscillation of the gas molecules is C_i', C_p^0 and $C'(T)$ are replaced by $\frac{5}{2}R$ and $C_i'(T)$ respectively. This can be done for light gases such as hydrogen and helium.

5. Fig. 4.6 is the phase diagram for the Cu-Ag system. The region above AEB is the liquid phase, to the right of ACF is the α-solid solution phase, and to the left of BDG is the β-solid solution phase. The triple point E is called the eutectic point.

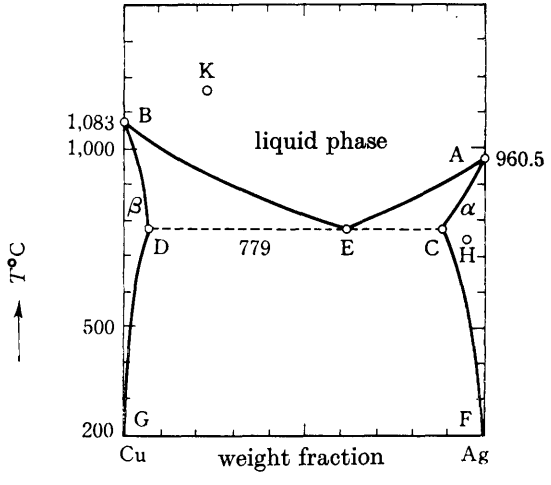


Fig. 4.6.

(i) How will a solution behave if it is cooled down from the liquid state K in the figure?

(ii) How will it behave if an α-solid solution is heated up from the point H in the figure?

SOLUTION

(i) The temperature merely drops in the liquid phase along the vertical line passing through K until it reaches the intersection K′ (Fig. 4.7) with curve BE. At the temperature of K′ the β phase of the solid solution starts to solidify the concentration of which is given by K″. Since the solid solution which solidifies has a smaller concentration of Ag than the liquid phase, the

Ag concentration of the remaining liquid becomes greater. So, as the temperature decreases further, the β phase solid solution freezes out with increasing Ag-concentration. Thus, the state of the liquid solution travels along K′E and accordingly the β phase solid solution along K″D. When the liquid

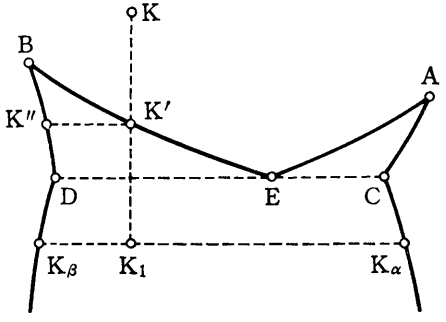


Fig. 4.7.

reaches the point E, the α-phase solid solution starts to freeze out and thereafter, the concentration of the liquid phase remain constant while the α-phase (C) and β-phase (D) solids are freezing out until all is solidified. (When the temperature is further decreased to, say, K_1 and a sufficiently long time has passed, then the solid solutions corresponding to K_α and K_β should exist as stable solid phases. The ratio for the numbers of atoms $N(K_\alpha)/N(K_\beta)$ is equal to $\overline{K_\beta K_1}:\overline{K_1 K_\alpha}$. However this process takes a very long time because it is a reaction between solid phases.)

(ii) Similarly, when the temperature is raised from H, the α-phase remains unchanged until it reaches H′, when the liquid phase starts to appear with a concentration corresponding to H″. The Ag concentration is less than that

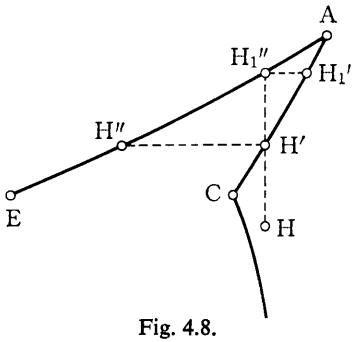


Fig. 4.8.

of the solid. If a sufficiently long time is allowed, the α-phase moves to that with higher concentrations of Ag, namely to the right in the figure. Correspondingly, the liquid phase also becomes richer in Ag, so that both H′ and H″ move to the right. Finally, H′ arrives at H_1' in the figure when H″ arrives at H_1'' and all becomes liquid. H_1'' must have the same concentration as the original point H, because all is liquid. This condition determines the position of H_1'. After this stage, heating merely increases the temperature of the melt. If, however, the melted solution is constantly separated, the solid phase continues past H_1' and will first become pure solid silver at A and then become pure liquid Ag.

6. In terms of the activity a_1 of the solvent show that, for a general solution, the vapor pressure p_1, the osmotic pressure π, and the boiling point elevation (or freezing point depression) can be approximated as follows:

$$p_1 = p_1^0 a_1 ,$$

$$\pi \bar{V}_1^0 = \frac{\Delta T}{T_1^0} \bar{L}_1 = - RT_1^0 \log a_1 ,$$

where p_1^0, $\bar{V}_1^0$, T_1^0 and $\bar{L}_1$ are, respectively, the saturation vapor pressure, molar volume, boiling point (or melting point) and the molar latent heat of vaporization (or freezing) of the pure solvent. In treating the boiling point elevation or freezing point depression, assume that the gas that evaporates or the solid that precipitates is a pure solvent.

SOLUTION

(i) By (4.42) the chemical potential of the solvent is

$$\bar{G}_1 = \bar{G}_1^0(T, p) + RT \log a_1 , \tag{1}$$

where $\bar{G}_1^0$ is the chemical potential of the pure solvent. The chemical potential of the gas phase, assuming it is ideal, is

$$\bar{G}_{1,\,\mathrm{gas}} = \bar{G}_{1,\,\mathrm{gas}}(T, p) = \bar{G}_{1,\,\mathrm{gas}}^0 + RT \log p_1 ,$$

where p_1 is the vapor pressure of solvent 1. The equilibrium condition $\bar{G}_1 = \bar{G}_{1,\,\mathrm{gas}}$ becomes

$$\bar{G}_1^0(T, p) + RT \log a_1 = \bar{G}_{1,\,\mathrm{gas}}^0(T) + RT \log p_1 . \tag{2}$$

Now the saturated vapor pressure p_1^0 of the pure solvent is given as

$$\bar{G}_1^0(T, p_1^0) = \bar{G}_{1,\,\mathrm{gas}}^0(T, p_1^0) = \bar{G}_{1,\,\mathrm{gas}}^0 + RT \log p_1^0 . \tag{3}$$

Subtract (3) from (2). Using (4.14) we obtain

$$p_1 = p_1^0 a_1 \exp \frac{\bar{G}_1^0(T, p) - \bar{G}_1^0(T, p_1^0)}{RT}.$$

Since $\bar{G}_1^0(T, p) - G_1^0(T, p_1^0) \approx (p - p_1^0)\, \bar{V}^0_{1\,\mathrm{liq}} \ll RT = p_1^0 \bar{V}^0_{1\,\mathrm{gas}}$, we may put the exponential on the right side equal to unity to obtain

$$p_1 = p_1^0 a_1 . \tag{4}$$

(ii) The equilibrium condition when a pure solvent (pressure p_0) and a solution (pressure p) are separated by a semi-permeable membrane at temperature T is, by (1),

$$\bar{G}_1^0(T, p_0) = \bar{G}_1^0(T, p) + RT \log a_1 .$$

Therefore, using

$$\bar{G}_1^0(T, p) - \bar{G}_1^0(T, p_0) = \bar{V}_1^0 (p - p_0)$$

(since the change in volume due to osmotic pressure is extremely small, this approximation is sufficient) and using the definition of osmotic pressure,

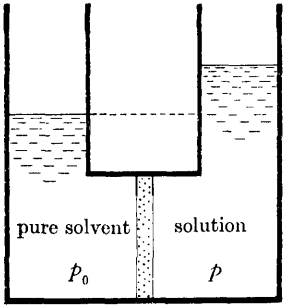


Fig. 4.9.

$\pi \equiv p - p_0$, we obtain

$$\pi \bar{V}_1^0 = - RT \log a_1 . \tag{5}$$

(iii) Since the vaporized gas is pure solvent the boiling point is equal to the temperature at which the vapor pressure of the pure solvent is equal to the external pressure, p_0. If the boiling point of the pure solvent is T_1^0 and the boiling point of the solution is T_1, (3) and (2) can be written as

$$\bar{G}_1^0(T_1^0, p_0) = \bar{G}^0_{1,\,\mathrm{gas}}(T_1^0, p_0) \qquad \text{(pure solvent)}, \tag{6}$$

$$\bar{G}_1^0(T_1, p_0) + RT_1 \log a_1 = \bar{G}^0_{1,\,\mathrm{gas}}(T_1, p_0) \qquad \text{(solution)}. \tag{7}$$

Subtract (7) from (6) and use $\partial G/\partial T = -S$ to obtain an expansion to first order of $T_1 - T_1^0$:

$$\begin{aligned} -RT_1 \log a_1 &= \bar{G}_1^0(T, p_0) - \bar{G}_1^0(T_1^0, p_0) - \{\bar{G}_{1,\,\mathrm{gas}}^0(T_1, p_0) - \bar{G}_{1,\,\mathrm{gas}}^0(T_1^0, p_0)\} \\ &= (T_1 - T_1^0)\{-\bar{S}_1^0(T_1^0, p_0) + \bar{S}_{1,\,\mathrm{gas}}^0(T_1^0, p_0)\} = (T_1 - T_1^0)\,\bar{L}_1/T_1^0, \end{aligned}$$

hence

$$-\log a_1 = \frac{\bar{L}_1}{R}\left(\frac{1}{T_1^0} - \frac{1}{T_1}\right). \tag{8}$$

If $T_1 - T_1^0 = \Delta T \ll T_1^0$, we have

$$-\log a_1 = \bar{L}_1\,\Delta T/R(T_1^0)^2, \tag{9}$$

where

$$\bar{L}_1 = T_1^0\{\bar{S}_{1,\,\mathrm{gas}}^0(T_1^0, p_0) - \bar{S}_1^0(T_1^0, p_0)\}$$

is the heat of vaporization of the solvent at pressure p_0 and temperature T_1^0.

The problem of the freezing point depression is similar. If the freezing point of the pure solvent under pressure p_0 is T_1^0 and the temperature at which the pure solid solute freezes out is T_1, the right-hand sides of eqs. (6) and (7) only need to be replaced by $\bar{G}_{1,\,\mathrm{solid}}^0(T_1^0, p_0)$ and $\bar{G}_{1,\,\mathrm{solid}}^0(T_1, p_0)$. Then $\bar{L}_1$ in (8) or (9) becomes

$$\bar{L}_1 = T_1^0\{\bar{S}_{1,\,\mathrm{solid}}^0 - \bar{S}_1^0\} = -\text{ heat of freezing} < 0. \tag{10}$$

Thus the freezing point is depressed in contrast to the elevation of the boiling point.

NOTE: Observe that the signs of the boiling point elevation and freezing point depression may be reserved if a_1 is larger than 1.

7+. Consider a regular solution of two components for which the heat of mixing, eq. (4.37), is given by $\Delta\bar{H} = Ax_1x_2$. Examine the relationship of the vapor pressure and the composition. In particular, discuss the case where the two phases separate out. Draw the phase diagram.

SOLUTION

Let n_1 and n_2 be the mole numbers of the components. Then the enthalpy of mixing ΔH, is

$$\Delta H = An_1n_2/(n_1 + n_2). \tag{1}$$

Since the solution is regular, the Gibbs free energy of the solution and the entropy of mixing are given by

$$\left.\begin{aligned} G(n_1, n_2) &= n_1\bar{G}_1^0 + n_2\bar{G}_2^0 + \Delta H - T\,\Delta S, \\ \Delta S &= -R(n_1 \log x_1 + n_2 \log x_2), \end{aligned}\right\} \tag{2}$$

where $x_1 = n_1/(n_1+n_2)$, $x_2 = n_2/(n_1+n_2)$. The partial free energies of the components are obtained by the formulae $\bar{G}_1 = \partial G/\partial n_1$ and $\bar{G}_2 = \partial G/\partial n_2$:

$$\bar{G}_i = \bar{G}_i^0 + A(1-x_i)^2 + RT\log x_i, \qquad i = 1, 2 \tag{3}$$

(see eq. (4.38)). The vapor pressure is given by the equation, $\bar{G}_i = \bar{G}_{i,\text{gas}}$. Assuming the vapor to be an ideal gas, we can use eq. (4.16), to obtain

$$\bar{G}_i^0(T, p) + A(1-x_i)^2 + RT\log x_i = \bar{G}_{i,\text{gas}}(T) + RT\log p_i, \tag{4}$$

where p_1 and p_2 are the partial pressures of the components 1 and 2, respectively, and $p = p_1 + p_2$ is the total pressure. The solution is also under the pressure p, but its free energy may be assumed almost independent of the pressure because liquids are nearly incompressible. Therefore the p-dependence of $\bar{G}_i^0(T, p)$ in eq. (4) can be ignored, and eq. (4) yields

$$p_i = p_{i0} x_i \exp[A(1-x_i)^2/RT], \tag{5}$$

where $p_{i0}(T) = \exp[\{\bar{G}_i^0(T) - \bar{G}_{i,\text{gas}}\}/RT]$ is the saturation vapor pressure of the pure liquid i at temperature T and is a function of T. The relation between p_i and x_i is linear (Raoult's law) if $A = 0$, but it is generally non-linear when $A \neq 0$.

(i) $A < 0$. Mixing decreases the enthalpy. The two components are easily mixed so that the pressure p_i should be lower than that given by Raoult's law. See Fig. 4.10.

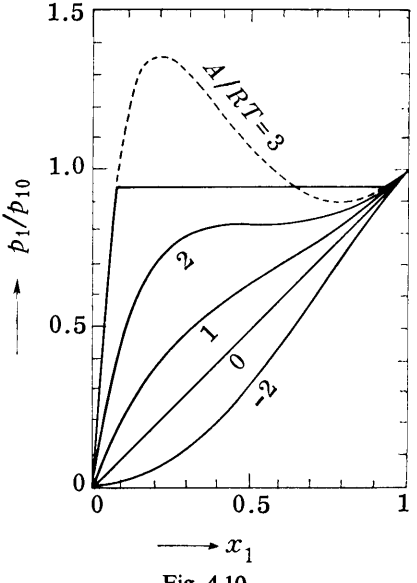


Fig. 4.10.

(ii) $A>0$. The enthalpy is increased by mixing. The components are not easily mixed, so that the pressure p_i should be higher than that given by Raoult's law (the solute is easily vaporized). If the ratio A/RT is large, the initial slope will be large for the increase of p_i from $x_i=0$. On the other hand, p_i as given by eq. (5) approaches the line $p_i=p_{i0}x_i$ as $x_i\to 1$. Then the pressure p_i can have a maximum and a minimum as shown in Fig. 4.10.

From eq. (4),

$$RT\frac{\partial \log p_i}{\partial x_i}=\frac{\partial \bar{G}_i}{\partial x_i}$$

so that the inequality $\partial p_i/\partial x_i<0$ implies $\partial \bar{G}_i/\partial x_i<0$, which is a thermodynamically unstable condition. (This resembles the unstable states of a van der Waals gas.) Such unstable states may appear if there are maxima and minima in the p_i-x_i curve. We have, from eq. (5),

$$\frac{\partial \log p_i}{\partial x_i}=\frac{1}{x_i}-\frac{2A}{RT}(1-x_i)=\frac{2A}{RTx_i}\left\{\left(x_i-\frac{1}{2}\right)^2-\frac{1}{4}\left(1-\frac{2RT}{A}\right)\right\}, \tag{6}$$

which shows that if $A/RT>2\,(0<2RT/A<1)$ we have extrema of p_i in the range $0\leqq x_i\leqq 1$. If, on the other hand, $A<0$ or $0<A/RT<2$, we have always $\partial p_i/\partial x_i>0$. Therefore the condition for the occurrence of two separated phases is

$$A/2RT>1. \tag{7}$$

One can obtain the same result by examining

$$\bar{G}(x_1,x_2)=x_1\bar{G}_1^0+x_2\bar{G}_2^0+Ax_1x_2+RT(x_1\log x_1+x_2\log x_2), \tag{8}$$

following example 2. Equation (1) of the solution of example 2 and eq. (4) in this solution give

$$\frac{\partial \bar{G}}{\partial x_1}=\bar{G}_1-\bar{G}_2=(\bar{G}_1^0-\bar{G}_2^0)+A\{(1-x_1)^2-x_1^2\}+RT\log\frac{x_1}{1-x_1}, \tag{9}$$

from which we obtain

$$\frac{\partial^2\bar{G}}{\partial x_1^2}=-2A+\frac{RT}{x_1(1-x_1)}\geqq 4RT-2A \tag{10}$$

(as $[x_1(1-x_1)]^{-1}\geqq 4$; the equality holds for $x_1=\frac{1}{2}$). Therefore, if eq. (7) holds, we have $\partial^2\bar{G}/\partial x_1^2<0$ for $x_1=\frac{1}{2}$. Then there exists a common tangent to the graph of $\bar{G}$ against x_1, and so there occurs a separation into two phases. In order to find mole fractions x_1' and x_1'' of the two phases as functions of

temperature, one only has to find the points of contact from eq. (9). Since eq. (9) is symmetric with respect to $x_1 = \frac{1}{2}$, the points of contact, x_1' and x_1'' are determined by the equation

$$A(1 - 2x_1) + RT \log \frac{x_1}{1 - x_1} = 0,$$

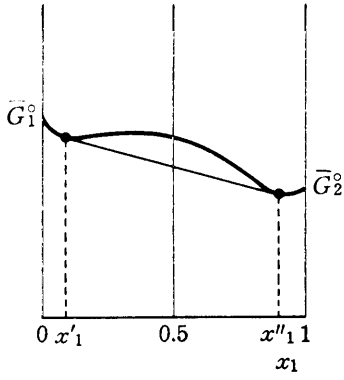


Fig. 4.11.

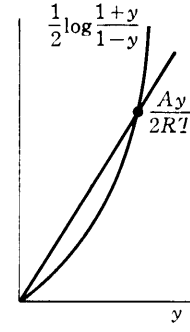


Fig. 4.12.

which may be written as

$$\tfrac{1}{2} \log \frac{1 + y}{1 - y} = \frac{Ay}{2RT} \qquad (0 \leqq y \leqq 1) \tag{11}$$

or

$$y = \tanh \frac{Ay}{2RT}, \tag{12}$$

by putting

$$x_1' = \tfrac{1}{2}(1 - y), \qquad x_1'' = \tfrac{1}{2}(1 + y). \tag{13}$$

Fig. 4.12 shows the method of graphical solution of eq. (12). Eq. (7) is the condition that the equation has solutions other than $y=0$. (The tangent at $y=0$ of the curve for the function on the left-hand side of eq. (11) is at a 45 degree angle. Therefore the curves have an intersection besides $y=0$ if $A/2RT > 1$, whereas there is no intersection other than $y=0$ if $A/2RT < 1$.) Fig. 4.13 is the plot of x_1' and x_1'' against T, which is obtained by inserting the solution for $y(T)$ from eq. (12) into eq. (13). This is the phase diagram of the solution. The shaded portion is the two phase region where the system cannot exist as a single phase. At higher temperatures,

$$T > T_c = A/2R \tag{14}$$

where condition (7) no longer holds, a single phase solution is realized for all concentrations. The temperature T_c, eq. (14), is called the *critical temperature* of the solution.

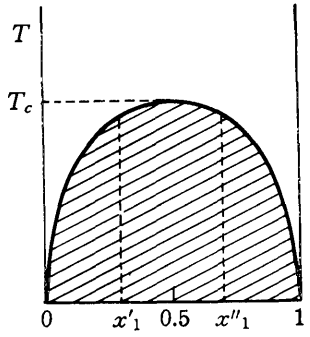


Fig. 4.13.

8⁺. For a dilute solution of a strong electrolyte, which dissociates as

$$A_{\nu_+}B_{\nu_-} \rightarrow \nu_+ A^{z^+} + \nu_- B^{z^-},$$

the osmotic pressure may be written as

$$\pi = \frac{\nu C_2 RT}{1000} g.$$

Prove that the osmotic coefficient* g is given by the formula

$$g = 1 + \frac{1}{m_2} \int_0^{m_2} m_2 \left(\frac{\partial \log \bar{\gamma}}{\partial m_2} \right)_{T,p} \mathrm{d}m_2. \tag{1}$$

[For the notation, see eqs. (4.40) and (4.51).] (*Hint*: Use eq. (4.52).)

SOLUTION

Following the solution of example 6, we have only to calculate the activity a_1 of the solvent. The chemical potential $\bar{G}$ of the solute is given by eq. (4.52), which can be inserted into the Gibbs-Duhem relation, (3.12),

$$n_1 \, \mathrm{d}\bar{G}_1 + n_2 \, \mathrm{d}\bar{G}_2 = 0 \qquad (T, p \text{ constant})$$

* The *osmotic coefficient* g is generally defined as follows: Let x_1 be the mole fraction of the solvent in a solution, the chemical potential of which is given by

$$\bar{G}_1 = \bar{G}_1^0 + gRT \log x_1.$$

Then the osmotic coefficient g is related to the activity γ_1, eq. (4.43), by the equation

$$\log \gamma_1 = (g - 1) \log x_1.$$

to yield the equation

$$\mathrm{d}\log a_1 + \nu\frac{x_2}{1-x_2}\{\mathrm{d}\log x_2 + \mathrm{d}\log\bar{\gamma}\} = 0, \tag{2}$$

which determines a_1. Since $a_1 = 1$ for $x_2 = 0$, this equation can be integrated to give

$$\log a_1 = -\nu\int_0^{x_2}\left\{\frac{1}{1-x_2} + \frac{x_2}{1-x_2}\frac{\partial\log\bar{\gamma}}{\partial x_2}\right\}\mathrm{d}x_2$$

$$= -\nu\left\{-\log(1-x_2) + \int_0^{x_2}\frac{x_2}{1-x_2}\frac{\partial\log\bar{\gamma}}{\partial x_2}\mathrm{d}x_2\right\}. \tag{2'}$$

If we insert this result into the equation $\pi\bar{V} = -RT\log a_1$, we obtain (for $x_2 \ll 1$)

$$\pi = \frac{\nu RT}{\bar{V}_1^0}\left\{-\log(1-x_2) + \int_0^{x_2}\frac{x_2}{1-x_2}\frac{\partial\log\bar{\gamma}}{\partial x_2}\mathrm{d}x_2\right\}$$

$$\approx \frac{\nu x_2 RT}{\bar{V}_1^0}\left\{1 + \frac{1}{x_2}\int_0^{x_2} x_2\frac{\partial\log\bar{\gamma}}{\partial x_2}\mathrm{d}x_2\right\}. \tag{3}$$

Using eqs. (4.40) and (4.41), one finds that

$$x_2/\bar{V}_1^0 = m_2\bar{M}_1/1000\bar{V}_1^0 = m_2\rho/1000 = C_2/1000,$$

so that the above result may be written as

$$\pi \approx \frac{\nu C_2 RT}{1000}\left\{1 + \frac{1}{m_2}\int_0^{m_2} m_2\frac{\partial\log\bar{\gamma}}{\partial m_2}\mathrm{d}m_2\right\}.$$

NOTE: The osmotic coefficient g characterizes the deviation of the osmotic pressure from the ideal relationship of van 't Hoff,

$$\pi = \frac{\nu C_2 RT}{1000}.$$

By solving equation (1) for $\bar{\gamma}$, we obtain

$$-\log\bar{\gamma} = \int_0^{m_2}\frac{\mathrm{d}\{(1-g)m_2\}}{m_2},$$

where we used the condition that $\bar{\gamma} \to 1$ as $m_2 \to 0$. The above equation is used to find the activity coefficient when $g(m_2)$ is known.

9. The thermal dissociation of metallic vapors

$$A \rightleftarrows A^+ + e$$

is a violent process in the atmospheres of some stars. Apply the law of mass action to find how the degree of dissociation α varies with temperature and pressure. Assume the energy of dissociation to be W per mole of the vapor.

SOLUTION

When the degree of dissociation is α, the molar ratio of A, A^+ and e is $1-\alpha:\alpha:\alpha$, so that the partial pressures of the components are

$$p_A = \frac{1-\alpha}{1+\alpha}p, \qquad p_{A^+} = \frac{\alpha}{1+\alpha}p, \qquad p_e = \frac{\alpha}{1+\alpha}p.$$

Therefore the mass action law, eq. (4.65), gives

$$\frac{p_{A^+}p_e}{p_A} = \frac{\alpha^2}{1-\alpha^2}p = \exp\left(-\frac{\Delta\bar{G}^0}{RT}\right). \tag{1}$$

If we ignore any internal degrees of freedom of the constituents, eq. (4.15) gives

$$\begin{aligned}\Delta\bar{G}^0 &= \bar{G}^0_{A^+} + \bar{G}^0_e - \bar{G}^0_A \\ &= U_{0A^+} + U_{0e} - U_{0A} - \tfrac{5}{2}RT\log T - RT(i_{A^+} + i_e - i_A)\end{aligned}$$

as the standard free energy of the reaction. If this is inserted into eq. (1), we find

$$\frac{\alpha^2}{1-\alpha^2}p \propto T^{\frac{5}{2}}\exp\left(-\frac{W}{RT}\right),$$

where

$$W = U_{0A^+} + U_{0e} - U_{0A}$$

is the energy of dissociation.

NOTE: The ionization energy of the process $A \to A^+ + e$, is generally much smaller than that of the process $A^+ \to A^{++} + e$. This is the reason why one may often ignore higher-order ionization processes.

10. Apply the equilibrium condition, eq. (4.73), to the phases in the Daniell cell, and derive the formula (4.71) for the electromotive force (potential

difference) between the two terminals* (which are made of copper) of the cell. Assume that there is no potential difference on the boundary of the $CuSO_4$ solution and the $ZnSO_4$ solution.

SOLUTION

The different phases and the terminals of the cell are denoted by

$$\underset{\mathrm{I}}{\mathrm{Cu}}\,|\,\underset{\mathrm{II}}{\mathrm{CuSO_4\,(aq)}}\,|\,\underset{\mathrm{III}}{\mathrm{ZnSO_4\,(aq)}}\,|\,\underset{\mathrm{IV}}{\mathrm{Zn}}\,|\,\underset{\mathrm{V}}{\mathrm{Cu}}$$

and the potential of each phase is denoted by Φ_{I}, Φ_{II} etc. The equilibrium conditions of two neighboring phases are:

$$\text{I-II (with respect to } Cu^{++}\text{):} \quad \overset{\mathrm{I}}{\mu}_{Cu^{++}} + 2e\Phi_{\mathrm{I}} = \overset{\mathrm{II}}{\mu}_{Cu^{++}} + 2e\Phi_{\mathrm{II}}, \tag{1}$$

$$\text{II-III (with respect to } SO_4^{--}\text{):} \quad \overset{\mathrm{II}}{\mu}_{SO_4^{--}} - 2e\Phi_{\mathrm{II}} = \overset{\mathrm{III}}{\mu}_{SO_4^{--}} - 2e\Phi_{\mathrm{III}}, \tag{2}$$

$$\text{III-IV (with respect to } Zn^{++}\text{):} \quad \overset{\mathrm{III}}{\mu}_{Zn^{++}} + 2e\Phi_{\mathrm{III}} = \overset{\mathrm{IV}}{\mu}_{Zn^{++}} + 2e\Phi_{\mathrm{IV}}, \tag{3}$$

$$\text{IV-V (with respect to electrons)} \quad \overset{\mathrm{IV}}{\mu}_{e} - e\Phi_{\mathrm{IV}} = \overset{\mathrm{V}}{\mu}_{e} - e\Phi_{\mathrm{V}}. \tag{4}$$

Further one may put

$$\overset{\mathrm{I}}{\mu}_{Cu} = \overset{\mathrm{I}}{\mu}_{Cu^{++}} + 2\overset{\mathrm{I}}{\mu}_{e}, \qquad \overset{\mathrm{IV}}{\mu}_{Zn} = \overset{\mathrm{IV}}{\mu}_{Zn^{++}} + 2\overset{\mathrm{IV}}{\mu}_{e} \tag{5}$$

becaus $Cu = Cu^{++} + 2e$ in copper and $Zn = Zn^{++} + 2e$ in zinc. Since we assumed $\Phi_{\mathrm{II}} = \Phi_{\mathrm{III}}$, eq. (2) becomes $\overset{\mathrm{II}}{\mu}_{SO_4^{--}} = \overset{\mathrm{III}}{\mu}_{SO_4^{--}}$, and may be neglected. By taking (1)+(3)−(4)×2, we obtain

$$\overset{\mathrm{I}}{\mu}_{Cu^{++}} + \overset{\mathrm{III}}{\mu}_{Zn^{++}} - 2\overset{\mathrm{IV}}{\mu}_{e} + 2e\Phi_{\mathrm{I}} = \overset{\mathrm{II}}{\mu}_{Cu^{++}} + \overset{\mathrm{IV}}{\mu}_{Zn^{++}} - 2\overset{\mathrm{V}}{\mu}_{e} - 2e\Phi_{\mathrm{V}},$$

which can be written as

$$2e(\Phi_{\mathrm{I}} - \Phi_{\mathrm{V}}) = \overset{\mathrm{II}}{\mu}_{Cu^{++}} - \overset{\mathrm{I}}{\mu}_{Cu} + \overset{\mathrm{IV}}{\mu}_{Zn} - \overset{\mathrm{III}}{\mu}_{Zn^{++}}$$

with the use of eq. (5). The above result is equivalent to

$$2\mathfrak{F}\cdot E = -\Delta\bar{G}(Cu^{++} + Zn \rightarrow Cu + Zn^{++}).$$

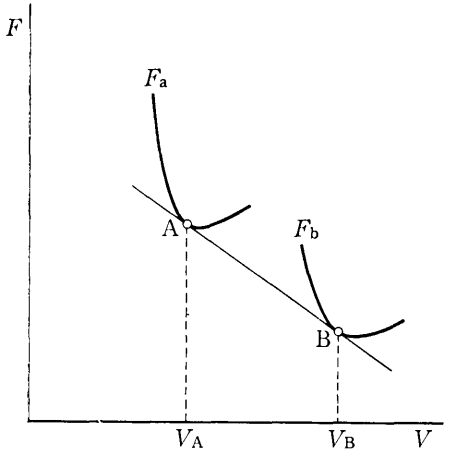
* If both terminals are not of the same metal, there exists a contact potential between them. The electromotive force of a cell is defined as the potential difference of two open terminals made of the same kind of metal, avoiding the appearance of a contact potential.

Problems

[A]

1. (i) Let the Helmholtz free energies F_a and F_b of a homogeneous substance in an a-phase and a b-phase be known as functions of T and V. Show that the transition point between these phases can be determined by drawing a common tangent for the curves of F_a and F_b plotted as functions of V for a given T (see the figure).

(ii) From the above point of view, derive Maxwell's rule which is explained in the note to example 1 of this chapter.



2. The heat of fusion of ice is 80 cal/g at 0 °C, 1 atm. The ratio of the specific volume of ice and water is 1.091:1.000. Estimate the change of melting point due to the change of pressure.

3. The pressure coefficient of the boiling point temperature of water at 100 °C, 1 atm, is given by

$$\frac{dT}{dp} = \frac{1}{27.12}\ \text{deg/mmHg}.$$

Estimate the heat of vaporization of water at 100 °C.

4. Near the triple point, the equilibrium curve (p-T curve) between the solid phase and the gas phase has generally a steeper gradient with respect

to the temperature axis compared to that between the liquid phase and the gas phase. Give a thermodynamical explanation for this fact.

5. The heat of fusion of ice is 80 cal/g at 0 °C, 1 atm, and the ratio of the specific volume of water to that of ice is equal to 1.000:1.091. The saturated vapor pressure and the heat of vaporization of water at 0 °C are 4.58 mm Hg and 600 cal/g, respectively. Estimate approximately the temperature of the triple point using the above data.
[*Hint*: Note that the triple point is very near to 0 °C, because the pressure change of the equilibrium temperature between ice and water is very slight.]

6. Show that the saturated vapor pressure p_s of a liquid is given by

$$p_s \propto \exp(-L/RT)$$

when (a) the temperature is not too close to the critical temperature so that the pressure is sufficiently small and (b) the latent heat L of vaporization may be considered as constant over the temperature range of interest.

7. Let ρ_1 and ρ_2 be the principal radii of a curved surface, the surface tension of which is denoted by γ. Show that the pressure difference Δp between the two sides of the surface is given by

$$\Delta p = \gamma\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) \qquad \text{(Laplace's formula)}.$$

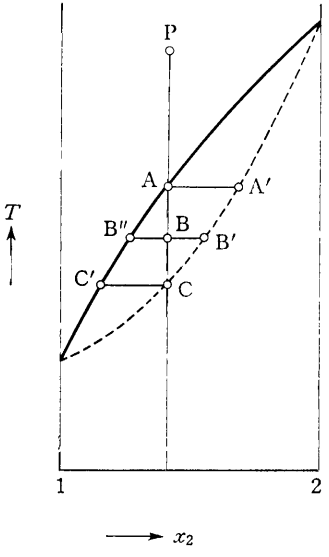
8. Give the formula for the heat which is absorbed by the isothermal expansion of a surface film, assuming the surface tension $\gamma(T)$ is known as a function of temperature (see example 3). Next, show that the temperature change caused by the adiabatic expansion is given by the condition

$$\sigma(\mathrm{d}\gamma/\mathrm{d}T) = \text{constant}.$$

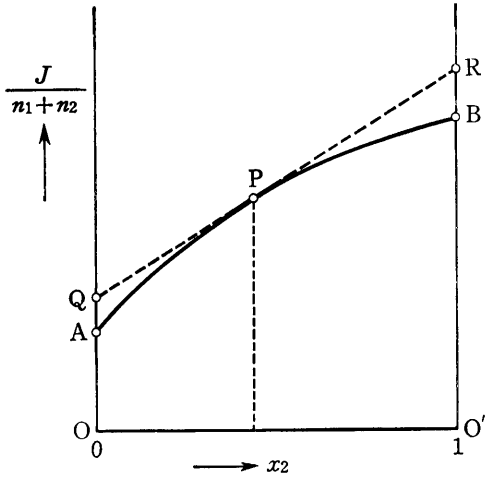
9. Consider the phase equilibrium between a binary solution and its vapor. The figure shows that relationship between the mole fraction in the liquid or the gas phase and the temperature under constant pressure. The gas phase is above the solid curve and the liquid phase lies below the dotted curve. Suppose now that the gas mixture at the point P in the figure is cooled down gradually. At point A, the liquid phase appears and at point C, the gas phase disappears completely.
   (i) Find the mole fractions of the solute at A.

(ii) Find the mole fractions in the gas at C.

(iii) Find the mole fractions in the liquid and the gas at an intermediate stage represented by a point B in the figure. Show that the ratio of the mass in the gas and the liquid phases at this point is given by $\overline{BB'}/\overline{BB''}$.



10. Consider a binary solution which contains n_1 moles of the constituent 1 and n_2 moles of 2. Let J be some extensive quantity of this solution. $J/(n_1+n_2)$ changes with the mole fraction x_2, for instance, as shown by the solid line in



the figure. The broken line QPR shows the tangent to this curve at P. Prove the relations

$$\mathrm{QO} = \left(\frac{\partial J}{\partial n_1}\right)_{p,T,n_2} \equiv J_1\,,$$

$$\mathrm{RO}' = \left(\frac{\partial J}{\partial n_2}\right)_{p,T,n_1} \equiv J_2\,.$$

11. Let the fugacities (see (4.22)) of the components in a gas mixture be $v_i (i=1,\ldots,c)$. Show that the following relation holds at constant pressure and temperature,

$$\sum_{i=1}^{c} n_i \,\mathrm{d}\log v_i = 0\,,$$

where $n_i (i=1,\ldots,c)$ is the mole fraction of component i.

12. Let the mole fractions be x_1 and x_2 in a binary solution of two components. When the chemical potential of one component is given by

$$\bar{G}_1 = \bar{G}_1^*(T,p) + RT\log x_1\,,$$

show that the chemical potential of the other component is given by

$$\bar{G}_2 = \bar{G}_2^*(T,p) + RT\log x_2\,.$$

13. In the ideal dilute solution of two components, the vapor pressure p_1 of the solvent obeys Raoult's law,

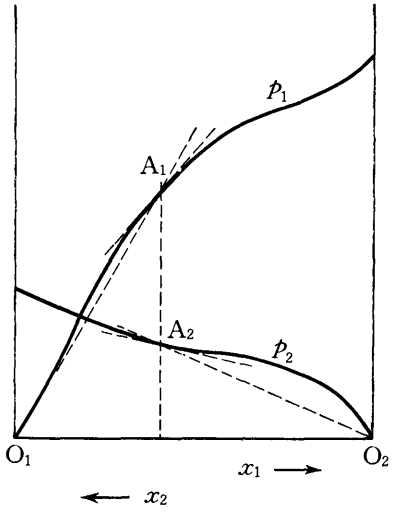
$$p_1 = x_1 p_1^0$$

(at constant temperature, p_1^0 being the vapor pressure of the pure solvent), which holds in the limit as $x_1 \to 1$. Using this law and the Gibbs-Duhem relation, derive Henry's law (4.29) for the vapor pressure p_2 of the solute and the formula (4.30b) for the chemical potential of the solute.

14. Prove the following statements concerning the graph which gives the vapor pressure p_1 or p_2 as function of the mole fraction x_1 (or x_2) for a binary solution.

(i) Let the gradients of the tangents of these curves at the points A_1 and A_2 be α_1 and α_2 respectively, and the gradients of the lines which connect the points A_1 and A_2 with the origins O_1 and O_2 be β_1 and β_2, respectively. We then have the relation

$$\alpha_1/\beta_1 = \alpha_2/\beta_2\,.$$



(ii) When the tangent at the point A_1 goes through the origin O_1, the tangent at the point A_2 goes through O_2.

15. For an ideal binary solution, formula (4.34) for the chemical potential of the i-th component,

$$\bar{G}_i = \bar{G}_i^0(T, p) + RT \log x_i,$$

always holds, where x_i is the mole fraction of the i-th component and $\bar{G}_i^0$ is the chemical potential in its pure state.

Prove the following statements for such an ideal solution when it is made by mixing pure component liquids.

(i) There is no volume change.

(ii) No heat is absorbed or emitted.

(iii) The entropy changes by the amount of the mixing entropy (4.19). Also find the change of internal energy.

16. Show that in an ideal solution the vapor pressure is approximately proportional to the mole fraction (eq. (4.36)), if the ideal gas formula can be used for the vapor, and further show that this approximation is valid in most cases.

17. Derive the formula for the osmotic pressure in the case of an ideal binary solution.

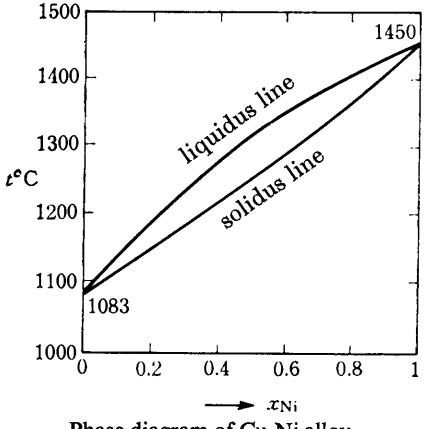
18. In the case of an ideal dilute solution, the pressure p_1 of the saturated vapor of the solvent is nearly proportional to the mole fraction $x_1 (\approx 1)$ of the solvent. Based on this fact, show that the variation of the boiling point of this solution is proportional to the mole fraction $x_2 (\ll 1)$ of the solute. (Note that the solute can also vaporize.)

19. The concentration of the solute in the solid phase which precipitates from a dilute solution x_2' is proportional to the concentration of the solute (mole fraction x_2) in the solution (liquid phase); $x_2' = kx_2$. Here k is a function of the temperature. Derive the relation between the variation of the freezing point and the mole fraction x_2 under the assumptions of an ideal dilute solution for the liquid phase and an ideal dilute solid solution for the solid phase.

20. Consider two kinds of metal 1 and 2 (with melting points T_1 and T_2 and heats of fusion L_1 and L_2, respectively), which mix well with each other in the liquid phase, but do not mix at all in the solid phase. Derive the equation for the phase diagram, and give the equation which determines the eutectic point. Assume, for the sake of simplicity, that the heat of fusion does not show any appreciable change with temperature.

21. Suppose that two kinds of metals A and B mix well both in the liquid and the solid phases. Assume that the mixtures are ideal and let T_1, T_2 and L_1, L_2 be the melting points and heats of fusion of A and B (per mole), respectively.

(i) Derive the general equations which give the solidus and the liquidus lines in the phase diagram.



Phase diagram of Cu-Ni alloy.

(ii) Simplify the above general equations by use of the following assumptions, and show that one has a cigar-shaped phase diagram shown in the figure.

Assumptions: (a) the entropies of fusion of A and B (per mole) are equal, and are of the order of the gas constant R. (b) The temperature variation of L_1 and L_2 can be neglected. (c) $|T_1 - T_2| \ll T_1, T_2$.

22. Consider the gas reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightleftarrows l\mathrm{L} + m\mathrm{M} + \cdots$$

under constant temperature and volume. Prove that the quantity defined below depends only on the temperature

$$\frac{[\mathrm{L}]^l\,[\mathrm{M}]^m \cdots}{[\mathrm{A}]^a\,[\mathrm{B}]^b \cdots} = K_c(T) \qquad \text{(Guldberg and Waage, 1867)}.$$

where the square brackets indicate the number of moles per unit volume. Assume the ideal gas formula for each component.

23. For a chemical reaction in the ideal gas mixture, derive the reaction isochore

$$\frac{\mathrm{d}\log K_c}{\mathrm{d}T} = \frac{\Delta\bar{U}}{RT^2}$$

and

$$\frac{\mathrm{d}\log K_p}{\mathrm{d}T} = \frac{\Delta\bar{H}}{RT^2} \qquad \text{(van 't Hoff, 1885)},$$

where $\Delta\bar{U}$ and $\Delta\bar{H}$ are the standard internal energy and the standard enthalpy per mole of the reaction.

24. Let us assume that the equilibrium constant of the reaction $\mathrm{A}_2 \rightleftarrows 2\mathrm{A}$, occurring in an ideal gas phase at 18 °C, is given by

$$K_c(18\ ^\circ\mathrm{C}) = \frac{[\mathrm{A}]^2}{[\mathrm{A}_2]} = 1.70 \times 10^{-4}\ \mathrm{mol/cm^3},$$

where the square brackets indicate the number of moles per unit volume. Determine the degree of dissociation when the pressure of the gaseous mixture is 1 atm. What value is expected at 19 °C and 1 atm for the degree of dissociation, if the heat of reaction is 5.0×10^4 cal/mol?

25. Let us consider the occlusion of a gas A_2 by a solid C. What relation is

expected between the gas pressure p_{A_2} and the concentration of A in C, if we assume that in C the molecule A_2 is dissociated into atoms A?

26. Solid calcium carbonate ($CaCO_3$), if heated, dissociates into solid calcium oxide (CaO) and carbonic acid gas. The observed value of the dissociation pressure (the pressure p_{CO_2} of CO_2 gas) can be expressed by

$$\log_{10} p_{CO_2} = -\frac{11355}{T} - 5.388 \log_{10} T + 26.238$$

between 1100 °K and 1500 °K, the pressure being measured in atm. Determine the standard enthalpy change of this dissociation reaction ΔH_T^0.

27. The net reaction in the electrochemical cell (4.67b) is

$$\mathrm{Ag(c)} + \tfrac{1}{2}\mathrm{Hg_2Cl_2(c)} \rightarrow \mathrm{AgCl(c)} + \mathrm{Hg(l)}.$$

At 25 °C and 1 atm, the experimental values of the electromotive force and of its temperature dependence are given by $E = 0.0455$ V and $(\partial E/\partial T)_p = 0.000338$ V/deg. Determine the free energy, enthalpy, and entropy of this reaction.

28. Evaluate the chemical constant i of mercury, based on the following data and on the assumption that the vapor of mercury may be regarded as a monatomic ideal gas. The melting point is $T_m = 234.2$ °K. The value of entropy of solid mercury at T_m evaluated by numerical integration of the specific heat at 1 atm is given by

$$S_s(234.2°) = \int_0^{234.2} C_p \, dT/T = 59.9 \times 10^7 \text{ erg/mol·deg}.$$

The heat of fusion is 2330×10^7 erg/mol. The boiling point is $T_b = 630$ °K. The increase in entropy of liquid mercury determined from the observed specific heat at constant pressure, 1 atm, is

$$S_l(630°) - S_l(234.2°) = \int_{234.2}^{630} C_p \, dT/T = 26.2 \times 10^7 \text{ erg/mol·deg}.$$

The heat of vaporization is 59300×10^7 erg/mol.

29. When a metal is heated to a sufficiently high temperature, electrons are

emitted from it. Show that the chemical constant of the thermal electrons can be found by measuring the temperature dependence of the pressure of the electron gas in equilibrium with the metal, if the chemical potential of the electrons within the metal is assumed to be constant.

30. The electrode reaction in an electrochemical cell

$$(\mathrm{Pt})\ \mathrm{H_2}\ (\mathrm{g})\ (\text{hydrogen electrode})\,|\mathrm{HCl}\ (\mathrm{aq},\ x)|\ \mathrm{AgCl}\ (\mathrm{c})\ \mathrm{Ag}\ (\mathrm{c})$$

is given by

$$\tfrac{1}{2}\mathrm{H_2}\ (\mathrm{g}) \rightarrow \mathrm{H^+}\ (\mathrm{HCl},\ \mathrm{aq},\ x) + \mathrm{e},$$
$$\mathrm{AgCl}\ (\mathrm{c}) + \mathrm{e} \rightarrow \mathrm{Ag}\ (\mathrm{c}) + \mathrm{Cl^-}(\mathrm{HCl},\ \mathrm{aq},\ x).$$

What is the net reaction? Prove that the electromotive force E of this cell can be expressed in the form

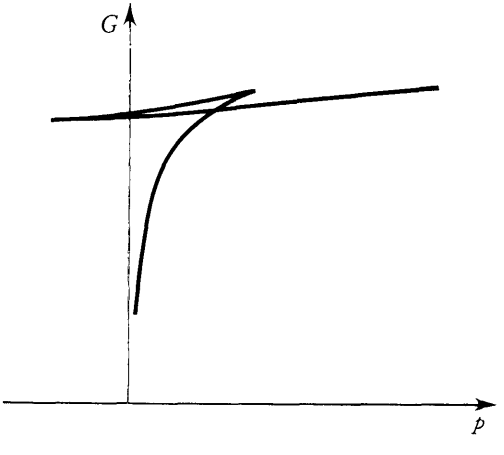
$$E = E^\circ - \left(\frac{2RT}{\mathfrak{F}}\right)\log(x\bar{\gamma}) + \left(\frac{RT}{\mathfrak{F}}\right)\log p_{\mathrm{H_2}}^{\frac{1}{2}},$$

where x denotes the concentration of HCl, $\bar{\gamma}$ the mean activity of ions, and $p_{\mathrm{H_2}}$ the pressure of the hydrogen gas.

[B]

31. Consider a system obeying van der Waals' equation of state below the critical point. Show that the Gibbs free energy changes as shown in the figure as the pressure is increased at constant temperature.

Explain what change the system under consideration makes in this process below the critical temperature.



32. When two phases 1 and 2 are in equilibrium with each other, prove that the heat of transition from 1 to 2, L, changes with temperature according to the equation,

$$\frac{\mathrm{d}L}{\mathrm{d}T} = C_{p_2} - C_{p_1} + \frac{L}{T} - L\frac{\bar{V}_2\beta_2 - \bar{V}_1\beta_1}{\bar{V}_2 - \bar{V}_1}.$$

Here C_{p_1} and C_{p_2} stand for the molar heat capacities at constant pressure, and β_1 and β_2 for the coefficients of thermal expansion of the two phases. Show, in particular, that, if phase 1 is either a solid or a liquid and the other phase is an ideal gas, we may approximate the equation obtained above as

$$\frac{\mathrm{d}L}{\mathrm{d}T} \approx C_{p_2} - C_{p_1}.$$

33. Prove that the specific heat of saturated vapor, i.e. the specific heat corresponding to a heating process in which the vapor is kept saturated, is given at a temperature T by

$$c = c_p^{\mathrm{g}} - \frac{r}{T} = c_p^{\mathrm{l}} + \frac{\mathrm{d}r}{\mathrm{d}T} - \frac{r}{T} = c_p^{\mathrm{l}} + T\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{r}{T}\right),$$

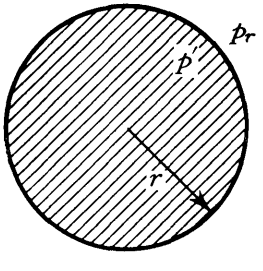
where r stands for the heat of vaporization per unit of mass, and c_p^{l} for the specific heat of the liquid at constant pressure.

Evaluate c for water at 100 °C, for which

$$c_p^{\mathrm{l}} = 1.01\,\frac{\mathrm{cal}}{\mathrm{g\cdot deg}}, \qquad \frac{\mathrm{d}r}{\mathrm{d}T} = -0.64\,\frac{\mathrm{cal}}{\mathrm{g\cdot deg}}, \qquad r = 539\,\frac{\mathrm{cal}}{\mathrm{g}}.$$

What is meant by $c<0$?

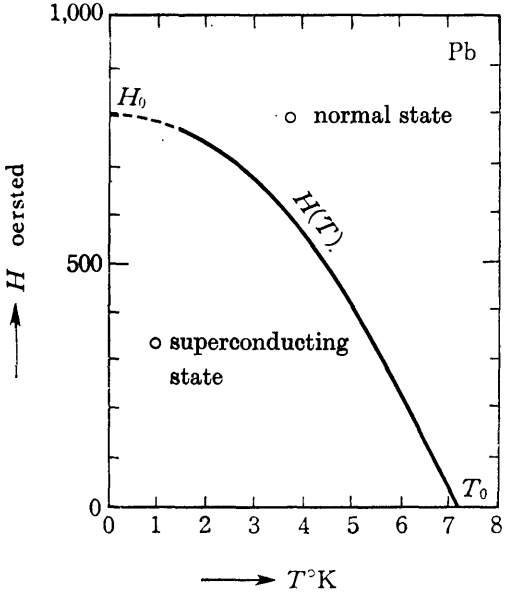
34. Due to the effect of surface tension, the saturated vapor pressure p_r in the case of a liquid drop of radius r is larger than the pressure p_∞ (the usual value of the saturated vapor pressure) in the case of a planar boundary of the liquid phase.



(i) Determine the relation between p_r and r.
(ii) What is the critical value of the radius r_c of such a liquid drop that it can grow in the supersaturated vapor with $p > p_\infty$?

35. Based on the fact that the specific heat c of the saturated vapor is negative (see problem 33), explain why supersaturated vapor is produced by a sudden expansion of the Wilson chamber.
[*Hint*: Consider the adiabatics and the saturated vapor pressure curve in a p-T plane.]

36. Some kinds of metal become superconductive at low temperatures. In this superconducting state, they have a remarkable property (the Meissner effect) that the magnetic flux does not enter into the metal even when an external magnetic field is imposed ($B=0$ even when $H \neq 0$). However, the superconducting state collapses and changes into the normal state, and the interior B becomes equal to H, if the external magnetic field exceeds a certain critical value $H_c(T)$ (if $|H| > H_c$, then $B=H$). The curve of the critical magnetic field $H_c(T)$ versus T is shown in the figure, and it divides the H-T plane into two phases corresponding to the superconducting state s and the normal state n.
(i) Determine the latent heat of the s→n transition at $H \neq 0$ and $T < T_0$.



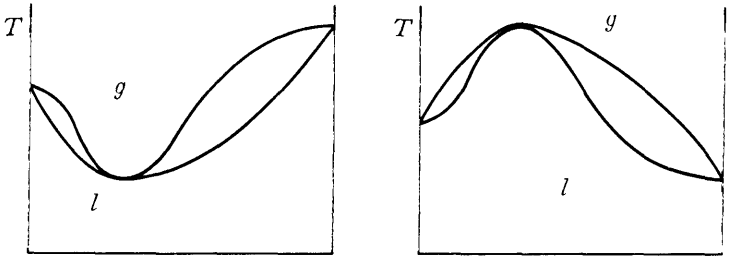
(ii) Derive Rutgers' equation

$$\left(\frac{dH_c}{dT}\right)^2_{T=T_0} = \frac{4\pi}{\bar{V}}\left(\frac{C_s - C_n}{T}\right)_{T=T_0},$$

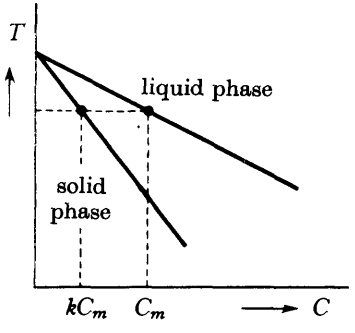
where C_s and C_n stand for the molar heats in the superconducting state and in the normal state, respectively, and $\bar{V}$ for the molar volume.

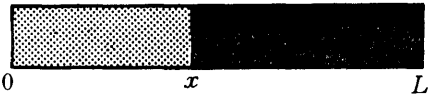
(iii) What is the relation between C_s and C_n at an arbitrary temperature, when $H_c = H_0\{1-(T/T_0)^2\}$ is assumed to be valid?

37. There are cases in which the composition of a solution agrees with that of its vapor at some temperature and composition, when a mixture of two different kinds of liquid is being distilled. This situation is called *azeotropy*. Show that the temperature mentioned above corresponds to either a maximum or a minimum of the gaseous line and of the liquidus in the phase diagram like those shown in the figure.



38. Consider a substance A containing an impurity constituent B. In the region of its phase diagram corresponding to the lower concentration of B, the liquidus and the solidus may be approximated by straight lines. When the concentration of B in the solid phase precipitating from the liquid phase of concentration C_m is denoted by C, $C/C_m = k$ is called the *segregation constant*.





Show that the concentration of B at a distance x from the left end of a molten rod of length L is given by

$$C(x) = kC_{\mathrm{m}}^{0}\left(1 - \frac{x}{L}\right)^{k-1},$$

if the molten rod with concentration C_{m}^{0} is cooled from its left end and solidifies. Assume that diffusion of atoms does not occur in the solid phase, but it occurs so rapidly in the liquid phase that the concentration is always kept uniform. (The principle of the zone melting method.)

39. For some kinds of high-polymer solutions, the chemical potentials of solvent and solute are approximately given by the equations

$$\bar{G}_1 = \bar{G}_1^0(T, p) + RT\left\{\log\phi_1 + \left(1 - \frac{1}{r}\right)(1 - \phi_1)\right\} + w(1 - \phi_1)^2,$$
$$\bar{G}_2 = \bar{G}_2^0(T, p) + RT\{\log\phi_2 - (r - 1)(1 - \phi_2)\} + rw(1 - \phi_2)^2,$$

where r stands for the degree of polymerization, and ϕ_i for the volume fractions

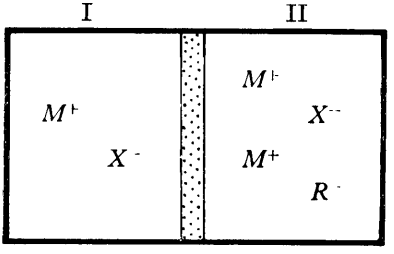
$$\phi_1 = \frac{N_1}{N_1 + rN_2}, \qquad \phi_2 = \frac{rN_2}{N_1 + rN_2}.$$

Here N_1 and N_2 are the numbers of solvent molecules and of solute high-polymer molecules, respectively. It is assumed that each polymer molecule consists of r monomers, and that the volume of a monomer approximately equals the volume of a solvent molecule. Then

(i) prove that the chemical potentials given above satisfy the Gibbs-Duhem relation;
(ii) compare the entropy of mixing of this solution with that of an ideal solution;
(iii) derive the relation of the heat of mixing to the concentration of this solution; and
(iv) examine the relations of the osmotic pressure and of the vapor pressure of the solvent to the concentration of this solution.

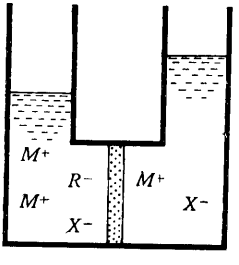
40. An aqueous solution of M^+X^- of concentration x_1^0 is poured into room I, and another solution M^+R^- of concentration x_2^0 into the other room II, which is separated from the room I by a semi-permeable membrane permeable for M^+ ions and X^- ions but not for R^- ions. What are the concentrations of M^+X^- in room I and II, x_1' and x_1'', when the equilibrium (Donnan's membrane equilibrium) is reached by diffusion of M^+ and X^-

ions through the membrane? For the sake of simplicity, assume that the solutions are very dilute, and may be regarded as ideal dilute solutions. [*Hint*: the solution must always be electrically neutral.]



41. In the case of the preceding problem, a voltage difference appears on both sides of the semi-permeable membrane. Derive the formula for this voltage difference, by considering the electrochemical potentials.

42. As is shown in the figure, a semi-permeable membrane, impermeable to R^- ions is inserted into a U-tube, and in one branch a M^+R^- solution is poured. Then the osmotic pressure is measured. When an electrolytic solution of M^+X^-, able to pass through the membrane, is added, a decrease in the osmotic pressure is observed. Explain this phenomenon, by assuming, for simplicity, that the solution is ideal and dilute.



43. In the table, the observed values of the freezing point depression are given against the various values of the molality θ for the aqueous solution of HCl. Determine the osmotic coefficient g from these data, and compare it with the result obtained by the limit of the Debye-Hückel law (4.56). (See examples 6 and 8.)

$10^3 m_2$ (mol·kg^{-1})	$10^2\,\theta$ (deg)	$10^3 m_2$ (mol·kg^{-1})	$10^2\,\theta$ (deg)
0.627	0.228	3.526	1.286
1.179	0.434	4.520	1.644
1.245	0.455	6.879	2.494
1.474	0.542	10.633	3.843
2.228	0.815		

44. In an n-type impurity semiconductor, the impurity atom (donor) D is ionized by the reaction $D \rightleftarrows D^+ + e$, and a conduction electron e is produced. Regarding the crystal containing D and D^+ as an ideal dilute solid solution, and regarding the conduction electrons as an ideal gas derive the formula for the equilibrium density of conduction electrons by thermodynamics.

NOTE: Since conduction electrons move freely in the crystal, they may be regarded as a kind of gas. The ideal gas is a good approximation when the concentration of electrons is low.

45. Molten silver can easily dissolve in molten gold, i.e.

$$\mathrm{Ag\,(l)} \rightarrow \mathrm{Ag(in\ Au\ (l))}.$$

In order to make this process take place reversibly, Wagner and Engelhardt made an electrochemical cell

$$\mathrm{Ag\,(l)\,|\,AgCl,\ KCl\ mixed\,|\,Ag_xAu_{1-x}},$$

and measured its electromotive force. The experimental data are shown in the table for five values of concentration x. What value of electromotive force can be expected at $x=0.5$ and at 1360 °K, if Ag_xAu_{1-x} (liquid) is assumed as an ideal solution? The table gives observed values of the electromotive force at the same temperature. Determine from these data the activity coefficient γ defined by eq. (4.43).

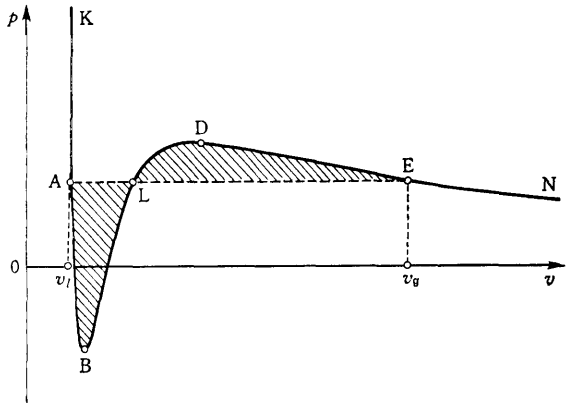
x	E (volt)
0.846	0.021
0.716	0.045
0.602	0.074
0.471	0.114
0.263	0.198

46. Le Chatelier's principle applied to a chemical equilibrium can be stated as follows. (i) If the temperature is raised under a constant pressure, the chemical equilibrium moves in such a direction that heat is absorbed. (ii) If the pressure is increased at constant temperature, the chemical equilibrium shifts in such a direction that the total volume of the system under consideration decreases. Prove these statements.

[C]

47. Prove Maxwell's rule described in example 1 for a van der Waals gas. Note, however, that the states on the p-V plane having $(\partial p/\partial V)_T > 0$ are nonphysical, because they violate the thermodynamic stability conditions, so that the equality of the Gibbs free energies at A and E must be proved by

considering a quasi-static process passing only through physical states and avoiding such non-physical states. Use the fact that C_v is a function of T only (see problem 34).



48. It is found that a ferromagnet has a magnetic susceptibility obeying the Curie-Weiss law

$$\chi_T = \frac{A}{T - T_c} \qquad (A \text{ is a positive constant})$$

in the paramagnetic region above its Curie temperature T_c. Discuss by thermodynamics the jump in the specific heat of this material at the Curie temperature and the spontaneous magnetization below the Curie temperature.

[*Hint*: Note that, if the free energy $F(M, T)$ can be expanded into the form $F(M, T) = F(0, T) + \frac{1}{2}\alpha(T)\, M^2 + \beta(T)\, M^4/4! + \cdots$, then $\alpha(T_c) = 0$ and $\beta(T_c) > 0$ must hold. As an approximation, retain the terms only up to M^4.]

49. Explain by thermodynamics why water drops condense around ions in water vapor, and why ion tracks are seen when the Wilson chamber is suddenly expanded.

[*Hint*: Note that the free energy is lowered in the polarization of water by the electric charge of the ion.]

50. Determine the conditions under which the high-polymer solution described in problem 39 separates into two phases.

Solutions

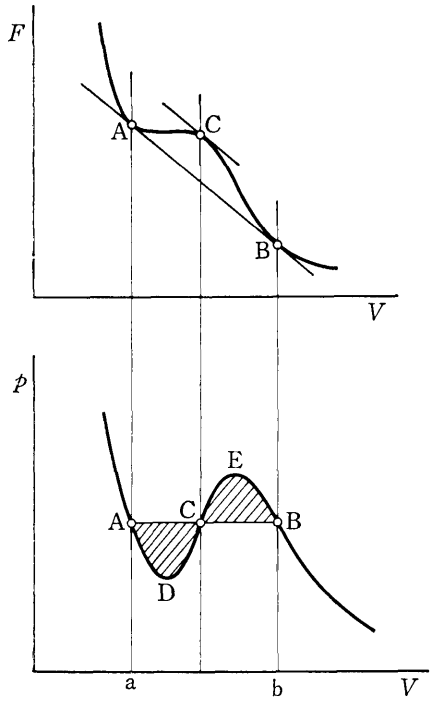
1. (i) The condition of thermal equilibrium between two phases is the establishment of equality of temperature, pressure and the Gibbs free energy $G=F+pV$ (per mole) between the two phases (see (4.1)–(4.3)). The pressure p is given by $p=-(\partial F/\partial V)_T$, that is, the negative gradient of the curve $F(V)$ for a given T. Hence we have at equilibrium,

$$p=-\frac{\partial F_a}{\partial V_a}=-\frac{\partial F_b}{\partial V_b}. \tag{1}$$

Further, from $G_a=G_b$, that is, from $F_a+pV_a=F_b+pV_b$ we have

$$p=-\frac{F_a-F_b}{V_a-V_b}. \tag{2}$$

Eqs. (1) and (2) show that equilibrium is established between the two states given by the contact points of the common tangent for the curves F_a and F_b (see the figure in the problem).



(ii) Assume that the F-V curve is given by a continuous curve as shown in the upper figure. Condition (2) above can be written as

$$-\int_a^b \frac{\partial F}{\partial V}\,\mathrm{d}V = p(V_b - V_a)$$

and therefore

$$\int_a^b p\,\mathrm{d}V = p(V_b - V_a). \tag{3}$$

Eq. (3) means (see the lower figure) that the area of ADCEBba = the area of ABba, that is, the area of ADCA = the area of CBEC. This is Maxwell's rule.

2. The Clausius-Clapeyron formula given in (4.4) can be used;

$$\frac{\mathrm{d}T_m}{\mathrm{d}p} = \frac{T_m(v_l - v_s)}{q_m} = \frac{273(-0.091)}{80} \times \frac{1}{3.13 \times 10^3}$$
$$= -0.99 \times 10^{-4}\ \mathrm{deg}\cdot(\mathrm{cm\ Hg})^{-1},$$

where the numerical value

$$1\ \mathrm{cal\ cm^{-3}} = 4.18 \times 10^7/13.6 \times 980\,\mathrm{cm\ Hg} = 3.13 \times 10^3\ \mathrm{cm\ Hg}$$

is used.

3. The Clausius-Clapeyron formula given in (4.4) can be used:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{q}{T(v_g - v_l)}.$$

The specific volume v_g of water vapor is very much larger than that of water v_l. Hence we can put $v_g - v_l \approx v_g$ and estimate v_g by the equation of state of an ideal gas:

$$v_g = \frac{RT}{pM_{H_2O}} = \frac{1.987 \times 373}{760 \times 18.02} = 5.41 \times 10^{-2}\ \mathrm{cal}\cdot(\mathrm{mm\ Hg})^{-1}\cdot\mathrm{g}^{-1}$$
$$= 1699\ \mathrm{cm^3\ g^{-1}}.$$

Thus we have

$$q = 27.12 \times 373 \times 5.41 \times 10^{-2} = 547\ \mathrm{cal}\cdot\mathrm{g}^{-1}.$$

NOTE: $q = 539.032\ \mathrm{cal}\cdot\mathrm{g}^{-1}$ is considered as the reliable observed value. Try the observed value $1672\ \mathrm{cm^3}\cdot\mathrm{g}^{-1}$ for v_g in the above estimation.

4. By Clausius-Clapeyron's formula (4.4), we have

$$\left(\frac{dp}{dT}\right)_{s-g} = \frac{S_g - S_s}{V_g - V_s} \qquad \text{(gas-solid)},$$

$$\left(\frac{dp}{dT}\right)_{l-g} = \frac{S_g - S_l}{V_g - V_l} \qquad \text{(gas-liquid)},$$

and we know $V_g \gg V_l$, V_s and $S_g > S_l > S_s$. Thus we find

$$\left(\frac{dp}{dT}\right)_{s-g} \fallingdotseq \frac{S_g - S_s}{V_g} > \frac{S_g - S_l}{V_g} \fallingdotseq \left(\frac{dp}{dT}\right)_{l-g}.$$

5. The triple point is defined as the intersection of the three equilibrium curves in a p–T plane: the equilibrium pressures p_{01}, p_{12} and p_{02} plotted as functions of temperature T where the suffices 0, 1 and 2 mean ice, water and vapor phase respectively. The gradient of the tangent of the equilibrium pressure curve is given by the Clausius-Clapeyron formula (4.4). The equilibrium pressure curve p_{01}–T between the water and the ice phases runs through the point (760 mm Hg, 0 °C) and has the gradient

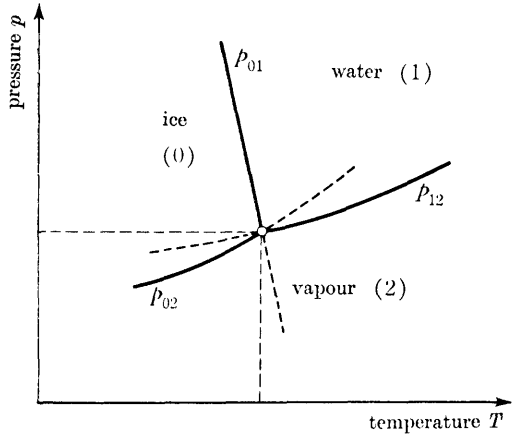
$$\frac{dp_{01}}{dT} = \frac{q_{01}}{T_0(v_0 - v_1)} = -\frac{80}{273\cdot(1.091 - 1)}\frac{\text{cal}}{\text{deg}\cdot\text{cm}^3} \tag{1}$$

at this point. On the other hand, the equilibrium curve p_{12}–T between the water and the vapor phases runs through the point (4.58 mm Hg, 0 °C) and has a gradient very much smaller than (1). (Although $q_{12} = 600$ cal is nearly 8 times larger than q_{01} in (1), the specific volume v_2 of the vapor at (4.58 mm Hg, 0 °C) is 10^5 times greater than v_0 or v_1.) This p_{12} curve can be approximated by a horizontal line and the temperature at the intersection with the p_{01} curve can be calculated from the ΔT which corresponds to $-\Delta p_{01} = (760 - 4.58)$ mm Hg. From (1), we have

$$\frac{dT}{dp_{01}} = -\,0.0075 \text{ deg/atm}.$$

Then ΔT is estimated as $\Delta T = 0.0075$ for $-\Delta p_{01} = 1$ atm. Hence the temperature at the triple point is about 0.0075 °C (the pressure is about 4.58 mmHg). NOTE: The reliable experimental values at the triple point are 4.579 mm Hg and 0.0098 °C. In 1954, the latter was put equal to 0.01 °C to define the centigrade temperature scale. The figure shows the curves p_{01}, p_{12} and p_{02}.

The curves given by broken lines are not stable equilibrium states but are only metastable. The equilibrium between water and vapor at (4.58 mm Hg, 0 °C) is thus metastable.



6. The Clapeyron-Clausius formula (4.4) can be written for this case as

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(v_g - v_l)},$$

where L means the latent heat of vaporization. By the condition (a), we have $v_g \gg v_l$. Dropping v_l and using the ideal gas approximation $v_g = RT/p$, we have

$$\frac{\mathrm{d}p}{p} = \frac{L}{RT^2}\,\mathrm{d}T.$$

Integrating this equation under the assumption (b), we obtain

$$p_s \propto \exp(-L/RT).$$

7. Use eq. (4.8). The condition for stable equilibrium (3.30a) applied to the present case is

$$\delta U \geqq 0$$

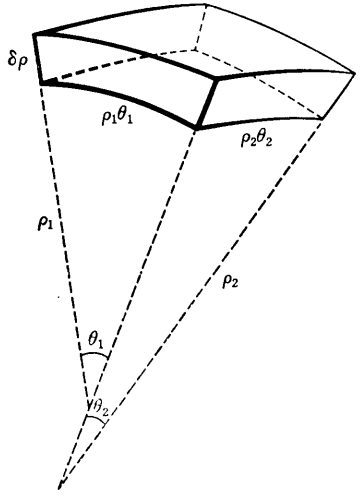
under the restrictions: the total volume is constant ($\delta v' + \delta v'' = 0$), the total entropy is constant ($\delta S = 0$), the number of particles in each phase is constant ($\delta N' = \delta N'' = 0$). Considering only the first order variation, we have

$$\delta U = (-p' + p'')\,\delta V' + \gamma\,\delta\sigma = 0,$$

so that

$$\Delta p = p' - p'' = \gamma \frac{\mathrm{d}\sigma}{\mathrm{d}V'}.$$

Consider an infinitesimal rectangle drawn along the geodesics as shown in the figure. Let θ_1 and θ_2 be the infinitesimal angles spanned by the edges of this rectangle at the respective centres of curvature. The area of this rectangle is given by $\rho_1\rho_2\theta_1\theta_2$. When the surface is displaced by $\delta\rho$ in the direction



of the radius, the infinitesimal volume $\mathrm{d}V' = \rho_1\rho_2\theta_1\theta_2\,\delta\rho$ is added due to the displacement and the area of the rectangle is increased by

$$\begin{aligned}\mathrm{d}\sigma &= (\rho_1 + \delta\rho)(\rho_2 + \delta\rho)\,\theta_1\theta_2 - \rho_1\rho_2\theta_1\theta_2 \\ &= (\rho_1 + \rho_2)\,\delta\rho\theta_1\theta_2.\end{aligned}$$

Therefore

$$\frac{\mathrm{d}\sigma}{\mathrm{d}V'} = \frac{1}{\rho_1} + \frac{1}{\rho_2},$$

so that the pressure difference Δp is given by

$$\Delta p = \gamma\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) = \frac{2\gamma}{\rho},$$

where $1/\rho$ is the mean curvature. Eq. (4.9) is a special case of this relation.

8. The entropy S_σ of the surface is given by

$$S_\sigma = -\sigma\frac{\mathrm{d}\gamma}{\mathrm{d}T}$$

as shown in example 3. The heat Q which is absorbed by the surface film when its area is expanded from σ_1 to σ_2 by a quasi-static isothermal process is given by

$$Q = T(S_\sigma(T, \sigma_2) - S_\sigma(T, \sigma_1)).$$

Hence

$$Q = -T\frac{\mathrm{d}\gamma}{\mathrm{d}T}(\sigma_2 - \sigma_1).$$

For a quasi-static adiabatic process, we have

$$\mathrm{d}S_\sigma = 0.$$

Hence

$$\sigma\frac{\mathrm{d}^2\gamma}{\mathrm{d}T^2}\mathrm{d}T + \frac{\mathrm{d}\gamma}{\mathrm{d}T}\mathrm{d}\sigma = 0,$$

or

$$\frac{\mathrm{d}\sigma}{\sigma} + \frac{\mathrm{d}(\mathrm{d}\gamma/\mathrm{d}T)}{\mathrm{d}\gamma/\mathrm{d}T} = 0.$$

Thus we have

$$\sigma\frac{\mathrm{d}\gamma}{\mathrm{d}T} = \text{const.}.$$

This is the condition for the adiabatic process, and T_2 is then obtained from the equation

$$\sigma_1\frac{\mathrm{d}\gamma(T_1)}{\mathrm{d}T_1} = \sigma_2\frac{\mathrm{d}\gamma(T_2)}{\mathrm{d}T_2},$$

for given σ_1, T_1 and σ_2.

DIVERTISSEMENT 12.

Thermodynamics and life. It would not be surprizing to find thermodynamics and life science to be old friends. Their friendship started early in the cradle of thermodynamics when the young German doctor R. von Mayer was suddenly struck by the ingeneous idea of the equivalence of work and heat. Another founder of thermodynamics, Helmholtz was also a great physiologist (see Divertissement 1).

Scientists have not yet disclosed the mystery of life. But, do you not believe that the biological phenomena will be explained someday by those physical laws which we know very definitely govern inanimate objects? Although no one can deny the possibility of a revolutionary discovery of an entirely new principle which makes life operative, such a principle, if it ever is found to exist, will very unlikely invalidate the laws of physics and chemistry. Biologists and biophysicists seem to agree, at least in the belief that the only fruitful way to approach the mysteries of life is to

adopt the working hypothesis of the general validity of physical laws in biological processes.

There has been no indication that biological phenomena ever violate the first law of thermodynamics: conservation of energy. We cannot work without food. Biological observations were important elements in establishing the first law. As far as we know today, there is no form of energy peculiar to living organisms: it appears that every form of energy appearing in biological processes can be understood completely on physical or chemical grounds. However complex a biological process may look, it is always found that the bookkeeping of energy is always very strict.

More delicate is the question of the validity of the second law of thermodynamics. Entropy is a measure of disorder. This is an atomistic interpretation of this concept as is implied by statistical mechanics. Increase of entropy generally expresses the unavoidable tendency of nature to approach disorder, which can be prevented only if some effort – some work – is consumed.

"The view that the universe is running down into a condition where its entropy and the amount of disorder are as great as possible has had a profound effect on the views of many biologists on the nature of biological phenomena. It springs to the eye that the tendency of living organisms is to organize their surroundings, that is, to produce "order" where formerly there was disorder. Life then appears in some way to oppose the otherwise universal drive to disorder. What is the significance of this? Does it mean that living organisms do or may violate the second law of thermodynamics?" (Bridgeman, *The Nature of Thermodynamics* (Harvard Univ. Press, 1943) p. 208.)

Maxwell once imagined an extremely clever creature who guards a gate on the wall separating two vessels containing gas molecules and skillfully controls the gate so as to allow only the fast molecules to pass (see Divertissement 1, in R. Kubo et al., *Statistical Mechanics* (North-Holland Publ. Co., 1965) p. 13). If he functions properly, the gas on one side gets hotter and that on the other side cools down. This seems to violate the second law.

Whether a Maxwell demon really turns the wheel against nature is only decided when we find what is occurring inside of him. When a living organisms is driving to order from disorder, the decrease of entropy may well be compensated by something which is hidden behind the hopelessly complex mechanism of life.

At present, it is still extremely difficult to prove or disprove the existence of a Maxwell demon in living organisms. It seems that an exact experimental proof could be achieved only when life can be artificially created.

Those who are interested in the thermodynamic aspects of biological processes are recommended to refer to the booklet *Bioenergetics* by A. L. Lehninger (W. A. Benjamin, Inc., New York, 1965).

9. (i) The mole fraction x_2 of the solute in the liquid phase which appears at point A is given by the intersection A′ of the horizontal line drawn from the

point A and the dotted line (liquidus line). (ii) Also the mole fraction x_2 in the gas phase at point C is given by point C′. (iii) Generally at an intermediate temperature corresponding to point B, the mole fraction of the solute in the liquid phase and that in the gas phase are given by the x_2 coordinate of the point B′ and that of the point B″ respectively. Let the mole number in the gas phase be N_g and that of the liquid phase be $N_l (N_g + N_l = N_1 + N_2)$. Then one has

$$N_g x_2^g + N_l x_2^l = N_2 .$$

where x_2^g and x_2^l are the mole fractions in the gas phase and in the liquid phase, and are the x_2 coordinates of the point B″ and the point B′, respectively. If this is divided by the total mole number N, one obtains

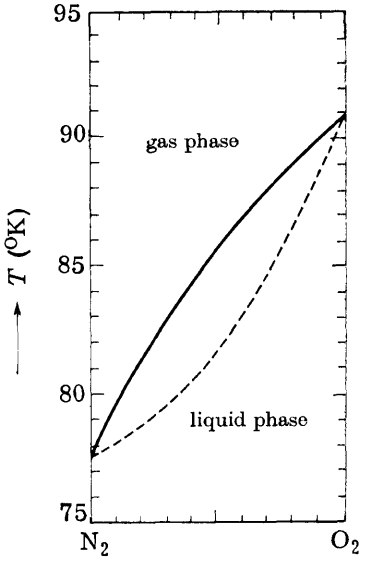
$$x_g x_2^g + x_l x_2^l = x \equiv x_2 (x_g + x_l)$$

and therefore

$$x_g/x_l = x_g/(1 - x_g) = (x_2^l - x_2)/(x_2 - x_2^g) = \overline{\mathrm{B'B}}/\overline{\mathrm{B''B}} .$$

This shows the required results.

NOTE: The liquid phase which appears in the above case is always homogeneous (contrary to the precipitation of solid phase from a liquid solution). The figure gives the example of $N_2 - O_2$ mixtures.



10. By assumption, J is extensive as a function of n_1 and n_2: that is,

$$J(\lambda n_1, \lambda n_2) = \lambda J(n_1, n_2). \tag{1}$$

Differentiate both sides by λ and put $\lambda = 1$, to get

$$J(n_1, n_2) = n_1 \frac{\partial J}{\partial n_1} + n_2 \frac{\partial J}{\partial n_2} = n_1 J_1 + n_2 J_2 \tag{2}$$

and

$$\frac{J}{n_1 + n_2} = (1 - x_2) J_1 + x_2 J_2 \qquad \left(x_2 = \frac{n_2}{n_1 + n_2}\right).$$

Therefore,

$$\frac{\mathrm{d}}{\mathrm{d}x_2} \frac{J}{(n_1 + n_2)} = J_2 - J_1 + (1 - x_2) \frac{\partial J_1}{\partial x_2} + x_2 \frac{\partial J_2}{\partial x_2} = J_2 - J_1. \tag{3}$$

(Here we have used the Gibbs-Duhem relation which will be derived as follows:

$$\mathrm{d}J \equiv \mathrm{d}n_1 \frac{\partial J}{\partial n_1} + \mathrm{d}n_2 \frac{\partial J}{\partial n_2} = J_1 \, \mathrm{d}n_1 + J_2 \, \mathrm{d}n_2.$$

From eq. (2), we have, $\mathrm{d}J = J_1 \, \mathrm{d}n_1 + J_2 \, \mathrm{d}n_2 + n_1 \, \mathrm{d}J_1 + n_2 \, \mathrm{d}J_2$. Hence $n_1 \, \mathrm{d}J_1 + n_2 \, \mathrm{d}J_2 = (n_1 + n_2)((1 - x_2) \, \mathrm{d}J_1 + x_2 \, \mathrm{d}J_2) = 0$.) Now the equation of the tangent QPR is given by

$$y = (1 - x_2') J_1 + x_2' J_2 + (J_2 - J_1)(x_2 - x_2') = J_1 + (J_2 - J_1) x_2,$$

where x_2' is the coordinate of the point P.

At the point Q: $x_2 = 0$, $\overline{\mathrm{OQ}} = J_1$.

At the point R: $x_2 = 1$, $\overline{\mathrm{RO'}} = J_2$.

11. The Gibbs-Duhem relation becomes, for constant pressure and temperature,

$$\sum n_j \, \mathrm{d}\bar{G}_j = 0. \tag{1}$$

From $p_j = p \cdot n_j / \sum n_i$, we have

$$\mathrm{d} \log p_j = \frac{\delta n_j}{n_j} - \frac{\sum \delta n_i}{\sum n_i},$$

and

$$\sum_j n_j \, \mathrm{d} \log p_j = \sum_j \delta n_j - \sum_j n_j \cdot \sum_i \delta n_i / \sum_i n_i = \sum_j \delta n_j - \sum_i \delta n_i = 0.$$

Putting the definition of $\bar{G}_j$, (4.21), into (1) and using the above relation, we obtain the required result.

12. Use the Gibbs-Duhem relation (3.12) for constant pressure and temperature:

$$x_1\,\mathrm{d}\bar{G}_1 + x_2\,\mathrm{d}\bar{G}_2 = 0 \qquad (x_1 + x_2 = 1).$$

If $\bar{G}_1$ is given, we have

$$\mathrm{d}\bar{G}_1 = RT\frac{\mathrm{d}x_1}{x_1} = -RT\frac{\mathrm{d}x_2}{x_1}$$

and therefore

$$\mathrm{d}\bar{G}_2 = RT\frac{\mathrm{d}x_2}{x_2}.$$

After integration, we get

$$\bar{G}_2 = \bar{G}_2^*(T, p) + RT\log x_2.$$

13. Let the chemical potential (per mole) of the solvent be $\bar{G}_1$ and that of the solute be $\bar{G}_2$. The Gibbs-Duhem relation is

$$x_1\,\mathrm{d}\bar{G}_1 + x_2\,\mathrm{d}\bar{G}_2 = 0, \tag{1}$$

for constant p and T. Using the definition (4.25) for $\bar{G}_1$ and $\bar{G}_2$, we obtain

$$x_1\,\mathrm{d}\log p_1 + x_2\,\mathrm{d}\log p_2 = x_1\frac{\mathrm{d}p_1}{p_1} + x_2\frac{\mathrm{d}p_2}{p_2} = 0. \tag{2}$$

(This relation for the vapor pressure is called the *Duhem-Margules relation.*) From Raoult's law:

$$\mathrm{d}p_1/p_1 = \mathrm{d}x_1/x_1,$$

and from $x_1 + x_2 = 1$: $\quad \mathrm{d}x_1 = -\,\mathrm{d}x_2$. Hence we have for $x_2 \sim 0$:

$$\frac{\mathrm{d}p_2}{p_2} = \frac{\mathrm{d}x_2}{x_2}. \tag{3}$$

Integrating, we have

$$p_2 = k_2 x_2 \qquad \text{(Henry's law)}, \tag{4}$$

where k_2 is a constant. Putting this into the defining equation (4.25), we get

$$\bar{G}_2 = \bar{G}_2^0(T, p_2^0) + RT\log\frac{k_2 x_2}{p_2^0} = \phi_2^0(T) + RT\log x_2, \tag{5}$$

where $\phi_2^0(T) = \bar{G}_2^0 + RT\log(k_2/p_2^0)$ is a function of the temperature.

NOTE: If the total pressure p is kept constant, relations (1) and (2) hold exactly. If we allow, however, the total pressure p to be equal to the sum of the partial pressures p_1 and p_2, the condition of constant pressure does

not hold exactly, and relation (2) must be replaced by

$$x_1 \, \mathrm{d} \log p_1 + x_2 \, \mathrm{d} \log p_2 = \bar{V} \frac{\mathrm{d}p}{RT}, \tag{6}$$

where $\bar{V}$ is the molar volume of the solution. Usually the right-hand side of (6) can be neglected compared to the terms on the left-hand side. For instance, let the order of the variation Δp of the pressure be 1 atm, $\bar{V}=0.1 \times 10^3 \mathrm{cm}^3$ and $T=300\,°\mathrm{K}$, then we have $\bar{V}\Delta p/RT \fallingdotseq 100 \times 1/82 \times 300 \fallingdotseq 0.004$. This will be less than 1/100 of the terms on the left-hand side.

14. From equation (6) of the solution of the previous problem, we have

$$\frac{x_1}{p_1}\frac{\partial p_1}{\partial x_1} = \frac{x_2}{p_2}\frac{\partial p_2}{\partial x_2}, \tag{1}$$

neglecting the right-hand side. For a given concentration (mole fraction) $x_i (x_1 > x_2)$, the gradient α_i of the tangent of the vapor pressure curve is given by $\alpha_i = \partial p_i / \partial x_i$ and the gradient β_i of the line which connects a point to the origin is given by $\beta_i = p_i / x_i$. Hence from (1), we have

$$\text{(i)} \quad \frac{\alpha_1}{\beta_1} = \frac{\alpha_2}{\beta_2}$$

and

$$\text{(ii)} \quad \alpha_2 = \beta_2 \qquad (\text{if } \alpha_1 = \beta_1).$$

NOTE: Relation (1) can be used as a check on the precision of an experiment.

15. The Gibbs free energy of the system is given by

$$G = \sum n_i \bar{G}_i = n_1 \bar{G}_1^0(T, p) + n_2 \bar{G}_2^0(T, p) + RT(n_1 \log x_1 + n_2 \log x_2)$$

(see (4.34)).

(i) The volume can be calculated to be

$$V = \sum n_i \left(\frac{\partial \bar{G}_i}{\partial p}\right)_{T,n} = n_1 \bar{V}_1^0 + n_2 \bar{V}_2^0.$$

No change is expected.

(iii) The entropy $(S = -(\partial G/\partial T)_{p,n})$ can be expressed as

$$S = n_1 \bar{S}_1^0 + n_2 \bar{S}_2^0 - R(n_1 \log x_1 + n_2 \log x_2).$$

Hence statement (iii) is proved.

(ii) The enthalpy $H = G + TS$ can be seen to be given by

$$H = n_1 \bar{H}_1^0 + n_2 \bar{H}_2^0 \qquad (\bar{H}_i^0 = \bar{G}_i^0 + T\bar{S}_i^0).$$

This shows that there is no heat of mixing. As for the internal energy, we do not expect any change because there is no work done. In fact, we have

$$U = H - pV = n_1 \bar{U}_1^0 + n_2 \bar{U}_2^0 \qquad (U_i^0 = \bar{H}_i^0 - p\bar{V}_i^0).$$

16. From (4.27) and (4.34), (4.36): $p_j = x_j p_j^0$ is obtained immediately. Here, however, we give a detailed derivation using the chemical potential (4.16) and (4.34). The condition of the equilibrium $\bar{G}_{j\,\mathrm{liq}} = \bar{G}_{j\,\mathrm{gas}}$ may be written as

$$\bar{G}_{j\,\mathrm{liq}}^0(T, p) + RT \log x_1 = \bar{G}_{j\,\mathrm{gas}}^0(T) + RT \log p_j,$$

and the vapor pressure p_j^0 of the pure state can be determined from

$$\bar{G}_{j\,\mathrm{liq}}^0(T, p_j^0) = \bar{G}_{j\,\mathrm{gas}}^0(T) + RT \log p_j^0.$$

Hence

$$p_j/p_j^0 = x_j \exp \frac{\bar{G}_{j\,\mathrm{liq}}^0(T, p) - \bar{G}_{j\,\mathrm{liq}}^0(T, p_j^0)}{RT}.$$

The exponent on the right-hand side can be estimated by an expansion around p_j^0:

$$\frac{\Delta \bar{G}_j}{RT} \approx \frac{\partial \bar{G}_{j\,\mathrm{liq}}^0}{\partial p} \frac{p - p_j^0}{RT} = \bar{V}_{j\,\mathrm{liq}}^0 \frac{p - p_j^0}{RT} = \frac{\bar{V}_{j\,\mathrm{liq}}^0}{\bar{V}_{j\,\mathrm{gas}}^0} \frac{p - p_j^0}{p_j^0} \ll 1.$$

Hence $p_j = x_j p_j^0$ holds in most cases.

17. When osmotic equilibrium is established through a semi-permeable membrane which allows only the solvent to go through, the condition of equilibrium is given by

$$\bar{G}_1(p', x_2) = \bar{G}_1^0(p''),$$

where p' is the pressure in the solution, p'' the pressure in the pure solvent and x_2 is the mole fraction of the solute. Using (4.34), we obtain

$$\bar{G}_1^0(T, p') + RT \log(1 - x_2) = \bar{G}_1^0(T, p'').$$

Putting $p' = p'' + \pi$ and assuming π to be small, we have

$$\bar{G}_1^0(T, p') - \bar{G}_1^0(T, p'') \fallingdotseq \pi \frac{\partial \bar{G}_1^0}{\partial p} = \pi \bar{V}_1.$$

Hence we obtain

$$\pi = -\frac{RT}{\bar{V}_1} \log(1 - x_2), \tag{1}$$

where $\bar{V}_1$ is the molar volume of the pure solvent.

NOTE: If $x_2 \ll 1$, (1) becomes

$$\pi \bar{V}_1 = RTx_2 .$$

This looks similar to the equation of state of an ideal gas.

18. Here the vapor pressure p_1 of the solvent is given by Raoult's law

$$p_1(T) = p_1^0(T)x_1$$

and that of the solute is given by Henry's law

$$p_2(T) = k(T)x_2 .$$

The boiling point T_b is determined by the condition

$$p = p_1 + p_2 = p_0 \qquad \text{or} \qquad p_1^0(T_b)x_1 + k(T_b)x_2 = p_0 . \tag{1}$$

The boiling point T_b^0 for the pure solvent is given by

$$p_1^0(T_b^0) = p_0 . \tag{2}$$

Putting $x_1 = 1 - x_2$, $T_b = T_b^0 + \Delta T$ and assuming that x_2 and ΔT are small, we can retain them to first order in eq. (1):

$$p_1^0(T_b^0) - p_1^0(T_b^0)x_2 + \frac{\partial p_1^0}{\partial T}\Delta T + k(T_b^0)x_2 = p_0 .$$

Using (2) and Clausius-Clapeyron's formula

$$\frac{\partial p_1^0}{\partial T} = \frac{\bar{L}}{T_b^0(\bar{V}_g - \bar{V}_l)} \doteqdot \frac{\bar{L}}{T_b^0 \bar{V}_g} = \frac{p_1^0 \bar{L}}{R(T_b^0)^2},$$

we obtain

$$\frac{\Delta T}{T_b^0} = \frac{RT_b^0}{\bar{L}}\left(1 - \frac{k}{p_1^0}\right)x_2 . \tag{3}$$

(Try another solution, using (4.30a, b) and following example 6.)
NOTE: When $k = 0$ (if the solute is non-volatile), $\Delta T / T_b^0 x_2$ is determined only by the properties of the solvent. As is well known, this fact can be used as a method for determining the molecular weight of the solute.

19. By the assumption of an ideal dilute mixture, the chemical potential of the solvent is given by (4.30a). Using $x_1 = 1 - x_2$, $x_1' = 1 - x_2'$, $x_2 \ll 1$, $x_2' \ll 1$, $\log x_1 \doteqdot -x_2$, $\log x_1' \doteqdot -x_2'$, we have, from the condition of equilibrium $\bar{G}_{1l}(T, x_2) = \bar{G}_{1s}(T, x_2')$,

$$\bar{G}_{1l}^0(T) - RTx_2 = G_{1s}^0(T) - RTx_2' , \tag{1}$$

where $\bar{G}^0_{1l}$ is the chemical potential of the pure solvent in the liquid, and $\bar{G}^0_{1s}$ that in the solid phase. Using the assumption $x'_2 = kx_2$, the temperature T_f of the precipitation of the solid phase (the freezing point) is determined by the relation

$$\bar{G}^0_{1l}(T_f) - \bar{G}^0_{1s}(T_f) = RT_f(1-k)x_2, \tag{2}$$

and the freezing point T^0_f of the pure solvent is determined from

$$\bar{G}^0_{1l}(T^0_f) - \bar{G}^0_{1s}(T^0_f) = 0. \tag{3}$$

Assuming $\Delta T_f = T_f - T^0_f$ to be small, we obtain

$$G(T_f) = G(T^0_f) - (T_f - T^0_f)\, S(T^0_f).$$

Hence from (2) and (3), retaining up to the first order terms in ΔT_f and x_2, we obtain

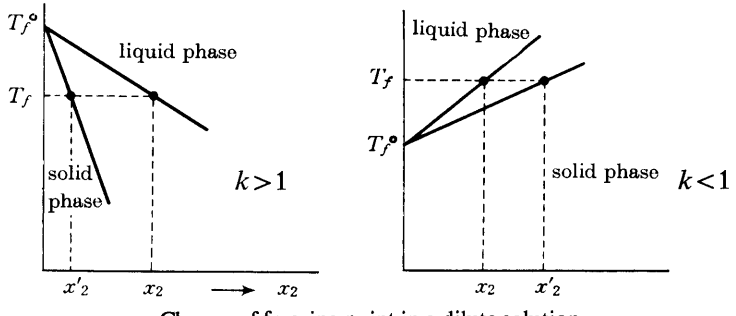
$$\Delta T_f\{-\bar{S}^0_{1l}(T^0_f) + \bar{S}^0_{1s}(T^0_f)\} = RT^0_f(1-k)x_2,$$

or

$$\frac{\Delta T_f}{T^0_f} = -\frac{RT^0_f}{\bar{L}_1}(1-k)x_2, \tag{4}$$

where $\bar{L}_1 = T^0_f(\bar{S}^0_{1l} - \bar{S}^0_{1s})$ is the heat of fusion of the solvent.

NOTE: $k<1$ corresponds to a depression of the freezing point and $k>1$ (this means that it is more favorable for the solute to go into the solid phase than into the liquid phase) corresponds to an elevation of the freezing point. The figures show the phase diagrams illustrating these two situations.



Change of freezing point in a dilute solution.

20. By assumption, the chemical potential of each component is given by (4.34). The conditions of equilibrium between the pure solid phase 1 and the liquid phase, and the pure solid phase 2 and the liquid phase are given by

$$\bar{G}^0_{1l} + RT\log x_{1l} = \bar{G}^0_{1s}, \qquad \bar{G}^0_{2l} + RT\log x_{2l} = \bar{G}^0_{2s}, \tag{1}$$

where x_{1l}, x_{2l} are the mole fractions in the liquid phase and $\bar{G}^0_{il}$, $\bar{G}^0_{is}$ are the chemical potentials of the pure i-th component in the liquid and the solid phase, respectively. Eq. (1) can be rewritten as

$$x_{1l} = e^{\lambda_1}, \qquad x_{2l} = e^{\lambda_2}, \tag{2}$$

where

$$\lambda_i = \frac{\bar{G}^0_{is} - \bar{G}^0_{il}}{RT} = -\int_{T_i}^{T} \frac{\bar{H}^0_{is} - \bar{H}^0_{il}}{RT^2}\,dT = \int_{T_i}^{T} \frac{L_i}{RT^2}\,dT \tag{3}$$

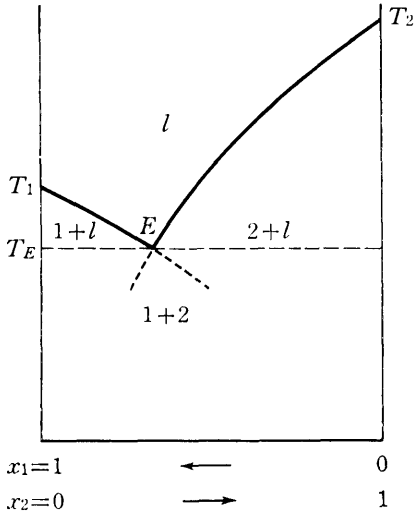
$$= \frac{L_i}{RT_i}\left(1 - \frac{T_i}{T}\right) = \alpha_i\left(1 - \frac{T_i}{T}\right). \tag{4}$$

Here $d(G/T)/dT = -H$ is used. (Note $\lambda_i = 0$ at $T = T_i$.) $L_i = \bar{H}^0_{il} - \bar{H}^0_{is}$ is the heat of fusion of the pure solid at the temperature T. This is assumed to be constant. $\alpha_i = L_i/RT_i$ is the entropy of melting $\Delta S_i = L_i/T_i$ measured in units R. Now we have

$$x_{1l} = \exp\left\{\alpha_1\left(1 - \frac{T_1}{T}\right)\right\} \quad (5a), \qquad x_{2l} = \exp\left\{\alpha_2\left(1 - \frac{T_2}{T}\right)\right\}. \quad (5b)$$

These give each a liquidus line and the intersection of (5a) and (5b) gives the eutectic point T_E:

$$\exp\left\{\alpha_1\left(1 - \frac{T_1}{T_E}\right)\right\} + \exp\left\{\alpha_2\left(1 - \frac{T_2}{T_E}\right)\right\} = 1. \tag{6}$$



Putting T_E into (5a) or (5b), we have the concentration at the eutectic point. Clearly, (5a) determines the liquidus line from $x_{1l}=1$ to the point E, and (5b) from E to $x_{2l}=1$.

21. (i) Let the suffices l and s indicate the liquid and the solid phase, respectively. Using (4.34), we can express the condition for equilibrium as

$$\left.\begin{aligned} \bar{G}^0_{1l} + RT\log x_{1l} &= \bar{G}^0_{1s} + RT\log x_{1s}, \\ \bar{G}^0_{2l} + RT\log x_{2l} &= \bar{G}^0_{2s} + RT\log x_{2s}. \end{aligned}\right\} \tag{1}$$

Through the introduction of λ_1 and λ_2, defined in the solution to problem 20, (1) can be rewritten as

$$\frac{x_{1l}}{x_{1s}} = e^{\lambda_1}, \qquad \frac{x_{2l}}{x_{2s}} = e^{\lambda_2}. \tag{2}$$

Recalling that

$$x_{1l} + x_{2l} = 1, \qquad x_{1s} + x_{2s} = 1, \tag{3}$$

we have from (2)

$$x_{1l}\,e^{-\lambda_1} + x_{2l}\,e^{-\lambda_2} = 1, \qquad \text{or} \qquad x_{2l} = \frac{1-e^{-\lambda_1}}{e^{-\lambda_2}-e^{-\lambda_1}}, \tag{4}$$

$$x_{1s}\,e^{\lambda_1} + x_{2s}\,e^{\lambda_2} = 1, \qquad \text{or} \qquad x_{2s} = \frac{e^{\lambda_1}-1}{e^{\lambda_1}-e^{\lambda_2}}. \tag{5}$$

(ii) By assumption (b), λ_i has the form given in the eq. (4) of the solution to problem 20. By assumption (a)

$$\lambda_i = \alpha(1 - T_i/T), \tag{6}$$

and by the assumption (c), $\lambda_i \ll 1$. From (4) and (5) we get

$$x_{2l} = \frac{\lambda_1}{\lambda_1-\lambda_2}\{1 + \tfrac{1}{2}\lambda_2 + \tfrac{1}{12}\lambda_2(\lambda_1+\lambda_2) + \cdots\}, \tag{7}$$

$$x_{2s} = \frac{\lambda_1}{\lambda_1-\lambda_2}\{1 - \tfrac{1}{2}\lambda_2 + \tfrac{1}{12}\lambda_2(\lambda_1+\lambda_2) + \cdots\}. \tag{8}$$

Using (6), we obtain finally

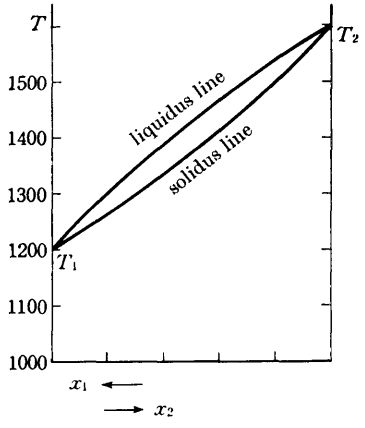
$$x_{2l} = \frac{T-T_1}{T_2-T_1} - \frac{1}{2}\frac{(T_2-T)(T-T_1)}{T(T_2-T_1)} + \cdots, \tag{9}$$

$$x_{2s} = \frac{T-T_1}{T_2-T_1} + \frac{1}{2}\frac{(T_2-T)(T-T_1)}{T(T_2-T_1)} + \cdots. \tag{10}$$

We know from these equations that if $T_1 < T_2$

$$T_1 \leqq T \leqq T_2, \qquad x_{2l} < x_{2s}.$$

The figure shows the result of the calculation from (9) and (10) for $T_1 = 1200$ °K, $T_2 = 1600$ °K and $\alpha = 1$. This is similar to the phase diagram of the Cu–Ni alloy illustrated in problem 21 (p. 233).



22. Let the Helmholtz free energy of the mixture of ideal gases A, B,... (n_A, n_B,... moles) in a volume V at a temperature T be

$$F(V, T, n_A, n_B, \ldots).$$

If the variations of n_A, n_B,... for a variation of the advancement of the reaction are taken to be

$$\delta n_A = \nu_A \, \delta\lambda, \qquad \delta n_B = \nu_B \, \delta\lambda,$$

the equilibrium condition may be written as

$$\left(\frac{\partial F}{\partial \lambda}\right)_{V,T} = 0,$$

or

$$\sum_{j=A,B,\cdots} \left(\frac{\partial F}{\partial n_j}\right)_{V,T} \delta n_j = \left(\sum_{j=A,B,\cdots} \nu_j \bar{G}_j\right) \cdot \delta\lambda = 0,$$

and hence

$$\sum \nu_j \bar{G}_j = 0. \tag{1}$$

This is the same as (4.63). The chemical potential expressed as a function

of concentration n_j/V has the form

$$\bar{G}_j = \bar{G}_j^0(T) + RT \log \frac{n_j RT}{V}.$$

Hence we have

$$\prod_{j=A,B,\ldots} \left(\frac{n_j}{V}\right)^{\nu_j} = (RT)^{-\Sigma\nu_j} \exp\left[-\frac{\sum \nu_j \bar{G}_j^0(T)}{RT}\right] \equiv K_c(T). \tag{2}$$

The left-hand side is nothing but the given expression if one puts $\nu_A = -a$, $\nu_L = l, \ldots$ etc.

NOTE: $K_c(T)$ and $K_p(T)$, defined by

$$K_p = \prod p_j^{\nu_j} \equiv K_p(T), \tag{3}$$

are related by

$$K_p(T) = (RT)^{\Sigma\nu_j} K_c. \tag{4}$$

Eq. (2) or (3) is called the *reaction isotherm.*

23. By (4.65), one obtains

$$\log K_p = -\frac{\Delta\bar{G}}{RT} = -\frac{1}{RT}\sum \nu_j \bar{G}_j^0(T),$$

and hence

$$\frac{\mathrm{d}\log K_p}{\mathrm{d}T} = -\frac{\mathrm{d}}{\mathrm{d}T}\frac{\Delta\bar{G}}{RT} = \frac{\Delta\bar{H}}{RT^2},$$

where $\Delta\bar{H} = \sum \nu_j \bar{H}_j^0$ is the standard enthalpy of reaction ((4.64b)). By eq. (2) of the solution to problem 22, we obtain

$$\log K_c = -\frac{1}{RT}\sum \nu_j(\bar{G}_j^0 + RT \log RT),$$

and hence

$$\frac{\mathrm{d}\log K_c}{\mathrm{d}T} = \frac{1}{RT^2}\sum \nu_j \bar{H}_j^0 - \frac{\sum \nu_j}{T} = \frac{1}{RT^2}\sum \nu_j(\bar{H}_j^0 - RT).$$

At a temperature T and the standard pressure p_j^0, we may use $p_j^0 \bar{V}_j^0 = RT$ (per mole). Then we have

$$\bar{H}_j^0 - RT = \bar{U}_j^0,$$

and hence

$$\Delta\bar{U} \equiv \sum \nu_j \bar{U}_j^0,$$

where $\Delta\bar{U}$ is the standard internal energy of reaction.

24. According to eq. (1.14),

$$[A] + [A_2] = \frac{p}{RT} = \frac{1.013 \times 10^6}{8.31 \times 10^7 \cdot (273 + 18)} = 4.19 \times 10^{-5}\ \text{mol/cm}^3.$$

Eliminating $[A_2]$ from this equation and the equation for K given in the problem, we obtain $[A]^2 = (4.19 \times 10^{-5} - [A]) \times 1.70 \times 10^{-4}$, or

$$[A] = 3.5 \times 10^{-5}\ \text{mol/cm}^3.$$

Therefore the degree of dissociation becomes

$$\frac{[A]}{[A] + 2[A_2]} = \frac{3.5}{2 \times 4.2 - 3.5} = 0.71.$$

To answer the second question, we use the reaction isochore derived in the preceding problem, $d \log K/dT = \Delta\bar{U}/RT^2$:

$$\frac{d \log K}{dT} = \frac{5.0 \times 10^4 \cdot 4.2 \times 10^7}{8.3 \times 10^7 \cdot (273 + 18)^2} = 0.30,$$

and thus

$$\log \frac{K(19\ ^\circ\text{C})}{K(18\ ^\circ\text{C})} = 0.30, \qquad \text{whence} \qquad K(19\ ^\circ\text{C}) = 1.35K(18\ ^\circ\text{C}).$$

Hereafter, we proceed in parallel with the calculation done above, to obtain $[A]^2 = (4.18 \times 10^{-5} - [A]) \times 1.35 \times 1.70 \times 10^{-4}$, and thus

$$[A] = 3.6 \times 10^{-5}\ \text{mol/cm}^3, \qquad \text{whence} \qquad \frac{[A]}{[A] + 2[A_2]} = 0.75.$$

25. The point is to determine the equilibrium condition of the reaction A_2 (gas)$\rightleftarrows$2A(in C). The condition is obviously $\bar{G}_{A_2(\text{gas})} = 2\bar{G}_{A(c)}$. According to eqs. (4.14′) and (4.34), this may be written as

$$\log p_{A_2} = 2 \log x_A + f(T),$$

($f(T)$ being a certain function of the temperature). Thus we obtain

$$x_A \propto p_{A_2}^{\frac{1}{2}}.$$

26. The equilibrium condition for the chemical reaction $CaCo_3(c) \rightleftarrows CaO(c) + CO_2(g)$:

$$\bar{G}_{CaCO_3(c)} = \bar{G}_{CaO(c)} + \bar{G}_{CO_2(g)}$$

may be written, if the pressure dependence of the chemical potentials for

$CaCO_3$ and CaO is neglected, in the following form:

$$RT \log p_{CO_2} = \bar{G}^0_{CaCO_3} - \bar{G}^0_{CaO} - \bar{G}^0_{CO_2(g)} = -\Delta\bar{G},$$

and therefore

$$\frac{d \log p_{CO_2}}{dT} = -\frac{d}{dT}\left(\frac{\Delta\bar{G}}{RT}\right) = \frac{\Delta\bar{H}_T}{RT^2}.$$

Here we have used eq. (4.14′), and $\Delta\bar{H}_T$ denotes the standard enthalpy change, and is evaluated by making use of the given formula to be

$$\Delta\bar{H}_T = 51.957 - 10.707\ T \text{ cal}.$$

27. Since the reaction under consideration contains pure substances only, the free energies of reaction are the same as the standard free energies of reaction, and hence

$$\begin{aligned}\Delta G &= \bar{G}^0_{AgCl(c)} + \bar{G}^0_{Hg(l)} - \bar{G}^0_{Ag(c)} - \tfrac{1}{2}\bar{G}^0_{Hg_2Cl_2(c)}\\ &= \Delta\bar{G} = -\mathfrak{F}\cdot E.\end{aligned}$$

From the observed values of E and $(\partial E/\partial T)_p$, $\Delta\bar{G} = -23068 \times 0.0455 = -1050$ cal, and

$$\Delta\bar{S} = \mathfrak{F}(\partial E/\partial T)_p = 23068 \times 0.000338 = 7.80 \text{ cal/deg},$$

so that

$$\Delta\bar{H} = \Delta\bar{G} + T\Delta\bar{S} = -1050 + 298.16 \times 7.80 = 1276 \text{ cal}.$$

28. According to the given data, the entropy of mercury gas is found to be

$$\bar{S}_{gas}(630°, 1 \text{ atm}) = \left(59.9 + \frac{2330}{234.2} + 26.2 + \frac{59300}{630}\right) \times 10^7 =$$
$$= 190.1 \times 10^7 \text{ erg/mol}\cdot\text{deg}.$$

From eqs. (4.14′) and (4.15), the entropy per mole is given by

$$\bar{S}(T, p) = R\left\{\tfrac{5}{2}\log T - \log p + \tfrac{5}{2} + i\right\}$$

(we have assumed that $C^0_p = \frac{5}{2}R$). The third law of thermodynamics requires that the latter value of the entropy at $T = 630$ °K and $p = 1$ atm should agree with the former value. Thus we have $190.1 \times 10^7/8.32 \times 10^7 = 16.1 - 0 + 2.5 + i$, or

$$i = 4.2 \text{ (atm)}.$$

The value convenient for the use of the common logarithms $j = i/\log 10$ is called the conventional chemical constant:

$$j = 1.83 \text{ (atm)}.$$

NOTE: The molecular theoretical expression given by Tetrode and Sackur is

$$i = \log\left[(2\pi m)^{3/2}k^{5/2}\omega h^{-3}\right],$$

where h is Plancks' constant, m the atomic mass, k Boltzmann's constant, and ω the statistical weight of the ground state of the atom. The value obtained above agrees well with the value calculated from the above expression by putting $\omega = 1$. Note that the unit of pressure is atm.

29. The chemical potential of the electron gas outside the metal is given, according to eqs. (4.14′) and (4.15), by

$$\bar{G}_e(T, p) = U_{e0} - \tfrac{5}{2}RT\log T - RTi + RT\log p.$$

The chemical potential within the metal $\bar{G}_i$ is constant, by assumption. From the equilibrium condition $\bar{G}_e = \bar{G}_i$, we thus obtain

$$p = e^i T^{5/2}\exp(-W/RT),$$

where $W = U_{e0} - \bar{G}_i$ is a constant. Since $\log(p/T^{\frac{5}{2}}) = i - W/RT$, we can determine i as the intersection of the ordinate and a straight line passing through the observed values plotted in a $(1/T, \log(p/T^{\frac{5}{2}}))$ plane: $i = \lim_{T\to\infty}\log(p/T^{\frac{5}{2}})$.

30. The net reaction of this cell is

$$\tfrac{1}{2}H_2(g) + AgCl(c) \rightarrow Ag(c) + HCl(aq, x)$$

and hence the free energy of reaction is given by

$$\Delta\bar{G} = \bar{G}_{Ag(c)} + \bar{G}_{HCl(aq)} - \tfrac{1}{2}\bar{G}_{H_2(g)} - \bar{G}_{AgCl(c)}.$$

In this expression we may use for Ag(c) and AgCl (c) the chemical potentials at standard pressure $\bar{G}^0_{Ag(c)}$ and $\bar{G}^0_{AgCl(c)}$. If we use eq. (4.14′) for $\bar{G}_{H_2(g)}$ and eq. (4.52) for $\bar{G}_{HCl(aq)}$, we obtain

$$\begin{aligned}\Delta\bar{G} &= \bar{G}^0_{Ag(c)} + \phi^0_{HCl} + 2RT\log(x\bar{\gamma}) - \tfrac{1}{2}(\bar{G}^0_{H_2(g)} + RT\log p_{H_2}) - \bar{G}^0_{AgCl(c)}\\ &= \Delta\bar{G}^0 + 2RT\log(x\bar{\gamma}) - RT\log p^{\frac{1}{2}}_{H_2}.\end{aligned}$$

Remembering eq. (4.71), we arrive at the electromotive force of the required form, where we introduce

$$\begin{aligned}E^0 &= -\Delta\bar{G}^0/\mathfrak{F}\\ &= [\bar{G}^0_{AgCl(c)} + \tfrac{1}{2}\bar{G}^0_{H_2(g)} - \bar{G}^0_{Ag(c)} - \phi^0_{HCl}]/\mathfrak{F}.\end{aligned}$$

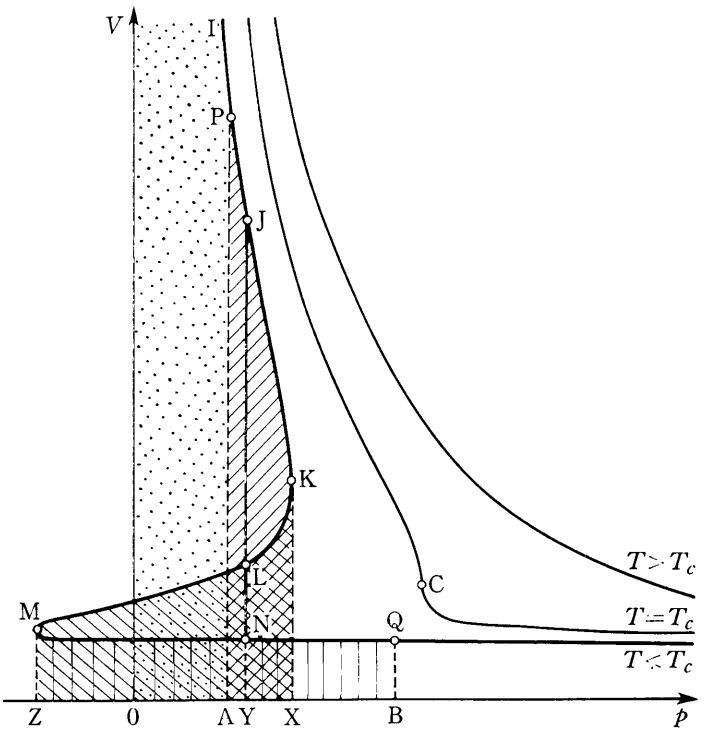
31. For the Gibbs free energy $G(p, T)$ we have $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$, where p, V and T denote the pressure, volume and temperature of the system. Then the pressure dependence of G is determined by

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \qquad \text{or} \qquad G(p, T) = \int_0^p V(p, T)\,\mathrm{d}p + \varphi(T). \tag{1}$$

$\varphi(T)$ is a function of T only. The volume V is obtained by solving the van der Waals equation of state

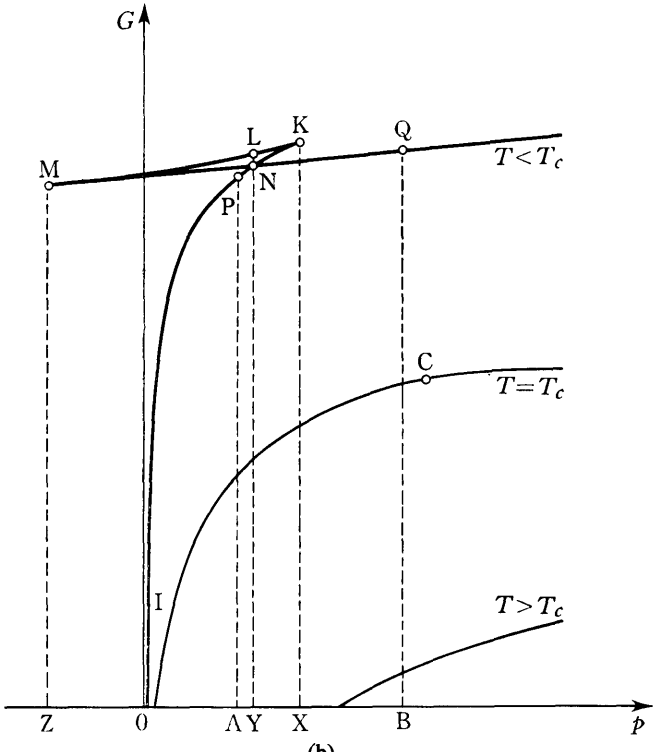
$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}. \tag{2}$$

It is not easy to solve this algebraically with respect to V for a temperature lower than the critical temperature $T_c = 8a/(27bR)$. In order to get an idea of the pressure dependence of G, it is convenient to use the fact that the right-hand member of eq. (1), except for the last term $\varphi(T)$, agrees with the area below the isotherm and above the p-axis in the p–V plane, as shown below.



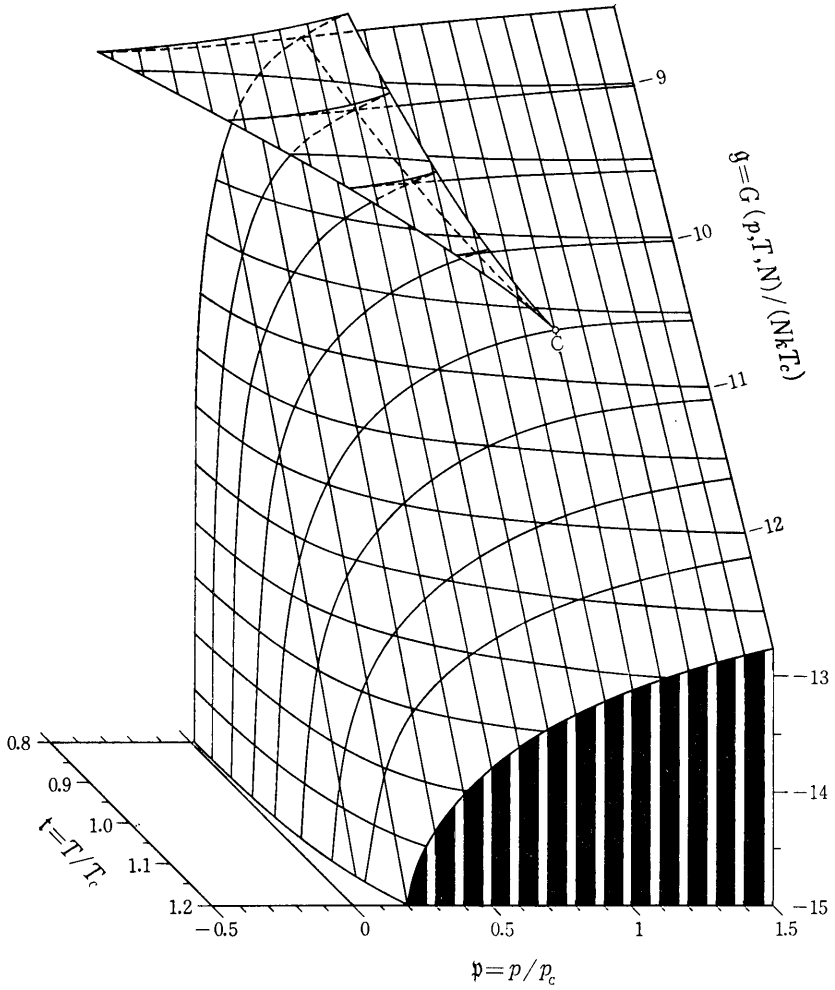
(a)

In figure (a), isotherms are drawn according to eq. (2). According to eq. (1), the value of the Gibbs free energy at a point P is equal to the area below the isotherm IP, i.e. to the area IPAOI (I being the point where the isotherm approaches the V-axis), in addition to $\varphi(T)$. This value is shown by the length PA in figure (b). As the point P moves along the isotherm and reaches the point K, the value of G increases and becomes the area IKXOI plus $\varphi(T)$, or KX in figure (b). When the point P moves further along the isotherm, the isotherm turns towards the negative p-axis. This means $dp<0$, and we have to give a negative sign to the corresponding area in eq. (1). At a point L, the Gibbs free energy decreases from the value at the point K by the area KXYLK, and at a point M by the area KXZMLK. Since the isotherm turns again towards the positive direction of the p-axis from the point M, the Gibbs free energy increases again, and reaches at the point Q the area QBZMNQ plus the value at point M, which is shown by QB in figure (b). Thus we obtain the curve of G against p, including KLM corresponding to the unstable state, by making faithful use of the van der Waals



(b)

equation. However, in stable equilibrium, the isotherm is not the curve JKLMN but the straight line JLN, which is drawn in parallel to the V-axis in such a way that the area JKLJ equals the area LNML in accordance with Maxwell's rule. The gas corresponding to the point J is in equilibrium with the liquid corresponding to the point N. Since Maxwell's rule is derived by the condition that the values of the Gibbs free energy at the points J and N coincide with each other, the points J and N are the same in figure (b).



The free energy as function of T and p, all quantities being expressed in reduced units. (The atomic mass of argon is used to evaluate the chemical constant.)

Therefore, if we apply eq. (1) to the new isotherm IPJLNQ, we obtain the curve IPNQ in figure (b). When the point P moves from J to N, the increasing rate of the area makes a jump, so that the G-curve has a kink, at the point J. It is clear that the parts JK and MN of the G-curve obtained from the van der Waals equation correspond to the metastable gas and liquid, respectively. For $T > T_c$, the G-curve becomes a smooth monotonically increasing function of p. At $T = T_c$, the G-curve is smooth at the critical point as it is reached from the high temperature side, while the G-curve has a kink when it is reached from the low temperature side.

When the gas is quasi-statically compressed at $T < T_c$, the density increases rapidly as the volume decreases, because the quantity of the material is kept constant, and liquefaction begins when the point J is reached. If some part of the gas is liquefied, our system becomes a one-component two-phase system. G obtained above is the Gibbs free energy of the whole system including gas and liquid, and is kept constant until the liquefaction ends. This is the reason why the point does not move in the p–G diagram, whereas it moves from the point J to the point N in the p–V diagram. When all the material contained in the system is liquefied, the point N is reached. If the pressure is increased further, the system is compressed as a liquid. The increase in the Gibbs free energy is the result of the supply of work and heat from the surroundings during the compression.

32. The heat of transition is given by the difference in enthalpies per mole: $L = \bar{H}_1 - \bar{H}_2$. Remembering $\bar{G}_1 = \bar{G}_2$, we have $L = T(\bar{S}_1 - \bar{S}_2)$. In the expression

$$\frac{\mathrm{d}L}{\mathrm{d}T} = \left(\frac{\partial L}{\partial T}\right)_p + \left(\frac{\partial L}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T},$$

$\mathrm{d}p/\mathrm{d}T$ is determined by the Clapeyron-Clausius equation: $\mathrm{d}p/\mathrm{d}T = L/T(\bar{V}_1 - \bar{V}_2)$. The other derivatives are obtained in the following way:

$$\left(\frac{\partial L}{\partial T}\right)_p = \frac{\partial(\bar{H}_1 - \bar{H}_2)}{\partial T} = C_{p_1} - C_{p_2},$$

$$\left(\frac{\mathrm{d}L}{\mathrm{d}p}\right)_T = \frac{\partial(\bar{H}_1 - \bar{H}_2)}{\partial p} = \bar{V}_1 - \bar{V}_2 + T\frac{\partial(\bar{S}_1 - \bar{S}_2)}{\partial p}.$$

Making use of the Maxwell relation $\partial\bar{S}/\partial p = -\partial\bar{V}/\partial T$, we have

$$\frac{\partial(\bar{S}_1 - \bar{S}_2)}{\partial p} = -\bar{V}_1\beta_1 + \bar{V}_2\beta_2,$$

and thus
$$\frac{\mathrm{d}L}{\mathrm{d}T} = C_{p_1} - C_{p_2} + \frac{L}{T} - \frac{L(\bar{V}_1\beta_1 - \bar{V}_2\beta_2)}{\bar{V}_1 - \bar{V}_2}.$$
Especially, if the phase 2 is an ideal gas, $\beta_2 = 1/T$ and $\bar{V}_1 \ll \bar{V}_2$, and therefore
$$\frac{L(\bar{V}_1\beta_1 - \bar{V}_2\beta_2)}{(\bar{V}_1 - \bar{V}_2)} \fallingdotseq \frac{L}{T}.$$
This gives $\mathrm{d}L/\mathrm{d}T \fallingdotseq C_{p1} - C_{p2}$.

33. Calculate $c = T\,\mathrm{d}s/\mathrm{d}T$ along the equilibrium line (the saturated vapor pressure curve) $p = p(T)$, or $c = T(\partial s/\partial T)_p + T(\partial s/\partial p)_T\,\mathrm{d}p/\mathrm{d}T$. Substituting Maxwell's relation $\partial s/\partial p = -\partial v/\partial T = -v\beta$ (β being the coefficient of thermal expansion) and the Clapeyron-Clausius equation $\mathrm{d}p/\mathrm{d}T = r/T(v^g - v^l)$, we obtain $c = c_p^g - v^g\beta r/(v^g - v^l)$. Making use of the fact that $v^g \gg v^l$ and of the ideal gas approximation $\beta = T^{-1}$, we arrive at $c = c_p^g - r/T$, which can be rewritten as $c = c_p^l + \mathrm{d}r/\mathrm{d}T - r/T = c_p^l + T\,\mathrm{d}(r/T)/\mathrm{d}T$, if we remember the approximate equation given in problem 32.

For water at 100 °C, we obtain a negative specific heat $c = -1.07$ cal deg^{-1}g^{-1} by inserting the values given in the problem. This means that, if an amount of heat is removed, the temperature of water vapor rises so as to keep thermal equilibrium with the water.

If we do not make an ideal gas approximation, there is an additional term $-rv^l\beta^l(v^g - v^l)$, and $c_s^g = c_s^l + T\,\mathrm{d}(r/T)/\mathrm{d}T$ is obtained. Here, c_s denotes the specific heat along the equilibrium line. However, the difference is of the order of 5×10^{-5} cal deg^{-1}g^{-1} for water, and may be neglected.

34. (i) If we denote the pressure within the liquid drop by p', the condition of mechanical balance (4.9) requires that
$$p' - p = 2\gamma/r. \tag{1}$$
The equilibrium condition concerning the exchange of material between the drop and the vapor is given by eq. (4.10′):
$$\mu_l\left(T, p_r + \frac{2\gamma}{r}\right) = \mu_g(T, p_r), \tag{2}$$
where p_r stands for the pressure of the vapor in balance with a drop of radius r, i.e. the saturated vapor pressure of the liquid drop. The usual saturated vapor pressure p_s is represented in this notation as $p_s = p_\infty$, and satisfies
$$\mu_l(T, p_\infty) = \mu_g(T, p_\infty). \tag{3}$$

From eqs. (2), (3) and (4.14), we obtain

$$\mu_l\left(p_r + \frac{2\gamma}{r}\right) - \mu_l(p_\infty) = kT \log\frac{p_r}{p_\infty}. \tag{4}$$

Remembering the fact that it is difficult to compress the liquid and that therefore the free energy of the liquid changes only slightly when the pressure is changed, and expanding the left-hand side of eq. (4)

$$\mu_l(p_r + 2\gamma/r) = \mu_l(p_\infty + p_r - p_\infty + 2\gamma/r)$$

with respect to

$$p_r - p_\infty + 2\gamma/r,$$

we obtain

$$\left(p_r - p_\infty + \frac{2\gamma}{r}\right) v_l = kT \log\frac{p_r}{p_\infty}, \tag{5}$$

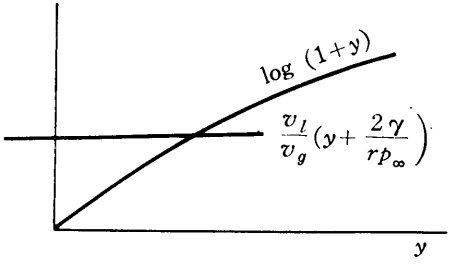
or

$$\log\frac{p_r}{p_\infty} = \frac{v_l p_\infty}{kT}\left(\frac{p_r}{p_\infty} - 1 + \frac{2\gamma}{r p_\infty}\right), \tag{6}$$

where we have used $\partial\mu_l/\partial p = v_l$. If we denote the specific volume of the vapor at pressure p_∞ and temperature T by v_g, we have $v_l p_\infty/kT = v_l/v_g \ll 1$. By writing $p_r/p_\infty = 1 + y$, (6) can be rewritten as

$$\log(1 + y) = (v_l/v_g)(y + 2\gamma/r p_\infty). \tag{6'}$$

Since v_l/v_g is usually a small quantity of the order of $10^{-3} \sim 10^{-4}$, we may neglect y in the parentheses on the right-hand member of eq. (6′) in order to determine the point of intersection of the functions on both sides (the



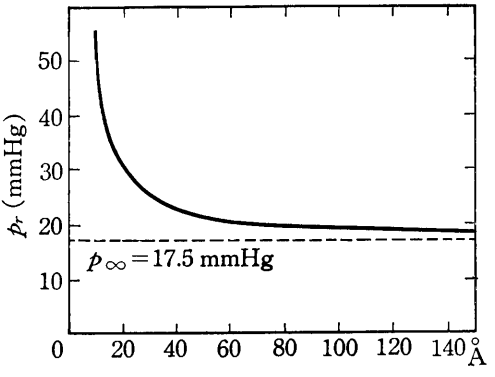
right-hand member represents an almost horizontal straight line; see the figure). This procedure is equivalent to approximating eq. (6) as

$$\log\frac{p_r}{p_\infty} = \frac{2v_l\gamma}{rkT}. \tag{7}$$

From eq. (7), we obtain

$$p_r = p_\infty \exp \frac{2v_l\gamma}{rkT}. \tag{8}$$

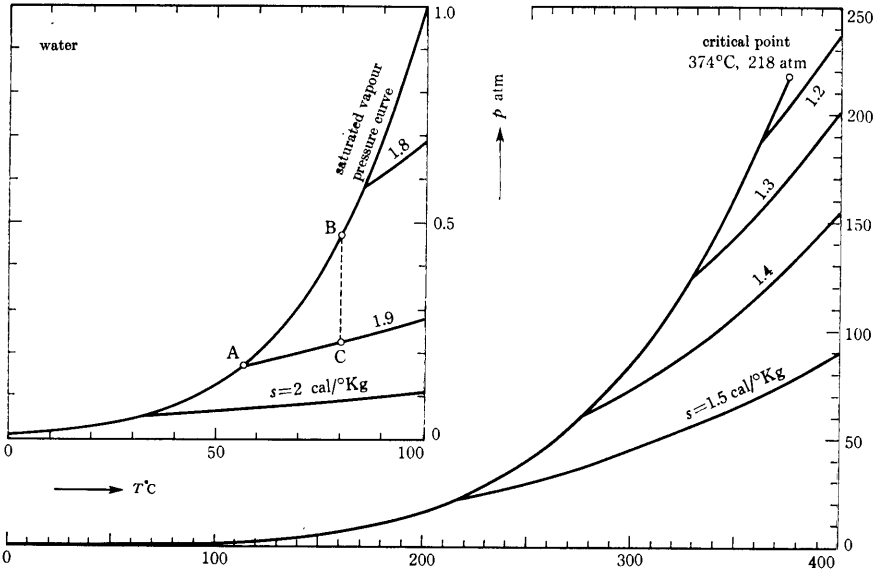
As an example, the relation between the vapor pressure and the radius of water drop at 20 °C is shown in the following figure.



(ii) The critical radius r_c is determined by $p = p_r = p_\infty \exp\{2v_l\gamma/rkT\}$ for a given $p > p_\infty$. Since the liquid drop having a radius smaller than r_c has a vapor pressure higher than p, such a drop, if it existed, would be vaporized. Thus r_c is the smallest radius with which a liquid drop can be stable.

NOTE: For this reason, a liquid drop cannot easily be produced in a vapor in which there are no nuclei for condensation, and the vapor is apt to become supersaturated. If there are fine particles like dust particles, liquid drops are produced around those particles under a vapor pressure higher than p_r, corresponding to the particle radius r.

35. In the following figure, AB denotes the saturated vapor pressure curve. The negative specific heat of the saturated vapor means that the entropy of vapor A is larger than that of vapor B. On the other hand, if the pressure is lowered along the isotherm from B, the entropy obviously increases $((\partial s/\partial p)_T = -(\partial v/\partial T)_p < 0)$, and the value of entropy at a state C on the isotherm agrees with that at A. Thus the isentropic line AC has a gentler slope than that of the supersaturated vapor pressure curve AB. This result can also be reached by comparing the Clapeyron-Clausius equation $\mathrm{d}p/\mathrm{d}T = L/T(v_g - v_l)$ with the equation $(\partial p/\partial T)_s = c_p/T(\partial v/\partial T)_p$. Remembering problem 33, show that the latter method is equivalent to determining the sign of the specific heat of



supersaturated vapor. Now we see that, if the Wilson chamber is suddenly expanded and the saturated vapor is expanded adiabatically, the state of the vapor passes along CA into a state of supersaturated vapor on the left of AB. NOTE: As was shown in the preceding problem, a liquid drop cannot easily be produced even in a supersaturated state, when there are no nuclei. If some radiation passes through the chamber and ions are produced along the path, and if the chamber is adiabatically expanded immediately afterwards to produce a supersaturated vapor, those ions act as nuclei for condensation and fog drops appear. Thus we can observe the path of radiation by the Wilson chamber. (See problem 49 for the reason why ions act as nuclei.)

36. (i) According to the solutions of problem 24 of Chapter 1 and of problem 29 of Chapter 3, the free energy per unit volume, including the energy of magnetic field, is given by $F/V = F_0(T)/V + (1/4\pi)\int H\,dB$, where $F_0(T)$ denotes the value for $H=0$ and $B=0$. In the present case, it is more convenient to use

$$G(H, T) = F - V\frac{BH}{4\pi} \tag{1}$$

in place of F, for H is considered as one of the independent variables. The Meissner effect is represented by the relations

$$B(H) = 0 \qquad \text{if} \qquad |H| < H_c$$

and

$$B(H) = H \qquad \text{if} \qquad |H| > H_c.$$

Thus we obtain

$$G_s = F_0(T) - \frac{V}{4\pi}\int_0^H B\,\mathrm{d}H = F_0(T) \qquad \text{if} \qquad |H| < H_c, \tag{2}$$

$$G_n = F_0(T) - \frac{V}{4\pi}\int_0^H B\,\mathrm{d}H = F_0(T) - \frac{V}{8\pi}(H^2 - H_c^2) \qquad \text{if} \qquad |H| \geqq H_c, \tag{3}$$

so that

$$S_s - S_n = -\frac{\partial G_s}{\partial T} + \frac{\partial G_n}{\partial T} = \frac{V}{8\pi}\frac{\mathrm{d}H_c^2}{\mathrm{d}T}, \qquad \text{or} \qquad Q = T(S_n - S_s) = -\frac{V}{8\pi}\frac{\mathrm{d}H_c^2}{\mathrm{d}T}. \tag{4}$$

(ii) For the heat capacity of the whole system of volume V, we have

$$C_n - C_s = T\frac{\partial(S_n - S_s)}{\partial T} = -\frac{TV}{8\pi}\mathrm{d}^2H_c^2/\mathrm{d}T^2$$

$$= -\frac{TV}{8\pi}\left\{2\left(\frac{\mathrm{d}H_c}{\mathrm{d}T}\right)^2 + 2H_c\frac{\mathrm{d}^2H_c}{\mathrm{d}T^2}\right\}. \tag{5}$$

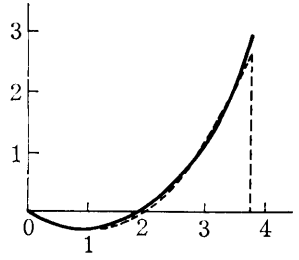
Putting $T = T_0$ and $H_c = 0$, and converting into the value per mole, we obtain

$$C_n - C_s = -\frac{T\bar{V}}{4\pi}\left(\frac{\mathrm{d}H_c}{\mathrm{d}T}\right)^2 \qquad (T = T_0). \tag{6}$$

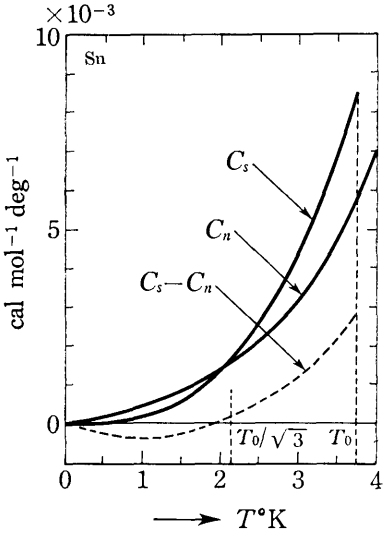
(iii) If we assume $H_c = H_0\{1 - (T/T_0)^2\}$, we obtain from eq. (5)

$$C_n - C_s = \frac{\bar{V}TH_0^2}{2\pi T_0^2}\left\{1 - 3\left(\frac{T}{T_0}\right)^2\right\}. \tag{7}$$

This value is plotted in the figure by the broken line (the full-drawn line corresponds to the experimental value).



NOTE: Typical graphs of C_n and C_s are shown in the second figure.



37. Let us denote the concentration x_1 or x_2 by x, and distinguish between the gaseous phase and the liquid phase by the suffixes g and l, respectively. The gaseous line $x_g(T)$ and the liquidus $x_l(T)$ are determined by

$$\left.\begin{aligned} \bar{G}_{1g}(T, x_g) &= \bar{G}_{1l}(T, x_l), \\ \bar{G}_{2g}(T, x_g) &= \bar{G}_{2l}(T, x_l). \end{aligned}\right\} \tag{1}$$

Their behavior near the azeotropic point $(T^0, x_g^0 = x_l^0)$ can be seen by inserting $T = T^0 + \delta T$, $x_g = x_g^0 + \delta x_g$, and $x_l = x_l^0 + \delta x_l$ into eq. (1), and by determining the relation among δT, δx_g and δx_l. Expanding in powers of δT, δx_g and δx_l, and retaining only the linear terms, we obtain from eq. (1)

$$-\bar{S}_{1g}\,\delta T + \frac{\partial \bar{G}_{1g}}{\partial x_g}\,\delta x_g = -\bar{S}_{1l}\,\delta T + \frac{\partial \bar{G}_{1l}}{\partial x_l}\,\delta x_l, \tag{2a}$$

$$-\bar{S}_{2g}\,\delta T + \frac{\partial \bar{G}_{2g}}{\partial x_g}\,\delta x_g = -\bar{S}_{2l}\,\delta T + \frac{\partial \bar{G}_{2l}}{\partial x_l}\,\delta x_l, \tag{2b}$$

where we have used $\partial \bar{G}/\partial T = -\bar{S}$, and denoted by $\bar{S}_{1g}, \ldots, \mathrm{d}\bar{G}_{1g}/\mathrm{d}x_g, \ldots$ their values at the azeotropic point. Remembering the Gibbs-Duhem relations $-\bar{S}_l\,\mathrm{d}T + x_{1l}\,\mathrm{d}\bar{G}_{1l} + x_{2l}\,\mathrm{d}\bar{G}_{2l} = 0$, and $-\bar{S}_g\,\mathrm{d}T + x_{1g}\,\mathrm{d}\bar{G}_{1g} + x_{2g}\,\mathrm{d}\bar{G}_{2g} = 0$, we can determine δT as follows. In order to eliminate δx_l, say, we multiply eq. (2a) by x_{1l}^0 and eq. (2b) by x_{2l}^0 and add together the results to obtain

$-(x_{1l}^0\bar{S}_{1l}+x_{2l}^0\bar{S}_{2l})\,\delta T=-\bar{S}_{1l}\,\delta T$ for the right-hand member, and $-\bar{S}_{1g}\,\delta T$ for the left-hand member, remembering $x_{1l}^0=x_{1g}^0$ and $x_{2l}^0=x_{2g}^0$. Since $\bar{S}_{1g}-\bar{S}_{1l}\neq 0$, we arrive at $\delta T=0$. This result means that δT is a quantity of at least second order along the gaseous line and the liquidus.

38. Let the cross-sectional area of the rod be equal to 1, and the impurity concentration in the liquid part of the rod be $C_m(x)$, when the rod is solidified up to a distance x from its left end. Then, when the solidification proceeds further over a distance dx, the amount of impurity removed from the liquid part is given by $kC_m(x)dx$. This amount should be the change $d\{C_m(x)(L-x)\}$ of the quantity of impurity in the liquid phase $C_m(x)(L-x)$, and therefore

$$d\{C_m(x)(L-x)\} = -kC_m(x)\,dx,$$

$$\frac{dC_m}{dx}\cdot(L-x) = -(k-1)\,C_m. \tag{1}$$

Integrating this equation, we obtain

$$C_m(x) = A\cdot(L-x)^{k-1} \qquad (A \text{ being a constant}). \tag{2}$$

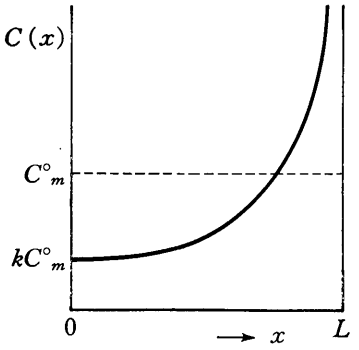
Since the impurity concentration of the initial liquid is C_m^0, we have $AL^{k-1}=C_m^0$, and thus

$$C_m(x) = C_m^0\left(1-\frac{x}{L}\right)^{k-1}. \tag{3}$$

The concentration of impurity in the solid phase precipitating at the point x becomes

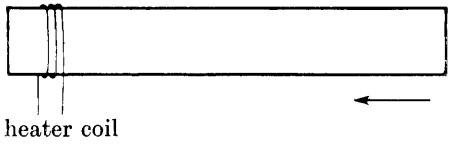
$$C(x) = kC_m(x) = kC_m^0\left(1-\frac{x}{L}\right)^{k-1}. \tag{4}$$

This value is plotted in the figure for $k<1$. (It is not correct that $C(x)\to\infty$



as $x \to L$. This error arises from the assumption of constant k, which is correct only for small C.) We see that the impurity is gathered towards the right end, and the left end of the rod becomes pure.

NOTE: *Zone refining:* in a process of purification of semi-conductor materials such as Si and Ge, a rod made of the material is made to pass through the coil of an induction heater. Then, when the part of the rod near the coil melts and re-solidifies, impurities are gathered towards the right-hand side (the molten part is kept from collapsing by the surface tension). The reason



is exactly that shown in the problem solved above. The method of obtaining very pure materials by repeating such zone melting is called the method of zone refining. Conversely, there is a case of obtaining a uniform concentration by adding impurities to a pure substance and by making use of zone melting (zone levelling).

39. (i) First, the relations between ϕ_i and the molecular fractions $x_i = N_i/\sum N_i$ are determined as

$$x_1 = r\phi_1/[r\phi_1 + \phi_2], \qquad x_2 = \phi_2/[r\phi_1 + \phi_2]. \tag{1}$$

By solving these, we have

$$\phi_1 = x_1/[x_1 + rx_2], \qquad \phi_2 = rx_2/[x_1 + rx_2]. \tag{2}$$

Now, by making use of the given expressions for $\bar{G}_i$, we obtain, under the condition of constant p and T,

$$\begin{aligned}\sum x_i \, \mathrm{d}\bar{G}_i &= [r\phi_1 + \phi_2]^{-1}\left(r\phi_1\left[RT\left\{\frac{1}{\phi_1} - \left(1 - \frac{1}{r}\right)\right\} - 2w(1-\phi_1)\right]\mathrm{d}\phi_1 + \right.\\ &\quad \left. + \phi_2\left[RT\left\{\frac{1}{\phi_2} + (r-1)\right\} - 2rw(1-\phi_2)\right]\mathrm{d}\phi_2\right)\\ &= [r\phi_1 + \phi_2]^{-1}([RT\{\phi_1 + r\phi_2\} - 2rw\phi_1\phi_2]\,\mathrm{d}\phi_1 + \\ &\quad + [RT\{\phi_1 + r\phi_2\} - 2rw\phi_1\phi_2]\,\mathrm{d}\phi_2) = 0\\ &\qquad\qquad (\text{since } \mathrm{d}\phi_1 + \mathrm{d}\phi_2 = 0).\end{aligned}$$

(ii) According to $\bar{S}_i = -\partial \bar{G}_i/\partial T$, we have

$$\bar{S}_1 = \bar{S}_1^0 - R\left\{\log \phi_1 + \left(1 - \frac{1}{r}\right)\phi_2\right\},$$
$$\bar{S}_2 = \bar{S}_2^0 - R\{\log \phi_2 - (r-1)\phi_1\},$$

and hence

$$\bar{S} = \sum x_i \bar{S}_i = \sum x_i \bar{S}_i^0 - R\left[x_1\left\{\log \phi_1 + \left(1 - \frac{1}{r}\right)\phi_2\right\} + \right.$$
$$\left. + x_2\{\log \phi_2 - (r-1)\phi_1\}\right]$$
$$= \sum x_i \bar{S}_i^0 - R[x_1 \log \phi_1 + x_2 \log \phi_2]. \tag{3}$$

In the expression for the entropy of mixing, the volume fractions ϕ_i's appear in place of the x_i's as the independent variables in the logarithmic functions, in contrast to the case of an ideal solution. If we write

$$-R[x_1 \log \phi_1 + x_2 \log \phi_2] =$$
$$= -R[x_1 \log x_1 + x_2 \log x_2] + R[\log\{1 + (r-1)x_2\} - x_2 \log r],$$

we find that this entropy is, in general, larger than that of an ideal solution when $r > 1$.

(iii) Next, by using $\bar{H}_i = \bar{G}_i + T\bar{S}_i$, we calculate the partial molar enthalpies, to obtain

$$\bar{H}_1 = \bar{H}_1^0 + w\phi_2^2, \qquad \bar{H}_2 = \bar{H}_2^0 + rw\phi_1^2,$$

and hence the heat of mixing is given by

$$\Delta \bar{H} = \sum x_i \bar{H}_i - \sum x_i \bar{H}_i^0 = w(x_1\phi_2^2 + rx_2\phi_1^2) = \frac{rx_1x_2}{x_1 + rx_2} w. \tag{4}$$

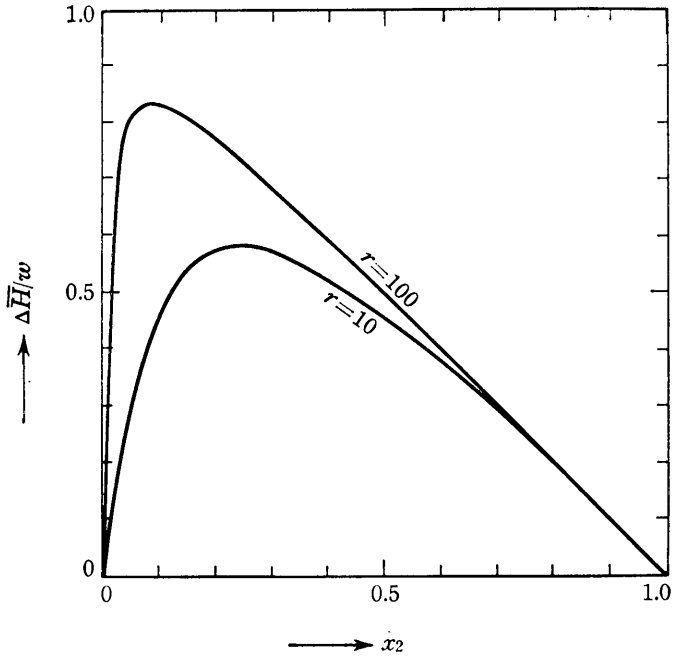
This vanishes at $x_2 = 0$ and 1, and reaches its maximum value $rw/(\sqrt{r}+1)^2$ at $x_2 = (\sqrt{r}+1)^{-1}$. Two examples for $r = 10$ and for $r = 100$ are plotted in the figure.

(iv) Finally, the vapor pressure and the osmotic pressure are computed. To calculate them, let us use the results of example 6. According to the given chemical potential, the activity of solvent a_1 is given as

$$a_1 = (1 - \phi_2)\exp\left\{\left(1 - \frac{1}{r}\right)\phi_2 + \frac{w}{RT}\phi_2^2\right\}. \tag{5}$$

Therefore we obtain

$$\frac{p_1}{p_1^0} = a_1 = (1 - \phi_2)\exp\left\{\left(1 - \frac{1}{r}\right)\phi_2 + \frac{w}{RT}\phi_2^2\right\}, \tag{6}$$



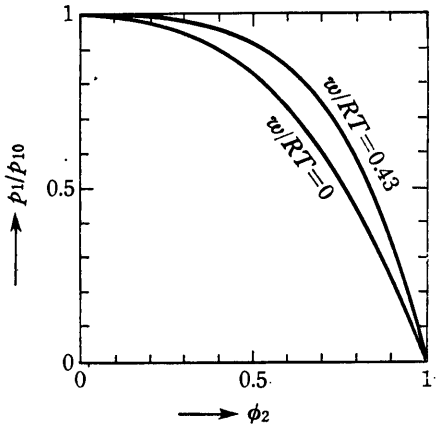
$$\begin{aligned}\frac{\pi\bar{V}_1^0}{RT} &= -\log a_1 = -\log(1-\phi_2) - \left(1-\frac{1}{r}\right)\phi_2 - \frac{w}{RT}\phi_2^2 \\ &= \frac{1}{r}\phi_2 + \left(\frac{1}{2}-\frac{w}{RT}\right)\phi_2^2 + \cdots \qquad (7)\\ &= \frac{x_2}{1+(r-1)x_2} + \left(\frac{1}{2}-\frac{w}{RT}\right)\left(\frac{rx_2}{1+(r-1)x_2}\right)^2 + \cdots \\ &\fallingdotseq x_2 + \left(\frac{1}{2}-\frac{w}{RT}\right)r^2x_2^2 + \cdots \qquad (r \gg 1).\end{aligned}$$

When the concentration is very low, van 't Hoff's law is valid as in the case of an ideal dilute solution. However, if the polymerization grade r is large, the deviation from that law occurs at relatively small mole fractions. Examples of the vapor pressure p_1/p_1^0 when $r \to \infty$ are plotted against ϕ_2 in the following figure.

40. According to the condition of electrical neutrality,

$$x'_{M^+} = x'_{X^-} \qquad (1a)$$

$$x''_{M^+} = x''_{X^-} + x_2^0, \qquad (1b)$$



although M^+ and X^- are exchanged between I and II. Also the conservation laws for M^+ and X^- require the equations

$$x'_{M^+} + x''_{M^+} = x_1^0, \qquad x'_{X^-} + x''_{X^-} = x_1^0. \tag{2}$$

On the other hand, the equilibrium condition is

$$\bar{G}_{M^+X^-(I)} = \bar{G}_{M^+X^-(II)}. \tag{3}$$

If an ideal dilute solution is assumed, the latter condition becomes

$$RT\log(x'_{M^+}x'_{X^-}) = RT\log(x''_{M^+}x''_{X^-}), \qquad \text{or} \qquad x'_{M^+}x'_{X^-} = x''_{M^+}x''_{X^-}, \tag{4}$$

where eqs. (4.33) have been used ($\phi^0_{M^+}$ and $\phi^0_{X^-}$ are the same for I and II). Substituting eqs. (1a), (1b) and (2), we obtain $(x'_{X^-})^2 = (x_1^0 - x''_{X^-})^2 = (x''_{X^-} + x_2^0)\, x''_{X^-}$, and hence

$$x''_{X^-} = \frac{x_1^{02}}{2x_1^0 + x_2^0}.$$

In the same way,

$$x'_{X^-} = \frac{x_1^0(x_1^0 + x_2^0)}{2x_1^0 + x_2^0}, \qquad \text{or} \qquad \frac{x'_{X^-}}{x''_{X^-}} = 1 + \frac{x_2^0}{x_1^0}.$$

This means that M^+X^- itself is distributed between I and II in the ratio $x_1^0 + x_2^0 : x_1^0$.

11. If the electrostatic potentials in the phases I and II are Φ_I and Φ_{II}, respectively, the electrochemical potentials are given by

$$\eta'_{M^+} = \mu'_{M^+} + e\Phi_I, \qquad \eta'_{X^-} = \mu'_{X^-} - e\Phi_I,$$
$$\eta''_{M^+} = \mu''_{M^+} + e\Phi_{II}, \qquad \eta''_{X^-} = \mu''_{X^-} - e\Phi_{II}.$$

The equilibrium conditions $\eta'_{M^+} = \eta''_{M^+}$ and $\eta'_{X^-} = \eta''_{X^-}$ give

$$\frac{x'_{M^+}}{x''_{M^+}} = \exp\left(\frac{-e(\phi_I - \phi_{II})}{kT}\right), \qquad \frac{x'_{X^-}}{x''_{X^-}} = \exp\left(\frac{e(\phi_I - \phi_{II})}{kT}\right), \tag{1}$$

where eqs. (4.33) have been used for $\mu'_{M^+}, \ldots$. Substituting the results obtained in the solution of the preceding problem into eq. (1), we obtain

$$\Phi_I - \Phi_{II} = \frac{kT}{e} \cdot \log \frac{x'_{X^-}}{x''_{X^-}} = \frac{kT}{e} \log\left(1 + \frac{x_2^0}{x_1^0}\right).$$

NOTE: From eq. (1) we can derive eq. (4) in the solution of the preceding problem, as should be the case.

42. This is also a problem concerning Donnan's membrane equilibrium. If the ionic concentrations on both sides of the membrane I and II are denoted by x'_{M^+}, x'_{X^-}, x''_{M^+}, x''_{X^-}, and x''_{R^-}, when M^+X^- is added, then the osmotic pressure is given by

$$\pi = \frac{RT}{\bar{V}}(x''_{M^+} + x''_{X^-} + x''_{R^-} - x'_{M^+} - x'_{X^-})$$

($\bar{V}$ being the molar volume of water). According to the solution of problem 40 (with $x_2^0 = x''_{R^-}$),

$$\frac{\pi \bar{V}}{RT} = 2(x''_{X^-} + x''_{R^-}) - 2x'_{X^-} = 2x''_{R^-}\left(\frac{x''_{R^-} + x_1^0}{x''_{R^-} + 2x_1^0}\right).$$

Therefore, the osmotic pressure starts from the value $(RT/\bar{V}) \cdot 2x''_{R^-}$ before the addition of M^+X^-, decreases gradually by the addition of M^+X^-, and approaches to one half of the initial value in the limit of the addition of a large amount of M^+X^-. This is an expected result. In phase II, R^-ions remain always with a concentration x''_{R^-}. Before adding M^+X^-, M^+ions do not pass through the semi-permeable membrane because of the electric attraction due to R^-ions, and remain in the phase II, so that the osmotic pressure has the value corresponding to the solution of concentration $2x''_{R^-}$. When M^+X^- is added, the differences of ionic concentrations of M^+ and X^- in the phases I and II decrease gradually (the effect of the existence of R^- ions decreases relatively), and become equal at last: the difference between the two phases comes only from the existence of R^- ions.

NOTE: It is very important in biological phenomena that a slight addition of electrolytes has a remarkable effect on the osmotic pressure in colloidal solutions of protein or starch, for instance. (Many of these colloids are so-called amphoteric electrolytes, and become either negative or positive ions according to the pH value.)

43. First let us derive the necessary relations. According to example 8, we have for a small x_2

$$\log a_1 = -\nu x_2 g = -\frac{\nu m_2 \bar{M}_1}{1000} g, \qquad g = 1 + \frac{1}{x_2}\int_0^{x_2} x_2 \frac{\partial \log \bar{\gamma}}{\partial x_2} \mathrm{d}x_2. \tag{1}$$

From example 6,

$$\Delta T = -\frac{RT_1^{02}}{L_1}\log a_1 = \nu \frac{RT_1^{02}}{L_1}\frac{\bar{M}_1 \cdot m_2}{1000} g \equiv -\nu\lambda m_2 g.$$

Inserting the values $\nu = 2$ (because $HCl \rightarrow H^+ + Cl^-$), $T_1^0 = 273.16$ deg, $L_1 = -1436$ cal/mol, and $R = 1.9870$ cal/deg mol and $\bar{M}_1 = 18.016$ g/mol into this, we obtain

$$\lambda \equiv -\frac{RT_1^{02}\bar{M}_1}{1000\,L_1} = 1.860 \text{ deg}\cdot\text{mol}^{-1}\text{ kg},$$

$$\theta = -\Delta T = 3.72\, m_2 g(\text{deg}) \qquad (m_2 \text{ in mol/kg}). \tag{2}$$

Making use of eq. (4.56) as the theoretical Debye-Hückel equation, and calculating A for $D = 88.23$, $e = 4.802 \times 10^{-10}$ e.s.u, $N_0 = 6.025 \times 10^{23}$ and $k = 1.38 \times 10^{-16}$ erg/deg, we have $A = 1.12$. Since we may put $C_2 = \rho_1 m_2 \doteqdot m_2$, we obtain

$$\log \bar{\gamma} = -\alpha\sqrt{m_2}, \qquad \alpha = 1.12. \tag{3}$$

Changing x_2 in eq. (1) to m_2:

$$g = 1 + \frac{1}{m_2}\int_0^{m_2} m_2 \frac{\partial \log \bar{\gamma}}{\partial m_2} \mathrm{d}m_2 = 1 - \frac{\alpha}{2m_2}\int_0^{m_2} m_2^{\frac{1}{2}}\, \mathrm{d}m_2$$

$$= 1 - \tfrac{1}{3}\alpha\sqrt{m_2} = 1 - 0.375\sqrt{m_2}. \tag{4}$$

Using eqs. (2) and (4), we can calculate $1-g$ from the table given in the problem to obtain the results given in the following table:

m_2 (mol·kg^{-1})	$1-g$ experiment	$1-g$ Debey-Hückel
0.627×10^{-3}	0.021	0.009
1.179	0.011	0.012
1.245	0.017	0.013
1.474	0.011	0.014
2.228	0.017	0.017
3.526	0.020	0.022
4.520	0.022	0.025
6.879	0.025	0.031
10.633	0.027	0.039

44. If the number densities of donors and of electrons are denoted by N_d and n_e, respectively, the number densities of D and D^+ are $N_d - n_e$ and n_e respectively. Making use of the ideal gas approximation for the conduction electrons ($p_e = n_e kT$), we obtain from eqs. (4.14′) and (4.15a) the chemical potential for an electron

$$\mu_e = \mu_e^0 - \tfrac{3}{2}kT \log T - kTi_e + kT \log n_e .$$

For D and D^+, according to the assumption of an ideal solid solution, we have

$$\mu_D = \mu_D^0(T, p) + kT \log \frac{N_d - n_e}{N_d},$$

$$\mu_{D^+} = \mu_{D^+}^0(T, p) + kT \log \frac{n_e}{N_d},$$

from eqs. (4.34). Therefore, in equilibrium, $\mu_D = \mu_{D^+} + \mu_e$ by eq. (4.63), and therefore

$$\frac{n_e^2}{N_d - n_e} \propto T^{\frac{3}{2}} \exp\left\{-\frac{1}{kT}(\mu_e^0 + \mu_{D^+}^0 - \mu_D^0)\right\}.$$

On the right-hand side, $\mu_e^0 + \mu_{D^+}^0 - \mu_D^0$ equals the ionization energy in the crystal E_d. Thus, when $n_e \ll N_d$, the answer becomes

$$n_e \propto N_d^{\frac{1}{2}} T^{\frac{3}{4}} \exp(-E_d/2kT).$$

45. The net reaction given in the problem is made in the two steps $Ag(l) \rightarrow Ag^+(AgCl-KCl) + e$ and $Ag^+(AgCl-KCl) + e \rightarrow Ag(Ag_xAu_{1-x})$ in the particular cell referred to in the problem. According to eq. (4.42), the electro-motive force is given by

$$\begin{aligned}\mathfrak{F}E &= \bar{G}_{Ag(Ag_xAu_{1-x})} - \bar{G}_{Ag(l)} \\ &= \bar{G}_{Ag(l)} + RT \log(x\gamma) - \bar{G}_{Ag(l)} = RT \log(x\gamma),\end{aligned}$$

where γ denotes the activity. If an ideal solution is assumed, we have $\gamma = 1$, and expect the value

$$-\frac{1.987 \times 1360}{23060} \cdot \log \frac{1}{2} = 0.082\ (V)$$

at $x = 0.5$ and $T = 1360$ °K. From the values of x and E given in the table, the values of γ are determined as given in the following table.

x	E	$\mathfrak{F}E/2.303RT$	$\log_{10} x$	$\log_{10} \gamma$	γ
0.846	0.021	0.078	− 0.072	− 0.006	0.986
0.716	0.045	0.167	− 0.145	− 0.022	0.950
0.602	0.074	0.274	− 0.220	− 0.054	0.884
0.471	0.114	0.422	− 0.327	− 0.095	0.804
0.263	0.198	0.734	− 0.580	− 0.154	0.701

46. A chemical reaction of the type

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightleftarrows l\mathrm{L} + m\mathrm{M} + \cdots \tag{1}$$

can be expressed, after eq. (4.59′), in the form

$$\sum \nu_k \mathrm{X}_k = 0 \qquad (\nu_a = -a\,, \quad \mathrm{X}_a = \mathrm{A}, \ldots). \tag{2}$$

The degree of advancement of the reaction λ is introduced by definition (4.60), where we put $\lambda = 0$ at the initial state. The Gibbs free energy of the whole system

$$G(n_\mathrm{A}, n_\mathrm{B}, \ldots, n_\mathrm{L}, \ldots) = \sum_k n_k \bar{G}_k \equiv G(\lambda)$$

is a function of λ. The chemical equilibrium is determined by the relation $(\partial G/\partial\lambda)_{p,T} = 0$, that is, by eq. (4.63):

$$(\partial \bar{G}/\partial\lambda)_{p,T} = \Delta G = \sum \nu_k \bar{G}_k = 0\,. \tag{3}$$

In order that the equilibrium be stable, $G(\lambda)$ should be a minimum at λ determined by eq. (3), i.e.,

$$(\partial^2 G/\partial\lambda^2)_{p,T} = (\partial \Delta\bar{G}/\partial\lambda)_{p,T} = \frac{\partial}{\partial\lambda}\sum \nu_k \bar{G}_k > 0\,. \tag{4}$$

(i) The change in the degree of advancement λ corresponding to a change in T at constant pressure is expressed by $(\partial\lambda/\partial T)_{p,\Delta\bar{G}}$. Note that $\Delta\bar{G}$ is kept constant at the value zero. We note that

$$\left(\frac{\partial\lambda}{\partial T}\right)_{p,\Delta\bar{G}} = \frac{\partial(\lambda, \Delta\bar{G})}{\partial(T, \Delta\bar{G})} = \frac{\partial(\lambda, \Delta\bar{G})}{\partial(\lambda, T)}\,\frac{\partial(\lambda, T)}{\partial(T, \Delta\bar{G})} = -\left(\frac{\partial\Delta\bar{G}}{\partial T}\right)_{p,\lambda} \Big/ \left(\frac{\partial\Delta\bar{G}}{\partial\lambda}\right)_{p,T}, \tag{5}$$

and that

$$\left(\frac{\partial}{\partial T}\Delta\bar{G}\right) = \frac{\partial}{\partial T}\sum \nu_k \bar{G}_k = -\sum \nu_k \bar{S}_k = -\Delta\bar{S} = -\frac{\Delta\bar{H}}{T} \tag{6}$$

(since $\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S} = 0$), where $\Delta\bar{H} = \sum \nu_k \bar{H}_k$ denotes the enthalpy change in the reaction and is written as $\partial H/\partial\lambda$ in correspondence to eq. (3). Eq. (5)

becomes

$$\left(\frac{\partial\lambda}{\partial T}\right)_{p,\Delta\bar{G}} = \frac{1}{T}\left(\frac{\partial H}{\partial\lambda}\right)_{p,T} \Bigg/ \left(\frac{\partial\Delta\bar{G}}{\partial\lambda}\right)_{p,T}. \tag{7}$$

The denominator on the right-hand side is positive, according to inequality (4), and hence $(\partial\lambda/\partial T)_{p,\Delta\bar{G}}$ and $(\partial H/\partial\lambda)_{p,T}$ have the same sign. If $\Delta\bar{H}>0$, the reaction is endothermic, and proceeds forwards (λ increases) as T increases. If $\Delta\bar{H}<0$, the reaction is exothermic, and the balance shifts in the reverse way when T is raised.

(ii) When p is changed at fixed T, we have, in a similar way,

$$\left(\frac{\partial\lambda}{\partial p}\right)_{T,\Delta\bar{G}} = -\left(\frac{\partial\Delta\bar{G}}{\partial p}\right)_{T,\lambda} \Bigg/ \left(\frac{\partial\Delta\bar{G}}{\partial\lambda}\right)_{p,T} = -\Delta\bar{V} \Bigg/ \left(\frac{\partial\Delta\bar{G}}{\partial\lambda}\right)_{p,T}, \tag{8}$$

where

$$\Delta\bar{V} = \sum \nu_k \bar{V}_k = \sum \nu_k (\partial\bar{G}_k/\partial p)_T = (\partial V/\partial\lambda)_{p,T}$$

means the volume change in the reaction. Since the denominators of eq. (8) are positive, $(\partial\lambda/\partial p)_{T,\Delta\bar{G}}$ and $\Delta\bar{V}$ have opposite signs. In the case of $\Delta\bar{V}>0$, i.e., if the volume increases as the reaction proceeds, the chemical equilibrium shifts leftwards in the reaction formula (1), while, if $\Delta\bar{V}<0$, it shifts rightwards. Thus, the reaction proceeds in such a direction that the whole volume is decreased.

47. The necessary conditions for equilibrium between the gas phase corresponding to the point E and the liquid phase corresponding to the point A are the equality of pressures p, temperatures T and the chemical potentials μ of the two phases. The first two conditions are automatically satisfied according to the way of selecting A and E. Maxwell's rule can be derived from the third condition

$$\mu_A(p, T) = \mu_E(p, T). \tag{1}$$

If the mass in the volume V is M, the Gibbs free energy in the state A is

$$G_A(p, T) = M\mu_A(p, T) = U_A - TS_A + pV_A.$$

For the state E, $M\mu_E(p, T) = U_E - TS_E + pV_E$, and eq. (1) can be written in the following form

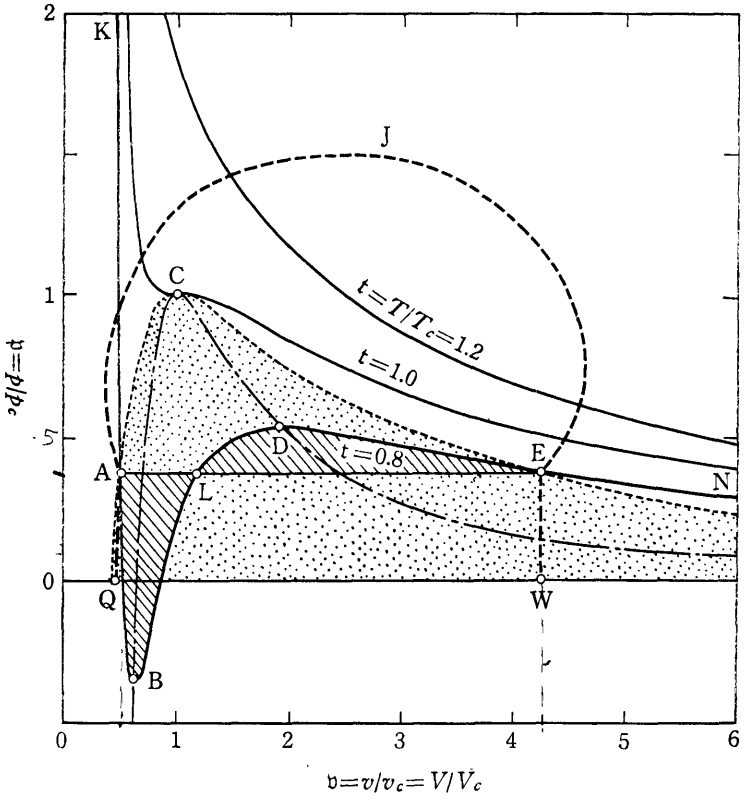
$$(U_E - U_A) - T(S_E - S_A) + p(V_E - V_A) = 0. \tag{2}$$

Thus we need to calculate the differences of internal energy $U_E - U_A$, and of entropy $S_E - S_A$.

If n moles of the gas are enclosed in volume V, the van der Waals equation has the form

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}, \tag{3}$$

where a and b are material constants, and R the gas constant. Note that in equilibrium, eq. (3) can be applied only to the parts KA and EN of the isotherm, i.e. to the region outside of ACE. If eq. (3) is applicable, the specific heat at constant volume c_V becomes a function of T only, as was



shown in the solution of problem 34 in Chapter 2. In order to calculate the entropy difference $S_E - S_A$ it is sufficient to take an arbitrary quasi-static process AJE connecting A with E through the region, in which eq. (3) is applicable, like the one shown in the figure by the broken line. If M is fixed,

S is a function of V and T, and

$$S_E - S_A = \int_A^E dS = \int_A^E \left\{ \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \right\}$$
$$= \int_A^E \left(\frac{\partial p}{\partial T}\right)_V dV + \int_A^E \frac{Mc_V(T)}{T} dT. \tag{4}$$

In the last step we have used the Maxwell relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V$. Since A and E are states at the same temperature, the last integral in eq. (4) must vanish. Making use of eq. (3), we thus obtain

$$S_E - S_A = \int_{V_A}^{V_E} \frac{nR}{V - nb} dV = nR \log \frac{V_E - nb}{V_A - nb}. \tag{5}$$

In a similar way, the difference in internal energy becomes

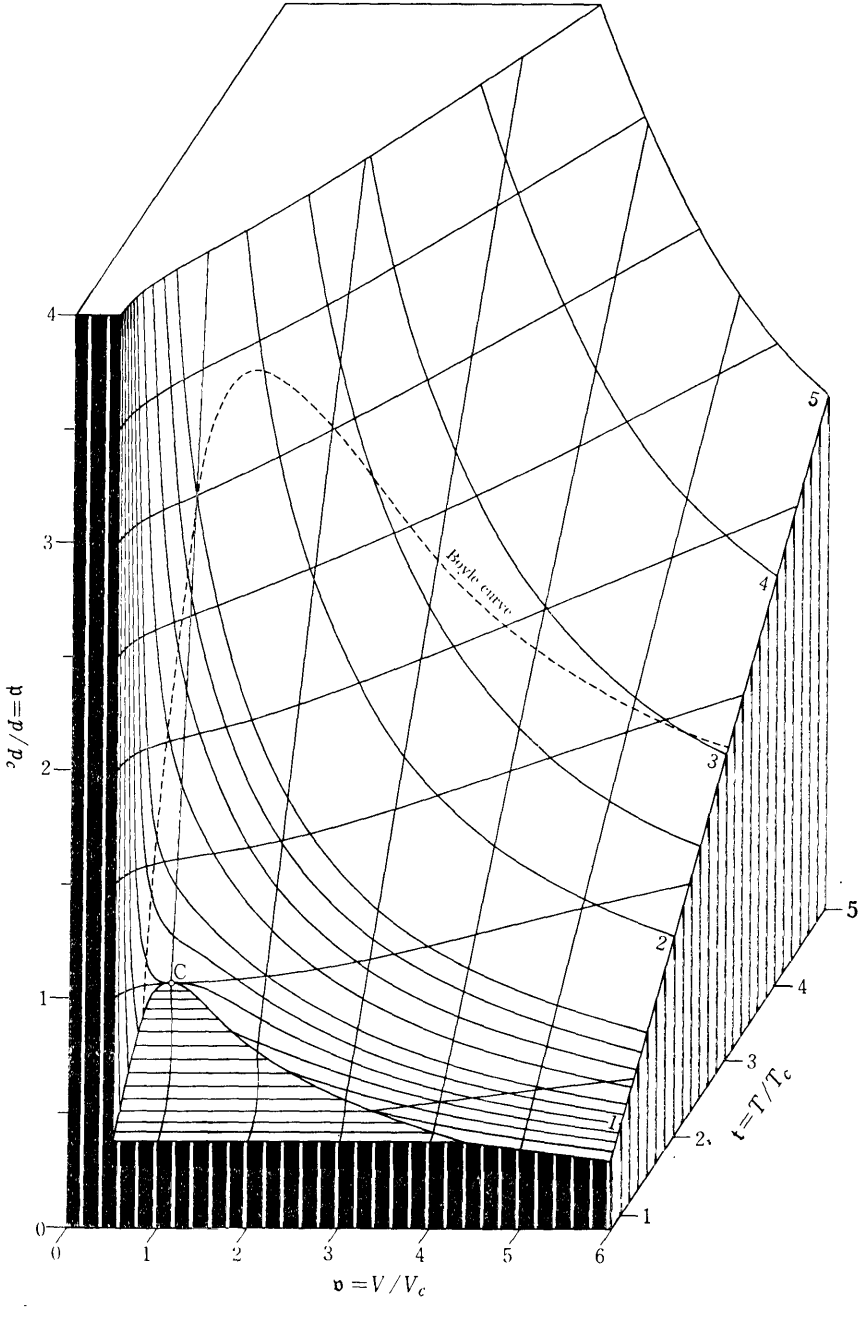
$$U_E - U_A = \int_A^E dU = \int_A^E \left\{ \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \right\}$$
$$= \int_A^E \left\{ T\left(\frac{\partial p}{\partial T}\right)_V - p \right\} dV + \int_A^E Mc_V(T)\, dT$$
$$= \int_{V_A}^{V_E} \frac{n^2 a}{V^2} dV + 0 = n^2 a \left(\frac{1}{V_A} - \frac{1}{V_E}\right). \tag{6}$$

Here we have used eq. (3.21b). From eqs. (5) and (6),

$$(U_E - U_A) - T(S_E - S_A) = -\left(nRT \log \frac{V_E - nb}{V_A - nb} + \frac{n^2 a}{V_E} - \frac{n^2 a}{V_A}\right). \tag{7}$$

This difference is found to be equal to the integral of $p\,dV$ along the isotherm ABLDE, based on the assumption that eq. (3) was valid for all states including metastable and unstable states:

$$\int_{ABLDE} p\, dV = \int_{V_A}^{V_E} \left(\frac{nRT}{V - nb} - \frac{n^2 a}{V^2}\right) dV = \left[nRT \log(V - nb) + \frac{n^2 a}{V} \right]_{V = V_A}^{V = V_E}. \tag{8}$$


Boyle curve
C
$\mathfrak{p} = p/p_c$
$\mathfrak{v} = V/V_c$
$\mathfrak{t} = T/T_c$
0
1
2
3
4
5
6

Therefore, remembering eq. (2), we arrive at

$$\int_{\text{ABLDE}} p\,\mathrm{d}V = p(V_{\mathrm{E}} - V_{\mathrm{A}}). \tag{9}$$

Since p is the value of pressure at the points A and E, the right-hand member of eq. (9) corresponds to the area of the rectangle AEWQA in the figure. The left-hand member corresponds to the area of the region ABLDEWQA between the isotherm ABLDE and the V-axis, and thus eq. (9) means that the area DELD is equal to the area ALBA. This is Maxwell's rule. To convert into the specific volume $v = V/M$, divide both sides of eq. (9) by the total mass M. The specific volumes at the points A and E, v_l and v_g, become functions of T (or p) only (p is determined by solving eq. (1) for a given T, and vice versa, as $T = 100$ °C is obtained at $p = 1$ atm for water, for example). NOTE: For reference, the relief of the van der Waals equation of state modified by introducing the horizontal line AE, which is determined by Maxwell's rule and corresponds to states of the coexisting gas an liquid phases, is shown in the figure on page 287.

48. Assuming that the volume change is negligible, let us consider the free energy per unit volume $F(M, T)$. Since we are considering a ferro-magnet near the Curie point, M may be regarded as small. We assume that $F(M, T)$ can be expanded as a function of M as

$$F(M, T) = F(0, T) + \alpha(T)\frac{M^2}{2!} + \beta(T)\frac{M^4}{4!} + \cdots. \tag{1}$$

(The odd powers of M do not appear, because one direction of magnetization is equivalent to the opposite direction.) The equilibrium condition in the presence of magnetic field H is that

$$F(M, T) - HM = \text{min.}, \tag{2}$$

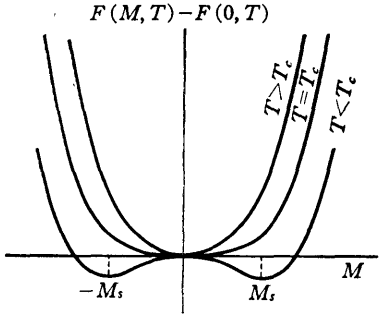
from which $M(H)$ is determined. First, for $T > T_c$, the magnetization $M = \chi_T H$ proportional to H should appear for $H \neq 0$ (not large $|H|$). Thus, retaining the terms up to M^2 in eq. (1), we find from condition (2)

$$\frac{\partial}{\partial M}(\tfrac{1}{2}\alpha M^2 - HM) = 0, \qquad \text{or} \qquad M = H/\alpha, \tag{3}$$

so that

$$\alpha = 1/\chi_T, \qquad \text{or} \qquad \alpha = (T - T_c)/A. \tag{4}$$

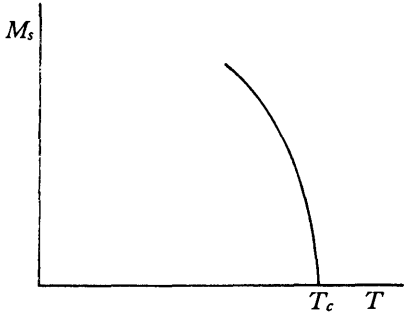
For $T<T_c$, α in eq. (1) becomes negative, and the curve of $F(M,T)$ versus M has a maximum at $M=0$. If $\beta>0$, $F(M,T)$ has two minima at $M\neq 0$ because of the M^4 term (see the figure). For $H=0$, these minima give the



spontaneous magnetization M_s. In order to discuss it near the Curie temperature, we may put $\beta(T)\sim\beta(T_c)$ and obtain

$$\alpha M_s + \tfrac{1}{6}\beta M_s^3 = 0 \qquad \text{and thus} \qquad M_s = \sqrt{-6\alpha/\beta} \doteqdot \{6(T_c - T)/A\beta(T_c)\}^{\frac{1}{2}}. \tag{5}$$

This gives the behavior of the spontaneous magnetization below T_c (see figure).



Therefore, for $H=0$ we obtain

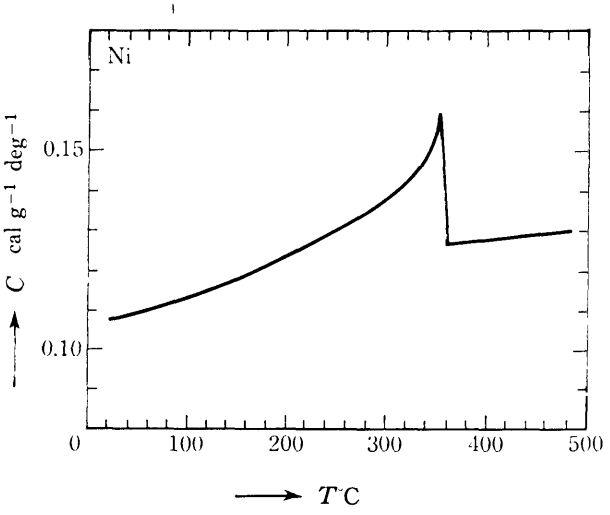
$$M = 0, \qquad F(T) = F(0, T), \qquad \text{if} \quad T > T_c; \tag{6a}$$

$$M = M_s, \qquad F(T) = F(0, T) - \frac{3\alpha^2}{\beta} + \cdots, \qquad \text{if} \quad T < T_c. \tag{6b}$$

By using these equations we can calculate $S=-\partial F/\partial T$ and $C=T\partial S/\partial T=-T\partial^2 F/\partial T^2$. The discontinuity in the specific heat originates in the second term of eq. (6b). We thus obtain

$$\Delta C = C_{T_c-0} - C_{T_c+0} = 6T_c/A^2\beta(T_c). \tag{7}$$

The figure shows qualitatively the behavior of the specific heat.



49. Let us suppose there is a water drop of radius r, at the center of which there is a particle (ion) of radius a and having an electric charge e. If the dielectric constant of water is ε, an electric field $E=e/\varepsilon\rho^2$ exists at a distance ρ from the center. As was shown in problem 29 of Chapter 3, the free energy of water decreases by $-(\varepsilon-1)E^2/8\pi$ per unit volume because of the polarization in this electric field. Integrating this decrease over the whole volume of the water drop, we obtain the change ΔF of the free energy of the drop:

$$\Delta F = -\int_a^r \frac{(\varepsilon-1)}{8\pi}\frac{e^2}{\varepsilon^2\rho^4}4\pi\rho^2\,\mathrm{d}\rho = -\tfrac{1}{2}e^2\left(1-\frac{1}{\varepsilon}\right)\left(\frac{1}{a}-\frac{1}{r}\right)\frac{1}{\varepsilon}$$

$$= e^2\left(1-\frac{1}{\varepsilon}\right)\Big/2r\varepsilon + \text{constant}. \tag{1}$$

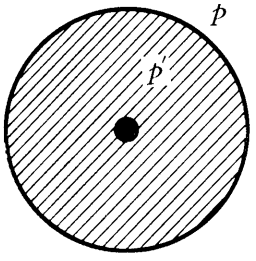
Regarding a region of sufficiently large volume of water vapor including the water drop as the system under consideration, and the remaining part of water vapor as its environment, we arrive at the equilibrium condition

(3.28):

$$\delta U - T\,\delta S + p\,\delta(V' + V'') - \mu\,\delta(N' + N'') > 0.$$

Here we have distinguished the liquid phase by a single prime. Substituting for δU the expression (4.8), which takes into account the surface energy, we arrive at

$$(p - p')\,\delta V' + \gamma\,\delta\sigma + \{\mu'(T, p') - \mu''(T, p)\}\,\delta N' + \delta\left\{\frac{e^2}{2r\varepsilon}\left(1 - \frac{1}{\varepsilon}\right)\right\} \geq 0.$$



By neglecting the density dependence of ε, and by the use of $\mathrm{d}\sigma = (2/r)\mathrm{d}V'$ and $\mathrm{d}r = (1/4\pi r^2)\,\mathrm{d}V'$, the relation obtained above can be rewritten as

$$\left\{-p' + p + \frac{2\gamma}{r} - \frac{e^2}{8\pi\varepsilon r^4}\left(1 - \frac{1}{\varepsilon}\right)\right\}\delta V' + \{\mu'(T, p') - \mu''(T, p)\}\,\delta N' \geq 0.$$

At equilibrium,

$$p' = p + \frac{2\gamma}{r} - \frac{e^2}{8\pi\varepsilon r^4}\left(1 - \frac{1}{\varepsilon}\right) \qquad \text{(J. J. Thomson's equation)} \qquad (2)$$

and

$$\mu'(T, p') = \mu''(T, p)$$

hold. From these two equations the critical radius r is determined.

Note that for a planar boundary, $\mu'(p_s) = \mu''(p_s)$ holds for the saturated vapor, while for the present case $\mu'(p') < \mu''(p)$ can hold not only for the supersaturated vapor $(\mu'(p) < \mu''(p))$ but also for the unsaturated vapor $(\mu'(p) > \mu''(p))$, because $p' < p$ holds by eq. (2) as long as r is sufficiently small $(\partial\mu/\partial p = v > 0)$. That is to say, the liquid phase is more stable (see § 4.2, 1)), and the water drop can grow. This effect of electric charges plays an important role, when the water vapor condenses into clouds and fog in the atmosphere. About the Wilson chamber, see the note to the solution of problem 35.

50. The general conditions for phase separation are given in example 2. After the solution of example 7, we treat the problem as a sequel to problem 39:

$$\Delta G/RT \equiv f(\phi) = x_1\bar{G}_1 + x_2\bar{G}_2 - (x_1\bar{G}_1^0 + x_2\bar{G}_2^0)$$
$$= \frac{1}{r-(r-1)\phi}\left[r(1-\phi)\log(1-\phi) + \phi\log\phi + \frac{rw}{RT}\phi(1-\phi)\right], \tag{1}$$

where we have written ϕ in place of ϕ_2. We shall write x for x_2 hereafter. The separation into two phases occurs, if the graph of $\Delta G/RT$ versus x has two minima. The sum of the first two terms in the square brackets of eq. (1) gives a curve having vertical tangents at $\phi \sim 0$ and $\phi \sim 1$ and being convex downwards for $0<\phi<1$, and the third term is convex upwards if $w>0$. Thus two minima and a maximum between the minima appear, if w/RT is sufficiently large. Let us examine this condition. First, we have

$$\frac{d\phi}{dx} = \frac{d}{dx}\frac{rx}{1+(r-1)x} = \frac{\phi^2}{rx^2}, \qquad \text{or} \qquad \frac{d}{dx}\frac{\Delta G}{RT} = \frac{f'(\phi)\cdot\phi^2}{rx^2}. \tag{2}$$

From $f(\phi)=g(\phi)/\{r-(r-1)\phi\}$ with

$$g(\phi) = r(1-\phi)\log(1-\phi) + \phi\log\phi + \frac{rw}{RT}\phi(1-\phi), \tag{3}$$

we have

$$f'(\phi) = g'(\phi)/\{r-(r-1)\phi\} + (r-1)g(\phi)/\{r-(r-1)\phi\}^2, \tag{4}$$
$$f''(\phi) = \frac{g''}{r-(r-1)\phi} + \frac{2(r-1)g'}{[r-(r-1)\phi]^2} + \frac{2(r-1)^2 g}{[r-(r-1)\phi]^3}$$
$$= \frac{g''}{r-(r-1)\phi} + 2(r-1)f'. \tag{5}$$

The conditions that make the three roots of $f'(\phi)=0$ coincide are $f''(\phi)=0$ and $f'''(\phi)=0$, which are found to be equivalent to $g''(\phi)=0$ and $g'''(\phi)=0$ (because we obtain $g''=0$ from eq. (5) since $f'=0$, and $g'''=0$ by deriving $f'''(\phi)$ from eq. (5) and setting it equal to zero). According to eq. (3), these conditions can be written as

$$\left.\begin{aligned} \frac{r}{1-\phi} + \frac{1}{\phi} - 2\frac{rw}{RT} &= 0, \\ \frac{r}{(1-\phi)^2} - \frac{1}{\phi^2} &= 0. \end{aligned}\right\} \tag{6}$$

Let us denote the root of these equations as ϕ_c. Since $0<\phi<1$ and

$0<1-\phi<1$, we obtain $1-\phi_c=-\sqrt{r}\,\phi_c$ from the second equation, and hence $\phi_c=1/(1+\sqrt{r})$. Inserting this into the first equation, we have

$$\frac{w}{RT_c}=\frac{1}{2}\left(1+\frac{1}{\sqrt{r}}\right)^2. \tag{7}$$

As described above, the separation into two phases occurs, when $w>0$ and $T<T_c(w/RT>w/RT_c)$. The concentrations in the separated phases ϕ' and ϕ'' are determined by $f'(\phi)=0$.

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