

Advanced Engineering Thermo- dynamics

2ND EDITION
(in SI Metric Units)

Rowland S. Benson



Advanced Engineering Thermodynamics

SECOND EDITION

BY

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PREFACE TO SECOND EDITION

The basic thermodynamics covered in a final year honour course has not changed since the first edition so that the text is essentially the same. In view of the almost general use of the S.I. system in thermodynamics the tables in the text have been presented in these units as well as a number of worked examples and exercises. Since the publication of the first edition there has been an increase in interest in combustion-generated pollution. The thermodynamics of these processes can be handled by the methods outlined in Chapter 4; to illustrate the technique this chapter has been extended with an example of the rate controlled nitric oxide reactions.

A number of readers have used the data in Table A1 to generate their own thermodynamic properties, in particular in cycle and combustion calculations in computer programs. To assist new readers these polynomial coefficients have been presented in a form suitable for computing and a few simple algorithms are presented in the text. Because these coefficients have been referred to in published papers with their original symbols these have been retained in the headings of Table A1 in addition to the new symbols.

The opportunity has been taken to correct some minor printing errors in the first edition. I wish to thank all those who notified me of them. Finally, I wish to thank my former secretary, Mrs. J.A. Munro, who typed the master script upon which the printed copy is based.

MANCHESTER, April 1976.

texts referred to above. In particular, the formulation of the thermodynamic data for gas mixtures has been devised in such a manner that the various expressions can be used directly in computer programming. This should be of value for cycle analysis. The order of presentation is, in general, different from current texts and courses. It is considered that a discussion on equilibrium is necessary before the general development of the subject - this topic is scarcely discussed in engineering courses; Chapter 1 is therefore concerned solely with equilibrium. The material in Chapter 2 on the general thermodynamic relations is a happy hunting ground for students with mathematical facility and is fairly straightforward. In Chapter 3 the approach follows elementary chemical thermodynamics with a brief discussion of the quantum theory; more advanced chemical thermodynamics is described in Chapter 4 with the introduction of the chemical potential. Certain new material is added at the end of Chapter 4, including a proof of Lighthill's ideal dissociating gas state equation as well as a discussion of "frozen" flow. The exercises in Chapters 3 and 4 have been devised to include a number of practical applications of classical thermodynamics to engineering subjects. The interest of engineers in direct conversion of heat to electricity and cryogenics has prompted the inclusion of some of this material in Chapter 5 - this has been covered by chemists and physicists for some years. The chapter ends with some irreversible thermodynamics, a new topic of importance to engineers in thermoelectricity and similar fields.

The range of units used by engineers is extensive and, whilst it would have been desirable to keep to one set of units, it was difficult to decide which was the best. The basic relations have, therefore, been developed without units. For numerical examples the units are given both in the text and in the exercises. The tables at the end of the text have been prepared using the latest thermodynamic data kindly provided by Dr. A. Russo of Cornell Aeronautical Laboratory, Buffalo, N.Y. The programmes for these tables were prepared under my direction by Mr. W.G. Cartwright and Mr. R. Dale of my department; the calculations were carried out on the Manchester University Atlas Computer. I would like to thank all concerned.

The manuscript was read by Mr. W.G. Cartwright to whom I wish to express my grateful thanks for his comments and suggestions. I would also like to thank the editor of the series, Professor J.H. Horlock, for his helpful comments. The body of the material has been included in courses in mechanical engineering in the Universities of Liverpool and Manchester, whilst for the past three years the original draft of this text has been used by third-year honours students in the Department of Mechanical Engineering, Faculty of Technology, University of Manchester. I would be grateful for any comments and criticisms.

Acknowledgement is made to the Senates of the Universities

of Manchester and Liverpool for permission to reproduce examination questions but responsibility for the solutions given is entirely the author's.

I would like to thank Mrs. M.S. Ehren and Mrs. J.A. Munro for the preparation of the typed manuscript and Mr. E. Clough for the drawings.

Finally, my grateful thanks are given to my wife and family for their patience and forbearance whilst I spent many evenings and week-ends preparing this book.

MANCHESTER, June 1966.

EDITORIAL INTRODUCTION

The books in the Thermodynamics and Fluid Mechanics Division of the Commonwealth Library have been planned as a series. They cover those subjects in thermodynamics and fluid mechanics that are normally taught to mechanical engineering students in a three-year undergraduate course.

Although there will be some cross-reference to other books in the division, each volume will be self-contained. Lecturers will therefore be able to recommend to their students a volume covering the particular course which they are teaching. A student will be able to purchase a short, low-price, soft-cover book containing material which is relevant to his immediate needs, rather than a large volume in which most of the contents are outside his current field of study.

The book meets the immediate requirements of the mechanical engineering student in his undergraduate course, and of other engineering students taking courses in thermodynamics and fluid mechanics.

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CHAPTER 1

EQUILIBRIUM OF THERMODYNAMIC SYSTEMS

Introduction to concept of equilibrium, maximum work of thermodynamic systems, development of Gibbs and Helmholtz functions. Equilibrium of thermodynamic systems, conditions for stability and spontaneous change.

Notation

a	constant in Van der Waals' equation	m_v	mass of vapour
b	constant in Van der Waals' equation	M	number of mols
E	internal energy	p	pressure
F	Helmholtz free energy function	Q	heat transfer to system
g	specific Gibbs free energy function	R_{mol}	universal gas constant
G	Gibbs free energy function	S	entropy
H	enthalpy	t	time
m	mass	T	temperature absolute
m_1	mass of liquid	U	internal energy in the absence of motion, gravity, etc.
		V	volume
		W	work from system
		W'	shaft work

Concept of Equilibrium, Spontaneous Change and Criterion of Stability

In the study of engineering situations the question of stability of systems is of major importance. We may be concerned with spontaneous changes in the state of a system or at the other extreme with the states of equilibrium. In thermodynamics we are interested in similar situations. For example, a vessel may contain two gases separated by a partition. If the partition is removed we may wish to establish whether the gases will remain separated or whether they will mix or if they mix under what conditions there will be no further change in state. Alternatively, the gases may react with one another and we may require to know whether a reaction is possible or not and if so what is the final composition of the gases. Or we may require to know whether some of the initial reactants are still present when the system settles to a steady state.

Before we start our study we must define our terms. We say that a system is in a state of equilibrium[†] if no active unbalanced tendency towards a change in state exists. The equilibrium may be stable, unstable, neutral or metastable. We will be primarily concerned with criteria for stable equilibrium. By stable equilibrium we mean that if we slightly perturb the state of the system it will return to its original state. A system is not in equilibrium if there is a spontaneous change in the state. It is important how we define the system. For example, let us consider two bars of metal, one at a uniform temperature T_1 and the other at a uniform temperature T_2 . If we enclose both bars in heat insulators then experience tells us that they will remain at the same temperature. Hence, the separate bars, or the two systems enclosing the bars, are in thermal equilibrium. If we now bring the two bars together and place them in contact, at the same time removing the insulating walls on the contact faces only, we know from experience that the temperature of one bar will drop and the other increase until they are both once again in thermal equilibrium, this time with each other. We will observe that on contact there was a spontaneous change in the state of both bars. It will be noticed, however, that in order to produce this change in state the boundaries defining the system were altered. Thus in defining the conditions for equilibrium we must also state at the same time the constraints on the system.

In the simple example given above we can measure directly

[†]J.H. Keenan, Thermodynamics, J. Wiley & Sons, New York, 1940.
S.R. Montgomery, The Second Law of Thermodynamics, Pergamon Press, 1965.

the condition for equilibrium by means of a thermometer. Of course it is important to remember that the measurement of temperature is dependent on the concept of equilibrium (in this case thermal equilibrium) and in this experiment we have, strictly speaking, only three known temperatures, the two temperatures corresponding to the initial temperatures of each bar and the third corresponding to the final temperature of the two bars. In many problems the equilibrium criterion is not so readily obtained. We must therefore look for some general criterion.

This criterion we can obtain from the second law of thermodynamics. In the sixth corollary[†] to the second law it is stated that the entropy of an isolated system either increases or in the limit remains constant. Now an isolated system is a system of constant internal energy. If such a system eventually reaches the maximum entropy level then, since the entropy cannot decrease, any disturbance to the system will only cause the state to return to the maximum entropy. Let us examine this by means of an example.

Any system plus surroundings can be considered to be an isolated system (Fig. 1.1). Let us consider a system B at uniform temperature T_2 immersed in the surroundings A also at a uniform temperature T_1 (as shown in Fig. 1.1). We will

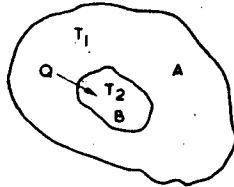


FIG. 1.1.

stipulate the following constraints, namely that the system and surroundings have fixed volume invariant with temperature. If the temperature T_1 is greater than T_2 , there will be a spontaneous heat interaction at the boundary of the system and surroundings. Let dQ be the quantity of heat transferred in a small interval of time dt . If both system and surroundings are maintained at the uniform temperature T_2 and T_1 respectively, then the entropy changes are:

[†]J.H. Keenan, Thermodynamics, J. Wiley & Sons, New York, 1940.
S.R. Montgomery, The Second Law of Thermodynamics, Pergamon Press, 1965.

For surroundings A, $dS_A = - \frac{dQ}{T_1}$. (1.1)

For system B, $dS_B = + \frac{dQ}{T_2}$. (1.2)

Since there are no changes in volume in A or B, the first law of thermodynamics states that the heat transferred equals the change in internal energy, that is $dQ = dE$. For the isolated system, comprising system B and surroundings A, the change in internal energy dE is zero or

$$dE = dE_A + dE_B = 0$$

and the total change in entropy will be

$$dS = dS_A + dS_B \quad (1.3)$$

Substituting (1.1) and (1.2) into (1.3)

$$dS = dQ \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1.4)$$

which after rearrangement becomes

$$dS = \frac{dQ}{T_1 T_2} (T_1 - T_2). \quad (1.5)$$

Since $T_1 > T_2$, then $dS > 0$.

If the entropy change dS takes place in time dt then equation (1.5) may be written in the form

$$\dot{S} = \frac{\dot{Q}}{T_1 T_2} (T_1 - T_2) \quad (1.6)$$

and

$$\dot{S} > 0 \quad (1.7)$$

-(using Newton's notation for time derivatives).

Hence the isolated system is producing entropy, or we can say the entropy is increasing. If the process is such that we

maintain uniform, but different, temperatures throughout A and B then as T_2 approaches T_1 the rate of entropy production is reduced.

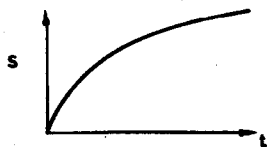


FIG. 1.2.

We might expect a curve of the type shown in Fig. 1.2. In the limit when $T_1 = T_2 = T$ there will be no further increase in entropy.

Let us assume that when the temperatures of system B and surroundings A are the same ($= T$) we can cause the temperature of A to rise dT_1 with a heat flow dQ from B at the same time producing a drop dT_2 in the temperature of B. To simplify the analysis we will assume that the heat capacities of the system and surroundings are equal, then $dT_1 = dT_2 = dT$. The change in entropies will be

$$dS_A = \frac{dQ}{T+dT} \quad (1.8)$$

$$dS_B = \frac{-dQ}{T-dT} \quad (1.9)$$

the total change in entropy for the isolated system

$$dS = dS_A + dS_B = dQ \left(\frac{1}{T+dT} - \frac{1}{T-dT} \right) \quad (1.10)$$

$$dS = \left(\frac{dQ}{T^2-dT^2} \right) (-2dT) = -2dQ \frac{dT}{T^2} \quad (1.11)$$

to the first-order small quantities.

In this case there is a decrease in entropy. The same results would have been obtained if we had raised the temperature of the surroundings. The point of maximum entropy has

clearly been obtained when both system and surroundings are at the same temperature and there is no change in volume.[†]

One other important point can be observed in this example. Since from the second law the entropy of an isolated system can only increase, it is clear that the variation in temperature dT discussed above cannot take place; in this case the volume is fixed (one of the initial constraints) and no other variations in state are possible in the system. The isolated system must therefore be in stable equilibrium. This follows since our perturbation of the state of the system (in this case the temperature) produces an absurd situation (decrease in entropy) and the system must immediately revert to its original state, which is the stable equilibrium state. We may observe the following three points from the systems we have examined but which apply quite generally:

- (1) If the properties of an isolated system change spontaneously there is an increase in entropy of the system.
- (2) When the entropy of an isolated system is at a maximum the system is in equilibrium.
- (3) If for all the possible variations in state of the isolated system there is a negative change in entropy then the system is in stable equilibrium.

In the last case we know that the possible variation cannot take place, but this we discover after we have made the test for the stability of the system. We note of course the constraints which we cannot vary (in this case the volume).

We may generalize and summarize therefore for an isolated system:^{††}

$$(i) \quad dS)_E > 0 \quad \text{Spontaneous change.} \quad (1.12)$$

$$(ii) \quad dS)_E = 0 \quad \text{Equilibrium.} \quad (1.13)$$

$$(iii) \quad \Delta S)_E < 0 \quad \text{Criterion of stability.} \quad (1.14)$$

[†]This method of examining a function is frequently used in mathematics to test for a maximum. In this case dS is negative both sides of the maximum value of S .

^{††}Where we use Keenan's notation $\Delta S)_E$ meaning variation in entropy at constant E . The E outside the half bracket indicates constant E . The Δ indicates an increment in S to any order of small quantities.

Equilibrium of System

In practice it is more convenient to formulate the above criteria for the system B only. Other state functions are used for this purpose.

Let us consider a system immersed in surroundings at constant temperature T . We impose a constraint on the system that the heat interactions can only occur at temperature T . Initially the system is at this temperature. Some process then occurs within the system in which heat and work interactions may take place. Finally the system is in equilibrium at temperature T and the entropy of the system and surroundings is at a maximum.

From the second law of thermodynamics we have for system plus surroundings (isolated system)

$$(dS)_{\text{system}} + (dS)_{\text{surroundings}} \geq 0 \quad (1.15)$$

and for the surroundings[†]

$$(dS)_{\text{surroundings}} = - \frac{dQ}{T} \quad (1.16)$$

hence

$$(dS)_{\text{system}} - \frac{dQ}{T} \geq 0 \quad (1.17)$$

Integrating between the initial and final states

$$T(S_2 - S_1) \geq Q \quad \text{for the system} \quad (1.18)$$

where Q is the heat transferred to the system.

Now from the First Law of Thermodynamics in the absence of motion, gravity, electricity, magnetism and capillarity

$$dQ - dW = dU \quad (1.19)$$

hence

$$Q - W = U_2 - U_1$$

for the system (1.12) and

$$W = Q - (U_2 - U_1). \quad (1.20)$$

[†]The negative sign is used since we are examining the system, heat flow to the system is $+dQ$, heat flow from the surroundings is $-dQ$.