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ABSTRACT

A time-sharing FORTRAN program is described. It was created to allow a student to design and perform classical thermodynamic experiments on three models of a working substance. One goal was to develop a simulation which gave the student maximum freedom and responsibility in the design of the experiment and provided only the primary experimental results, thereby affording him practice in planning and data analysis. The specific purpose was to develop a program the student could use to perform simulated thermodynamics experiments. The decisions about experimental variables to measure and control, and the values to use, were made by the student, although they could have been added to the program. An attempt was made to provide, as output, only those variables which are directly measurable in the laboratory. For example, if an assignment required the measurement of the specific heat vs. temperature curve for a given substance, the student must accept the limiting fact that specific heat is not directly measurable and must define what other parameters to measure, what conditions to use, and what analysis to make. (Author)

# A PROGRAM FOR SIMULATED THERMODYNAMIC EXPERIMENTS*

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This paper describes a time-sharing FORTRAN program which allowed a student to design and perform a variety of classical thermodynamic experiments on three common models of a working substance. An important goal of this project was to develop a simulation which gave the student maximum freedom and responsibility in the design of the experiment and provided only the primary experimental results. In this way the student obtained valuable practice in planning and data analysis. The particular purpose of the project was to develop a program which the student could use to perform simulated thermodynamics experiments. The decisions about experimental variables to measure and control, and the set of values to use, must be made by the student; the data analysis is left to the student, even if it could easily have been added to the program. An attempt has been made to provide, as output, only those thermodynamic variables which are directly measurable in the laboratory. As an example, an assignment may be to determine the specific heat vs. temperature curve for the substance under study. Specific heat is not directly measurable and it is the student's responsibility to determine what parameters to measure, what conditions to use, and what analysis to make.

## Program Description

PVTEXP is a program, written in Call-A-Computer FORTRAN, which simulates three of the most popular models for a real substance. These are (a) the ideal gas, (b) Van der Waals gas, and (c) a solid with a Debye specific heat curve. The program is used at our interactive, timesharing terminal, but this mode of operation is not felt to be necessary for successful operation.

The "User Instructions" attached to this paper are those given to our students. The instructions purposely omit the names of the models and refer to them only by number. This is done so that familiarity with "expected results" will not prevent discovery. Following these instructions, the student selects a working substance by number; chooses a fixed parameter (i.e., an isothermal, isobaric, isochoric or adiabatic process) with specified value; chooses to vary one of the remaining parameters; and enters an initial value, final value, and measurement interval. If he has chosen heat flow as one parameter, he will be asked to enter an additional P-V-T coordinate of the initial state since two such coordinates are required to specify a point on the state surface. For each of the models, not counting differences due to numerical values, there are fifteen ways of specifying the desired experiment. After appropriate selection of values and subsequent analysis of results, this set of 45 experimental choices may be combined in a wide variety of ways and made to answer many types of questions. The printed results are pressure in atmospheres, volume in liters, temperature in °K, and cumulative heat flow in calories at each step of the requested process. The units may be easily changed by an appropriate change of conversion factors in the DATA lines. In addition, the user will find it an easy matter to change model parameters (such as the Van der Waals constants or the Debye temperature) and study the effects of these changes.

Furthermore, since the program is essentially a series of subroutines, it is possible to introduce other models with relative ease. It does require, however, an equation of state (with algorithms for finding, P, V and T) and an expression for $C_p$ or $C_v$ in terms of these state variables. However, if no convenient algorithm for finding V(P,T), for example, is available, then a new model may still be introduced with the restriction that V is to be specified by the experimenter, either as a fixed or stepped parameter.

## Program Application

At Wofford, the program has found application at two places in the curriculum. One of these is with a class of freshman "non-scientists" who were given very little background information on thermodynamics. They had done some (non-thermo) laboratory experiments, statistical analysis of data, curve fitting, and a small amount of computer programming. The main theme in this course was the quantitative treatment of data in science. The thermodynamics program described here was introduced as an example of computer simulations of nature. Applications in this course included:

1. After a brief lecture on the nature of an equation of state and how such equations may be obtained experimentally, these students were asked to design experiments on "substance number 1" to obtain some information about its equation of state. Some "discovered" Boyle's law, some found Charles' law, and a few found combined results and reported something like T = CPV with a value of C and some indication of its variability.

2. After a brief discussion of specific heat and the fact that there are different specific heats for different processes, the students were asked to find, for substance number 1, $C_v$ at an assigned temperature.

3. After a classroom discussion of thermal expansion, the group was asked to select and perform experiments to determine the pressure dependence of the coefficient of expansion for substance number 2. Each student took data at one or more values of pressure and a plot was made of the group results. Subsequent discussion of the variability in these results proved fruitful for those who stuck with this problem.

I plan to make similar uses of the program with a new group of students in the spring semester.

The second application is in the thermodynamics course. A typical physics course in thermodynamics has no lab, but the experimental procedures for determination of specific heat, enthalpy, and other functions are important research methods. Furthermore, students are asked to work with several new abstract functions without the experience of seeing in a personal way how such functions are obtained from experiments. Therefore, this course is an ideal one for the introduction of simulated experimental planning and analysis. However, a literature search and other inquiries revealed very little work in the area and no programs with the desired capability.

With PVTEXP, students can be asked to observe system behavior, evaluate parameters, determine functional relationships, or investigate properties of thermodynamic cycles. A list of example assignments is given below. At Wofford, our experience with advanced students using the program is limited by the number of students who take the course. We have not exhausted the possibilities of the present program, but already recognize the need for an expanded version which will simulate phase changes and still allow the freedom of experimental design available with the present version.

## Sample Problem Ideas Using PVTEXP

1. Choose substance number 1 and evaluate beta and kappa near STP.

2. Choose substance number 2 and plot kappa as a function of temperature from 50°K to 1500°K at P = 1 atm.

3. Choose substance number 3, measure and plot beta as a function of temperature from 50°K to 2000°K.

4. Experimentally determine values for the Van der Waals constants, a and b, using substance number 2.

5. Choose substance number 2 and plot PV/PT against P from 1 to 800 atm. at several temperatures.

6. Find the work done in isothermally changing one mole of substance number 1 at 300°K and 1 atm. to 300°K and 5 atm.

7. Determine $C_p$ for substance number 1 in the neighborhood of STP.

8. Determine and plot $C_p$ of substance number 3 as a function of temperature from 10°K to 400°K.

9. Determine the enthalpy difference between 1 mole of substance number 2 at 300°K and at 500°K, both at 2 atm.

10. Determine and plot U as a function of T for substance number 1 from T = 100°K to T = 200°K at 1 atm. (Use an arbitrary reference level.)

11. Use substance number 1 and substance number 2 in separate throttling processes. Determine the Joule-Thompson coefficient of each substance in a region of interest to you.

12. Use substance number 1 in a Carnot cycle of your choice and calculate the efficiency from W and Q. Compare your result with the theoretical value.

13. Choose two Carnot cycles which have one boundary in common. With substance number 2 as the working fluid, experimentally determine the efficiency of each cyle and of the two cycles together.

14. Choose a Carnot cycle and an Otto cycle with the same temperature limits. Determine and compare their efficiencies with substance number 1 as the operating fluid.

15. Experimentally determine the Debye temperature for substance number 3.

16. Plot entropy as a function of temperature for substance number 3 from 0°K to 200°K.

## PVTEXP

## User Instructions

PVTEXP is a FORTRAN program to allow the user to design experiments and run selected processes on the P-V-T surfaces of several substances. The units for all input and output quantities are: pressure in atmospheres, volume in liters, temperature in degrees Kelvin, and heat flow in gram-calories. One gram-mole of substance is represented in each case. A process on the P-V-T surface may be chosen to be:

1. constant pressure (isobaric)
2. constant volume (isoboric)
3. constant temperature (isothermal)
4. constant Q (adiabatic)

NOTE: Q is not a state variable in thermodynamics. Only changes in Q have meaning. However, in this program, an adiabatic change is specified as Q = 0 and a process of controlled heat input may be specified as (for example) Q = 0, 200, 10 which is taken to mean "add heat in steps of 10 calories until 200 calories have been added."

There are three substances in the present program. The user selects one by responding 1, 2, or 3 to the first question which is "WHICH SUBSTANCE--TYPE NUMBER?".

In response to the question "SPECIFY FIXED PARAMETER?", a constant value for one of the four parameters is entered by typing an equation of the form T = 273. You may use any one of the variables P, V, T, or Q and assign its constant value in this way. (Other examples: P = 1.2, V = 24.3, Q = 0.) In entering equations, do not use a space anywhere before the equal sign.

The next question is "SPECIFY STEPPED PARAMETER WITH INITIAL AND FINAL VALUES AND STEP--SIZE?". A proper reply has the form P = 1,2,.2 which specifies a process beginning at P = 1 atmosphere, moving along the P-V-T surface (in the direction specified earlier) until P = 2 atmospheres, printing values of P,V, T and heat flow at each step of 0.2 atmospheres. Any one of the four variables may be specified in this way.

Two coordinates are required to locate the point from which you wish to start your process and Q is not a coordinate. If Q is specified as either the fixed or the stepped parameter, the next question will be "SPECIFY ANOTHER P-V-T COORDINATE OF THE STARTING POINT?". This is answered with another equation like V = 25.

Your replies to these questions have specified a path on the P-V-T surface--the starting point, the "direction", and the stopping criterion. Pressure, volume, temperature and net heat flow are then listed for points along this path, using the interval specified as "step-size" earlier.

When the tabulation is complete, the computer returns to the question "WHICH SUBSTANCE--TYPE NUMBER?" and you may continue with a new problem or you may wish to enter the previous final values of P, V, and T to begin a new part of a process under study. In this way, you may study closed cycles. Enter a zero (or an S) to stop the program.

Sample Run

```
PVTEXP    02:17   SAT.   03-24-73



WHICH SUBSTANCE -- TYPE NUMBER?2
SPECIFY FIXED PARAMETER?T=200
SPECIFY STEPPED PARAMETER WITH INITIAL AND FINAL VALUES AND STEP-SIZE
?P=.5,1.5,.25
     PRESSURE      VØLUME         TEMPERATURE    HEAT FLØW
       (ATM.)      (LITERS)      (DEG. KELVIN)  (CALØRIES)
        .50         32.8356      200.00           0.00
        .75         21.8943      200.00        -161.3181
       1.00         16.4237      200.00        -275.7905
      01.25         13.1413      200.00        -364.5873
       1.50         10.953       200.00        -437.1387


WHICH SUBSTANCE -- TYPE NUMBER?1
SPECIFY FIXED PARAMETER?V=25
SPECIFY STEPPED PARAMETER WITH INITIAL AND FINAL VALUES AND STEP-SIZE
?T=200,300,20
     PRESSURE      VØLUME         TEMPERATURE    HEAT FLØW
       (ATM.)      (LITERS)      (DEG. KELVIN)  (CALØRIES)
        .6565       25.00        200.00           0.00
        .7221       25.00        220.00          59.6478
        .7878       25.00        240.00         119.2955
        .8534       25.00        260.00         178.9433
        .9191       25.00        280.00         238.5911
        .9847       25.00        300.00         298.2388


WHICH SUBSTANCE -- TYPE NUMBER?3
SPECIFY FIXED PARAMETER?P=1
SPECIFY STEPPED PARAMETER WITH INITIAL AND FINAL VALUES AND STEP-SIZE
?T=100,1000,200
     PRESSURE      VØLUME         TEMPERATURE    HEAT FLØW
       (ATM.)      (LITERS)      (DEG. KELVIN)  (CALØRIES)
       1.00           .007       100.00           0.00
       1.00           .0071      300.00        1127.7404
       1.00           .0072      500.00        2347.7648
       1.00           .0073      700.00        3609.0076
       1.00           .0073      900.00        4910.6003
       1.00           .0074     1100.00        6256.9703


WHICH SUBSTANCE -- TYPE NUMBER?0



AT LINE NØ. 210: STØP    , RAN 216/6 SEC.
```

## Program Listing

PVTEXP

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100C VERSIØN ØF 22 AUGUST 1972, DAN W. ØLDS, WØFFØRD CØLLEGE
110 DIMENSIØN S(4),W(9)
120 REAL KAPPA
130 EQUIVALENCE (S(1),P),(S(2),V),(S(3),T),(S(4),Q)
140 CØMMØN FF(4)
150 1FØRMAT(1A1,1X,I15);2FØRMAT(1A1,1X)
160 READ,W,FF
170 R=8314.9
180 A5=24800;B5=.0266
190 BEGIN: PRINT,↑↑
200 PRINT"WHICH SUBSTANCE -- TYPE NUMBER",;INPUT,N1
210 IF(-N1)ØK;STØP
220 LETTR(M):
230 LETTR=(32-MØD(M/4096,20))/7;RETURN
240 VØL(P,T):
250 GØTØ(50,60,70)N1
260 50VØL=R*T/P;RETURN
270 60 V5=R*T/P;ITER=0
280 61V6=R*T/P+B5-A5/(P*V5)+A5*B5/(P*V5*V5)
290 IF(1E-5-ABS(1.-V6/V5))62;VØL=V6;RETURN
300 62IF(25-ITER)63;ITER=ITER+1;V5=V6;GØTØ61
310 70VØL=.0071*EXP(-1.34843E-2+4.15003E-5*T+1.15E-8*T*T-P*
320 +(6.7111E-12+2.71405E-15*T));RETURN
330 63PRINT,"VØLUME SØLUTIØN DØES NØT CØNVERGE--AVØID THIS REGIØN ØR
340 + SPECIFY VØLUME.";STØP
350 PRES(V,T):
360 GØTØ(150,160,170)N1
370 150 PRES=R*T/V;RETURN
380 160 PRES=R*T/(V-B5)-A5/(V*V);RETURN
390 170PRES=(ALØG(V/.0071)+1.34843E-2-4.15003E-5*T-1.15E-8*T*T)/
400 +(-6.7111E-12+2.71405E-15*T)
410 TEM(P,V):
420 GØTØ(250,260,270)N1
430 250 TEM=P*V/R;RETURN
440 260 TEM=(P+A5/V↑2)*(V-B5)/R;RETURN
450 270A1=4.15003E-5-2.71405E-15*P;A0=-1.34843E-2-6.7111E-12*P
460 TEM=(-A1+SQRTF(A1*A1-4.6E-8*(A0-ALØG(V/.0071))))/2.3E-8
470 CBK(P,V,T):
480 GØTØ(440,460,480)N1
490 440 CV=1.5*R
500 BETA=1/T
510 KAPPA=1/P
520 CP=CV+R
530 RETURN
540 460IF(50-T)462;CP=3.5*R;GØTØ464
550 462U=3070./T;CP=R*(3.5+(2*U/(EXP(U)-EXP(-U)))↑2)
560 464CP=CP+2*A5*P/(R*T*T)-(6*A5*B5/(R↑2*T↑3)-6*A5↑2/(R↑3*T↑4))*P↑2
570 BETA=R/(P*V-A5/(V+2*A5*B5/V↑2))
580 KAPPA =1/(-2*A5/(V*V)+R*T*V/(V-B5)↑2)
590 CV=CP-T*V*BETA↑2/KAPPA
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PVTEXP CØNTINUED

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600 RETURN
610 480 BETA=41.5E-6+T*23E-9-P*.271405E-14
620 KAPPA=6.7111E-12+2.71405E-15*T
630 X=215./T; IF(X-1) 482; DEB=0.; NT=2+10/X; DØ 481, CN=1, NT
640 481DEB=DEB+(X↑3+3*X↑2/CN+6*X/CN↑2+6/CN↑3)*EXP(-X*CN)/CN
650 DEB=3*(3.1415926↑4/15-DEB)/X↑3; GØTØ 483
660 482DEB=-3*X/8+1.+X*X/20.-X↑4/1680-X↑6/90720
670 483CV=3*R*(4*DEB-3*X/(EXP(X)-1))
680 CP=CV+T*V*BETA↑2/KAPPA
690 SLØPE(N2):
700 CALLCBK(P, V, T)
710 GØTØ(A, B, C, D, E, F)N2
720 A: SLØPE=CP/(BETA*V); RETURN
730 B: SLØPE=CP; RETURN
740 C: SLØPE=CV*KAPPA/BETA; RETURN
750 D: SLØPE=CV; RETURN
760 E: SLØPE=-T*V*BETA; RETURN
770 F: SLØPE=T*BETA/KAPPA; RETURN
780 PVT(L):
790 GØTØ(P, V, T)L
800 P:  PVT=PRES(V, T); RETURN
810 V:  PVT=VØL(P, T); RETURN
820 T:  PVT=TEM(P, V); RETURN
830 FG(X, Y, Z):
840 N3=N2-6
850 GØTØ(7, 8, 9, 10, 11, 12)N3
860 7 CALL  CBK(Z, Y, X)
870 F=Y*X*BETA/CP
880 G=-Y*CV*KAPPA/CP
890 RETURN
900 8  CALLCBK(Y, Z, X)
910 F=-BETA*X/(CV*KAPPA)
920 G=-CP/(KAPPA*Z*CV)
930 RETURN
940 9  CALLCBK(Y, X, Z)
950 F=-KAPPA*CV/(BETA*Z); G=CP/(Z*X*BETA); RETURN
960 10CALLCBK(P, Y, X)
970 F=1./CP; G=Y*BETA/CP; RETURN
980 11CALLCBK(Y, V, X); F=1./CV; G=BETA/(KAPPA*CV); RETURN
990 12CALLCBK(Y, X, T); F=KAPPA/(BETA*T); G=-1./(T*X*BETA); RETURN
1000 ØUTP(X, Y, Z):
1010 N3=N2-6
1020 GØTØ(20, 30, 40, 45, 47, 49)N3
1030 20CALLLINE(Z, Y, X, 0); RETURN
1040 30CALLLINE(Y, Z, X, 0); RETURN
1050 40CALLLINE(Y, X, Z, 0); RETURN
1060 45CALLLINE(P, Y, X, Z); RETURN
1070 47CALLLINE(Y, V, X, Z); RETURN
1080 49CALLLINE(Y, X, T, Z); RETURN
1090 ENDØUTP
```

PVTEXP CØNTINUED

```
1100 ØK;
1110 PRINT"SPECIFY FIXED PARAMETER",;INPUT1,I,VAL;I=LETTR(I);S(I)=VAL/FF(I)
1120 PRINT"SPECIFY STEPPED PARAMETER WITH INITIAL AND FINAL VALUES AND ST
1130 INPUT2,J;INPUT,VAL,STØP,STEP;J=LETTR(J);S(J)=VAL/FF(J);STØP=STØP/FF(J)
1140 STEP=STEP/FF(J)
1150 IF((3.5-I)*(3.5-J))70;N2=3*I+J-4;N2=N2-N2/4;S(6-I-J)=PVT(6-I-J)
1160 CALLTITLE
1170 Q=0;CALLLINE(P,V,T,Q)
1180 VAR=START=S(J)
1190 L=6-I-J
1200 597DQ=0
1210 DØ 598, JJ=0,8
1220 S(J)=VAR+JJ*STEP/8
1230 S(L)=PVT(L)
1240 598 DQ=SLØPE(N2)*W(JJ+1)+DQ
1250 Q=Q+STEP*DQ/24
1260 599 CALLLINE(P,V,T,Q)
1270 VAR=VAR+STEP
1280 IF(ABS(STØP-START)-ABS(VAR+.001*STEP-START))BEGIN,BEGIN,597
1290 70PRINT"SPECIFY ANØTHER P-V-T CØØRDINATE ØF THE STARTING PØINT",
1300 INPUT1,K,VAL;K=LETTR(K)
1310 S(K)=VAL/FF(K);CALLTITLE;S(10-J-K-I)=PVT(10-J-K-I)
1320 IF(3-J)80;N2=J+6;X0=S(MAX0(K,6-K-J));Y0=S(MIN0(K,6-K-J));GØTØ75
1330 80N2=I+9;X0=S(MAX0(K,6-I-K));Y0=S(MIN0(K,6-I-K))
1340 75Z0=S(J);CALLØUTP(X0,Y0,Z0);H=STEP
1350 CALLFG(X0,Y0,Z0)
1360 XX=X0+H*F
1370 YY=Y0+H*G
1380 Z=Z0+H
1390 CALLFG(XX,YY,Z)
1400 X1=.5*(X0+XX+H*F)
1410 Y1=.5*(Y0+YY+H*G)
1420 CALLØUTP(X1,Y1,Z)
1430 55CALLFG(X1,Y1,Z)
1440 X20=X2=X0+2.*H*F
1450 Y20=Y2=Y0+2*H*G
1460 F1=F;G1=G
1470 10CALLFG(X2,Y2,Z+H)
1480 X2NEW=X1+.5*H*(F1+F)
1490 Y2NEW=Y1+.5*H*(G1+G)
1500 IF(1.E-5-ABS(1.-X2/X2NEW)) 11
1510 IF(1.E-5-ABS(1-Y2/Y2NEW)) 11
1520 X2=X2NEW+.2*(X20-X2NEW);Y2=Y2NEW+.2*(Y20-Y2NEW)
1530 Z=Z+H
1540 CALLØUTP(X2,Y2,Z)
1550 IF(ABS(STØP-Z0)-ABS(Z+.001*H-Z0))BEGIN,BEGIN
1560 X0=X1;Y0=Y1;X1=X2;Y1=Y2
1570 GØTØ55
1580 11 X2=X2NEW;Y2=Y2NEW;GØTØ10
1590 SUBRØUTINE TITLE
```

PVTEXP CØNTINUED

```
1600 PRINT"      PRESSURE      VØLUME          TEMPERATURE     HEAT FLØW"
1610 PRINT"        (ATM.)      (LITERS)        (DEG. KELVIN)   (CALØRIES)"
1620 RETURN
1630 SUBRØUTINELINE(P, V, T, Q)
1640 CØMMØN FF(4)
1650 PRINT, P*FF(1), V*FF(2), T, Q*FF(4)
1660 RETURN
1670 $DATA
1680 1 4 2 4 2 4 2 4 1
1690 9.86927E-6 .999972 1. 2.3912E-4
```

PVTEXP

## Program Description
(Language: FORTRAN)

Line No. Comments

110 - 160 S is a vector containing the current values of P,V,T and Q to which it is equated by the EQUIVALENCE statement. W is a set of weight factors used in the integration routine and FF is a set of conversion factors to allow for the fact that MKS units are used internally and atmospheres, liters, and calories are used for input and output.

multiplying by FF(1) converts $nt/m^2$ to atmospheres
multiplying by FF(2) converts $m^3$/kgmole to liters/gmmole
multiplying by FF(3) converts from $^oK$ to $^oK$
multiplying by FF(4) converts from joules to calories.

170 - 180 R is the gas constant. A5 and B5 are the Van der Waals constants, a and b, and may be easily changed here.

190 - 210 The present code for substance number is: 1 = ideal gas; 2 = van der Waals gas; 3 = ideal Debye solid. If the substance number is not positive, the program stops.

220 - 230 LETTR convents letters to numbers such that:

P becomes 1
V becomes 2
T becomes 3
Q becomes 4

The numbers are then used as identifying parameters.

240 - 340 A solution of the equation of state for V(P,T). Other cases may be entered here if desired. The iterative solution for the Van der Waals case is suggested by Tribus. No attempt has been made to select an appropriate root when below the critical point. The convergence sometimes fails in this region. Therefore, to study the Van der Waals equation in this region, one should specify the volume.

The volume of the solid is calculated from

$$d(\ln V) = - \text{kappa} * dP + \text{beta} * dT$$

$$\text{kappa} = (680 + .275 * T)\ 10^{-9}/\text{atm}$$

$$\text{beta} = (41.5 + .023 * T) * 10^{-6}/^oC \text{ at } P = 1 \text{ atm.}$$

(These values are from Allis & Herlin p. 32, for copper.) The equation of state follows after converting to MKS values and integrating from the assumed initial state (1 atm., $7.1*10^{-3}$ $m^3$, $300^oK$) first along P=1 atm. until $T = T_f$, then along that isotherm until $P = P_f$. Clearly this stretches the data beyond its validity, but the result may be used for instructional purposes.

350 - 400 The pressure solutions.

410 - 460 The temperature solutions.

470 - 680 This routine supplies $C_p$, $C_V$, beta and kappa. Beta (the coefficient of expansion) and kappa (the compressibility) are obtained from the equations of state. For the ideal gas, $C_p$ and $C_v$ are those for a monotonic gas and independent of temperature. For the Van der Waals gas, $C_p$ is as given by combining the value for an ideal diatomic gas (Tribus, p. 177ff, $H_2$ values) with the Van der Waals corrections given by Crawford, p. 338ff. The hyperbolic term is completely negligible below $50^oK$. The Debye function expansions used for the solid are as given by Zharkhov and Kalinin, p. 241. Numerical tests show this

calculation to give nearly four-figure accuracy in the worst case (which is near the Debye temperature).

690 - 770 This routine sets the derivative to be used in the Simpson rule integration. The user has specified which variable is to be constant and which is the controlled variable. If only P, V, and T are involved, the other variable is determined from the equation of state and the appropriate derivative for Q may be expressed (by the usual methods) in terms of P, V, T, $C_p$, $C_V$, beta and kappa. Which derivative is required is determined by the value N2, set previously.

780 - 820 This routine determines P, V, or T from the equation of state. The variable to be determined is specified by the value of L.

830 - 990 If Q is one of the specified parameters, then <u>two</u> of the P-V-T variables must be determined by integration. F and G are the required derivatives. They are determined from the TdS equations for the particular case specified by N2, which carries information about both the fixed and stepped variables. For N2 = 7, 8, or 9, the stepped variable is P, V, or T, respectively, and the process is adiabatic. For N2 = 10, 11, or 12, the fixed variable is P, V or T, respectively, and Q is the stepped variable. In each case, two P-V-T variables must be determined by integration. F is the appropriate derivative for the first required integration and G is the derivative for the second. (The order is P, V, then T).

1000 - 1090 Since the variables X, Y, and Z may be one of several arrangements of the set P,V,T, and Q, it is necessary to sort them into proper order before printing. The selection of this order is determined by the value of N2.

1100 - 1140 This is the first part of the input routine. The equation is read, ignoring the = sign, the proper subscript is determined by LETTR, and the conversion factors are used.

1150 If either I or J was 4 (i.e., Q), another initial parameter is needed. Otherwise, N2 is set according to the following table and the remaining P-V-T value is obtained from the equation of state.

| I | J | N2 |
|---|---|---|
| 1 | 2 | 1 |
| 1 | 3 | 2 |
| 2 | 1 | 3 |
| 2 | 3 | 4 |
| 3 | 1 | 5 |
| 3 | 2 | 6 |

1160 - 1170 Prints a title, intializes Q, and prints the initial line.

1180 This line initializes the variable used in the Simpson rule integration and also stores the starting value for later reference.

1190 L becomes the subscript for the P-V-T value which will be determined from the equation of state.

1200 - 1280 A nine-point Simpson rule integration (see Pennington, p. 193ff) for Q. S(J) is the stepped variable and S(L) is determined from the equation of state. The other variable, S(I) is fixed. The stopping criterion in line 1260 allows for both negative and positive steps and for a small round-off error in the value of VAR.

1290 - 1310 This is similar to 1110 in case another P-V-T value was required.

1320 If J is not 4, then I = 4 here. The value of N2 is set and X0 and Y0 are the (ordered) variables to be determined by integration.

1330 If J is 4; similar to 1320.

1340 Initialize the stepped variable for integration and print the initial line.

| | |
|---|---|
| 1350 - 1580 | The integration of two simultaneous differential equations for the two variables (P, V or T) not determined by the input. Simultaneous equations are required since the slope at intermediate points along the path may depend upon the value of the *other* variable at those intermediate points. The method used here is taken from McCracken & Dorn, p. 343ff. |
| 1590 - 1620 | Prints title. |
| 1630 - 1660 | Prints a line of output data after converting to appropriate units. |
| 1670 - 1690 | The conversion factors in 1670 may be changed if another system of units for I-O is desired. |

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