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AVAILABLE ENERGY CONTOUR LINES ON T-S AND P-V PLANES

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## ABSTRACT

The primary objectives of this paper are : 1-To present the available energy balance equation for a non-reacting closed system. 2- To develop and discuss a computational method for plotting the available energy contour-lines of that system on the temperature-entropy, and pressure-volume planes. 3-To apply the method and present the contour-lines for three different cases for air : i - as a perfect gas (having perfect gas equation of state and constant specific heats), ii. as a semiperfect gas (having perfect gas equation of state and temperature-dependent specific heats), and iii- as a real gas (having Vander-Waals equation as an example for equation of state , and temperature-dependent specific heats).

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## INTRODUCTION

Available energy has been a subject in classical thermodynamics that can be traced back over a period of more than 100 years. However, there have been significant developments within the last few years. In the course of this extensive treatment of the subject, some reproduction of well-known material is unavoidable if clarity and continuity of presentation are to be maintained. Parts of the present work are thought to be original, particularly in the concise nature of the general methodology developed for plotting the available energy contour-lines for real substances.

The method developed here can easily be extended to represent the available energy surface in three dimensions. The importance of this work lies in the fact that it enables appropriate evaluation and design criteria to be set-up for many work-producing and work - absorbing systems. Examples of using the contour - lines to analyze cycle performance of I.C. engines are given in [1-2].

## AVAILABLE ENERGY BALANCE EQUATION

The available energy a, for a non-reacting closed system communicating only with the surroundings is defined, (e.g.[4] and [8]), as the maximum work which could be obtained by bringing the system to a state of thermodynamic equilibrium with the surroundings - to its dead state at pressure $P_{0}$ and temperature $T_{0}$. The value of a per unit mass of the system is given by:
$a=u+K E+P E+P_{0} v-T_{0} s-\left(u_{0}+P_{0} v_{0}-T_{0} s_{0}\right)+a_{0}$
where $u, K E$ and $P E$ are the values per unit mass of the internal, kinetic and potential energies, and $v$ and $s$ are specific volume and entropy of the system respectively. In the absence of KE and PE and with the available energy at dead state $a_{0}=0$, Eq. (1) reduces to :
$a=u-u_{0}+P_{0}\left(v-v_{0}\right)-T_{0}\left(s-s_{0}\right)$
The above equation is composed entirely of changes in properties and does not involve heat or work: It applies to all closed systems.

COMPUTATIONAL METHOD
The calculation of thermodynamic properties of any simple substance requires expressions of two types:
(1) an equation for constant volume specific heat at low density $c_{V}^{0}(T)$, and
(2) a $\mathrm{P}-\mathrm{v}-\mathrm{T}$ equation of state, which can be put in the form:
$P=\rho R T+F(\rho, T)$
where $R$ is the gas constant, and $F$ is a function of $\rho$ and $T$ with $F=0\left(\rho^{2}\right)$ as $\rho-0$, so that semiperfect behaviour is obtained at low densities( $P=\rho R T$ ). For the present work the above two expressions are assumed known. They will be used in the following manner.

The internal energy $u$ is generally a function in $T$ and $v$ and its differential
equation of change ( with $\left.c_{V}=\left(\frac{\partial u}{\partial T}\right)_{V}\right)$ is :
$d u=c_{v} d T+\left(\frac{\partial u}{\partial v}\right)_{T} d v$
An important thermodynamic relationship is :
$T d s=d u+P d v$ which can be put in the form $T\left(\frac{\partial s}{\partial v}\right)_{T}=\left(\frac{\partial u}{\partial v}\right)_{T}+P$. Using the Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_{T}=\left(-\frac{\partial P}{\partial T}\right)_{V}$ and the above equality, then
$d u=c_{v} d T+\left[T\left(\frac{\partial P}{\partial T}\right)_{v}-P\right] d v$
Integrating the above equation over the path shown in Fig.l, and using $d v=\frac{-d \rho}{\rho^{2}}$ and Eq. (3), then
$u-u_{0}=\int_{T_{0}}^{T} c_{v}^{0}(T) d T+\int_{0}^{\rho}\left(\frac{1}{\rho^{2}}\right)\left[F(\rho, T)-T\left(\frac{\partial F(\rho, T)}{\partial T}\right)\right] d \rho$


Fig.1. Path of integration for Eq.(5). Note that the first integration is at zero density and the second is at constant temperature.

The entropy is determined from the Gibbs equation: $d s=\left(\frac{1}{T}\right) d u+\left(\frac{P}{T}\right) d v$. Adding and subtracting $R(d \rho / \rho)$, integrating over the path shown in Fig.1, and using Eq.(3), the last equality can be rearranged into:
$s-s_{0}=\int_{T 0}^{T}\left(\frac{c^{0} v(T)}{T}\right) d T-R \ln (\rho)+\int_{0}^{\rho} \frac{1}{\rho^{2}}\left[\left(-\frac{\partial F(\rho, T)}{\partial T}\right)\right] d \rho$
Datums for $u$ and $s$ are chosen $s o$ that $u-u_{0}=0$ and $s-s_{0}=0$ for semiperfect gas at $T_{0}$ and $P_{0}$. This is done by adding
$\left[-\int_{0}^{\rho_{0}}\left(\frac{1}{\rho^{2}}\right)\left[F\left(\rho, T_{0}\right)-T_{0}-\frac{\partial F(\rho, T)}{\partial T}\right] d \rho\right] \&\left[\operatorname{Ren}\left(\rho_{0}\right)-\int_{0}^{\rho_{0}}\left(\frac{1}{\rho^{2}}\right)\left[-\frac{(\partial F(\rho, T)}{\partial T}\right] d \rho\right]$
to the R.H.S. of Eqs (6) and (7) respectively. Also substituting
$v-v_{0}=\frac{1}{\rho}-\frac{1}{\rho_{0}}$ into Eq. (2)., it reduces to :
$a=\int_{T_{0}}^{T} c_{V}^{0}\left(1-\frac{T_{0}}{T}\right) d T+T_{0} R \ln \left(\frac{\rho}{\rho_{0}}\right)+\frac{P_{0}}{\rho_{0}}\left(\frac{\rho_{0}}{\rho}-1\right)+\int_{0}^{\rho}\left(\frac{1}{\rho^{2}}\right)[F(\rho, T)+$
$\left.T_{0}\left(1-\frac{T}{T 0}\right) \frac{\partial F(\rho, T)}{\partial T}\right] d \rho-\int_{0}^{\rho 0}\left(\frac{1}{\rho^{2}}\right)[F(\rho, T)] d \rho$

(note that $a=0$ at $T_{0}$ and $P_{0}$ ). Equation (8) can be written in the compact form:
$z(a, \rho, T)=0$
Mathematically, the above equation is a level surface in the $z(a, \rho, T)$-space, (since grad $z=(\partial z / \partial a, \partial z / \partial \rho, \partial z / \partial T) \neq(0,0,0)$ at every point in the $z(a, \rho, T)$ space). The equation for the available energy contour-1 in es(level curves) is:
$z\left(a^{*}, \rho, T\right)=0, a^{*}=$ const
Equation (9) is a nonlinear equation in $\rho$ and $T$, and its degree of complexity depends on the expressions of $C_{V}(T)$ and $P(\rho, T)$ used in it, and a stable nonlinear technique must be used to solve it .

The general technique for the case of a perfect gas witi be outlined.Equation(8), for a perfect gas (with $\rho=\left(\frac{1}{V}\right)$, and $a=a^{*}=$ const.), reduces to :
$a^{*}=C_{v} T_{0}\left[\left(\frac{T}{T_{0}}-1-\ln \left(\frac{T}{T_{0}}\right)\right]+R T_{0}\left[\left(\frac{v}{v_{0}}\right)-1-\ln \left(\frac{v}{v_{0}}\right)\right]\right.$
or
$a^{*}=c_{v} T_{0} f\left(\frac{T}{T_{0}}\right)+R T_{0} f\left(\frac{v}{v_{0}}\right)$
where $f(x)=[x-1-\ln (x)]$ is always a non-negative function for $x>0$. Since $\left(\frac{T}{T_{0}}\right)>0$ and $\left(\frac{V}{V_{0}}\right)>0$, then Eq. $(10 \mathrm{~b})$ gives bounds for $f\left(\frac{T}{T_{0}}\right)$ and $f\left(\frac{\mathrm{~V}}{V_{0}}\right)$ as :
$0<f\left(\frac{T}{T_{0}}\right)<\left(\frac{a^{*}}{C_{v} T_{0}}\right)$, and $0<f\left(\frac{v}{v_{0}}\right)<\left(\frac{a^{*}}{R T_{0}}\right)$
This means that $T$ and $v$ can be defined only within these bounds. Also for any admissible value of $v$ ( or $T$ ), Eq. ( 10 b ) gives two corresponding T(or v) values. The computational procedure, in a global sense, reduces to solving Eq. (10b) by assuming admissible values for $T$ (or $v$ ) and solving for the two roots of the other variable. The procedure is to be repeated till the admissible domain of $T$ and $v$ is covered .

## CASE i. AIR AS A PERFECT GAS

Figures (2a) and (2b) show five constant available energy contour-lines on the $p-v$ and $T-s$ planes, along with lines of constant $p, v, T$ and $s$. In the first figure, the line $T=T_{0}$ is the locus of points on the available energy contour- lines where $(\mathrm{dp} / \mathrm{dv})=\infty$. Also in the second figure, lines of $p=\mathrm{p}_{0}$ and $v=v_{0}$ are the loci of points on the contour-lines where ( $\mathrm{dT} / \mathrm{ds}$ ) $=\infty$, and $(\mathrm{dT} / \mathrm{ds})=0$ respectively. In Fig. (2a), as $T$ decreases (below $T_{0}$ ), the contour-lines approach each other very fast specially as $p$ goes below $p_{0}$ and $v$ goes above $v_{0}$. Similar situation exists in Fig, (2b).

CASE ii. AIR AS A SEMIPERFECT GAS
Temperature- dependent specific heats, (shown in Fig. (3a) and (3b), and the perfect gas equation of state, are used to represent the air as a semiperfect gas. The temperature range covered by the specific heat equation is 273-3800 K, with maximum error $1.64 \%$. A comparison between the contour-1ines
of this case and that of case $i$ shows that there is no difference on the $p-v$ plane, while on the T-s plane, the difference,(case $i$ is greater than caseii) increases as $T$ increases. The maximum difference is a temperature shift of 12 K at $T=680 \mathrm{~K}$ for the contour-1ine $a^{\star}=100.0 \mathrm{KJ} / \mathrm{Kg}$.

CASE iii. AIR AS A REAL GAS
The Vander-Waals equation of state (given in Figs (4a) and (4b)) and the same temperature - dependent specific heat equations, used in case ii , are used to represent air as real gas. The contour - lines in this case are exactly the same as those of case ii .

## CONCLUSIONS

The method presented in this paper for plotting the contour - lines is quite general and can be used for any non-reacting closed system. The importance of these contour-lines in second law (exergy) analysis of workproducing and work - absorbing processes and cycles is comparable to the use of steam-tables and other thermodynamic charts in first law(energy) analysis. Finally, it is worth to mention that the graphes preseated here are computer plotted, and the computer program can be easily used to plot the contours for any non- reacting material, provided that $c_{v}^{0}(T)$ and

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## NOMENCLATURE

a
$c_{v}, c_{p}$
$\mathrm{c}_{\mathrm{V}}^{0}$
$F, f, z$ functions
$K E, P E$ sp. kinetic and potential energies
$P$ pressure
R,M gas constant and molecular wt. for air
Ro unjversal gas const.
s sp. entropy
T absolute temperature
$u \quad s p$. internal energy
$v$ sp. volume

- density

Subscript:
o condition at reference (dead) state.

i1g. 2a. dvallable enerzy contour-lines on the P-v plane for air as a perfect gas, $v_{0}=0.844 \mathrm{~m}^{3} / \mathrm{kg}$.


Fig. 2b. Available energy contour-lines on the T-s plane for air as a perfect 3as, $v_{0}=0.344 \mathrm{~m}^{3} / \mathrm{kg}$.

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Eig. 3a. Avallable energy contour-lines on the P-v plane for alr as a semperfect gas, $v_{0}=0.844 \mathrm{cum} / \mathrm{kg} ., c_{0}=0.661, c_{1}=0.213 \times 10^{-3}$ and $z_{2}=-0.031 \times 10^{-6}$.


Fig. 3b. Available energy contour-lines on the T-s plane for afr as a semiperfect gas, $\mathrm{v}_{0}=0.844 \mathrm{cu} \llbracket / \mathrm{kg}, c_{0}=0.661, c_{1}=0.213 \times 10^{-3}$ and $c_{2}=-0.031 \times 10^{-6}$.


1g. 4a. dvallable energy contour- lines on the ?-v plane for air as a
eal gas, $v_{0}=0.844 \mathrm{cu} \mathrm{m} / \mathrm{kg} ; c_{0}=0.661, c_{1}=0.213 \times 10^{-3}$ and $c_{2}=-0.031 \times 10^{-6}$,
and Vander-Haals constants: $a=0.1358 \mathrm{MPa} \cdot\left(\mathrm{a}^{3} / \mathrm{kgmole}\right)^{2}$ and $\mathrm{b}=0.0364 \mathrm{~m}^{3} / \mathrm{kgmole}$


Fi3. 40, Available energy contour-lines on the $\mathrm{T}-\mathrm{s}$ plane for air as d real gas, $v_{0}=0.844 \mathrm{cu} \mathrm{m} / \mathrm{kg}, c_{0}=0.661, c_{1}=0.213 \times 10^{-3}$ and $c_{2}=-0.031 \times 10^{-6}$, and Vander-Waals constants: $\mathrm{a}=0.1358 \mathrm{MPa} \cdot\left(\mathrm{m}^{3} / \mathrm{kgmole}\right)^{2}$ and $b=0.0364 \mathrm{~m}^{3} / \mathrm{kgmole}$.

