

物理化学力学进展

PROGRESS IN PHYSICS CHEMISTRY
MECHANICS

《物理化学力学进展》编委会

新热力学第二定律，耦合律 (LOC) (中国，1988):
“物系不能由低熵态趋于高熵态而又同时放出热量！”

	熵增加	熵不变	熵降低	
吸热	LOC (3): 发生过程	无此现象	无此现象	$\theta \wedge Q$
无热	LOC (4): 发生过程	LOC (5): 发生过程	无此现象	$\theta = Q$
放热	无此现象	LOC (2): 发生过程	LOC (1): 发生过程	$\theta \vee Q$
	$\Delta S > 0$	$\Delta S = 0$	$\Delta S < 0$	

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(4)

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1997

内 容 简 介

本卷含研究专论 14 篇。继卷 3 后，剖析了热力学状态场论理论体系，论述了地球环境无耗散系统、核素示踪原理、环境界面作用；开拓了固体材料热力学状态场论；以及反映了非线性断裂力学非局部平衡、断裂表面、磁性材料、有限元理论、低温核聚变等诸多前沿科学问题上的创新学术成果。全书反映物理-化学-力学交叠学科研究中的新进展。可供从事相关学科研究、教学的专家学者及研究生参考。

物 理 化 学 力 学 进 展 (4)

《物理化学力学进展》编委会

责任编辑：宋炳忠

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热力学统一场论 (S-F. TOT) 创始人刘叔仪教授 八十华诞志庆



本刊主编刘叔仪教授 1918 年 12 月诞生于贵州毕节，是中国科学技术大学物理化学一级教授（离休）。1943、1946、1949 年刘叔仪先生相继在原国立武汉大学、美国匹兹堡大学、美国克城凯斯（Case）理工学院获冶金学学士、化学冶金学硕士、物理（含力学）冶金学博士学位。尔后，刘先生在美国费城斯瓦斯莫（Swarthmore）大学任副研究员一年，主持造船钢板低温脆化研究。此时，中华人民共和国已屹立在世界的东方，年轻的刘博士学成业就思归，婉言谢辞了美国方面的挽留，于 1950 年 6 月 26 日登船东归。

经历两月余的漫长航程，怀着报效祖国的赤子之心，刘叔仪博士于当年 9 月中旬回到阔别多年的故土，并在天津应聘为北洋大学冶金系教授。直到 1956 年 8 月，因院系调整，刘教授先后执教于北洋大学、清华大学、华北工学院（现北京理工大学）、北京钢铁学院（现北京科技大学）；1951 年，仅 33 岁的北洋大学刘叔仪教授与复旦大学苏步青教授、中国科学院华罗庚教授、清华大学钱伟长教授四人，同时被高等教育部任命为首届部聘研究生导师。1956 年 8 月至 1960 年 3 月期间刘叔仪教授就任中国科学院 2 级研究员；1960 年 3 月调任中国科学技术大学任物理化学教授。

五十余年的科研、教学生涯中，刘叔仪教授治学严谨，诲人不倦而循循善诱，为祖国培养出了数以百计的具有现代高科技水平的栋梁之材。如今桃李芬芳，刘门弟子正肩负着国家党政、教育、科研和企业的重任。其中，一些已成为名驰海内外的跨世纪学科带头人。

刘叔仪教授积数十年之科学开拓，于 1979～1991～1997 年间创立并扩展了一个横跨物理、化学、力学三个基础学科的“新热力学派”的新学科：热力学状态场论 (S-F. TOT)。

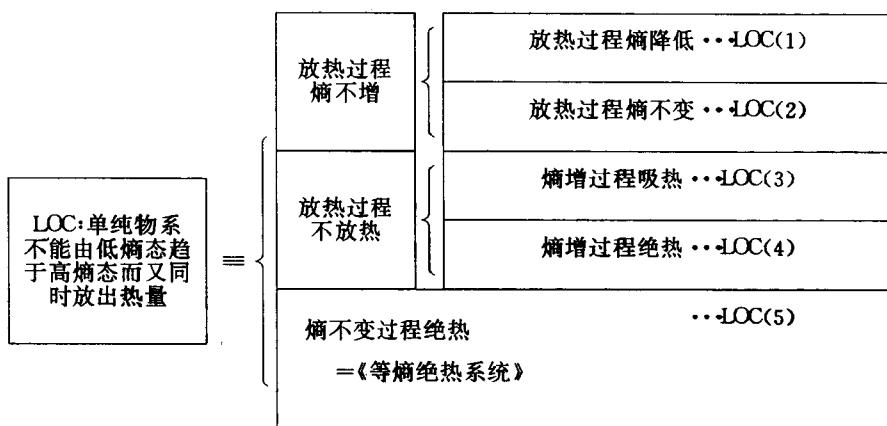
按数学：什么坐标系中有微分方程，那个坐标系所描述的空间内就有该微分方程所定的场 (Field) 和填满此空间的互不相交的场线簇。此种数学场论可按空间的物理本质之不同而分两大类：第一类是熟知的实几何空间 (x, y, z, t) 内的“输运场论”、“(固、液、气) 物态力学场论”、“电磁场论”、“量子场论”、以及爱因斯坦的“4 度几何空间的统一场论”。

第二类数学场论是刘叔仪教授在《纪念爱因斯坦百年华诞科学报告会》上提出的热力学状态坐标系 (y_1, y_2, \dots, y_f) 所描述的热力学状态空间 $\Omega^f (y_1, y_2, \dots, y_f)$ 内的《热力学状态场论 (S-F. TOT)》。例如：命 $(y_1, y_2) = (\text{体积 } V, \text{ 压强 } P)$ ，则有 $\Omega^2 (V, P)$ 平面中的《熵场理论》！泛言之：

因为由“整个宇宙”到 “ $V_{\min} = 10^{-18} \text{ cm}^3$ 的凝聚宏观微子系”之间的大大小小的一切宏观物系都服从 (S-F. TOT)，所以 (S-F. TOT) 与爱因斯坦“4 度几何空间的统一场论”是平行的。

由此，简称为《热力学统一场论》 \supset 《新创热力学第二定律：耦合律 (LOC)》：(LOC) 是由热力学第一定律在不知熵方程 $dS = ?$ 的条件下证出的《熵 (S) 定性存在定理》研究出来的《一句否定性的律文》 \equiv 《五句肯定性的律文》，称为《耦合律的五个分支》：LOC (1)、LOC

(2)、LOC (3)、LOC (4)、LOC (5)。一切宏观自然过程皆在这五个分支中：



详情如本卷封面及本卷两篇论文内之图解表所示，刘叔仪教授的《热力学统一场论》(LOC)已在科学前沿取得了重大突破！

值此《物理化学力学进展》(卷4)问世之际，适逢刘叔仪教授八十华诞！谨在此衷心祝愿刘教授健康长寿！恭祝刘教授开创的科学领域繁茂发展！

《物理化学力学进展》编辑委员会

1997.5

CELEBRATION OF THE EIGHTIETH BRIGHT ANNIVERSARY OF THE BIRTH OF PROFESSOR LIU SHUYI, THE FOUNDER OF THE UNITED FIELD THEORY OF THERMODYNAMICS

Professor Liu Shuyi of the University of Science and Technology of China (USTC) has established and vastly extended a New Discipline "**United Field Theory of Thermodynamics**" ⊃ "**A New (2ndLaw) of Thermodynamics, the Law of Coupling (LOC)**" which states "**It is impossible to approach a High Entropy state from a Low Entropy one with Evolution of Heat**" (1985). LOC ⊃ 5 Branches: LOC (1), LOC (2), LOC (3), LOC (4), LOC (5): All natural phenomena are in these 5 branches; But the 4 mathematical cases are not natural phenomena, as shown on the cover and in The Papers of (Vol. 4) PPCM.

We are happy to celebrate the bright eightieth anniversary of birth of professor Liu Shuyi on the day of publication of PPCM (Vol. 4). We heartily wish him a **joyful long life** so that he can **CEASELESSLY CREATE NEW IMPORTANT KNOWLEDGES** of the UNITED FIELD THEORY OF THERMODYNAMICS for the generations to come!

Editorial Committee of PPCM

May 1997

ER TONG BOOK

序

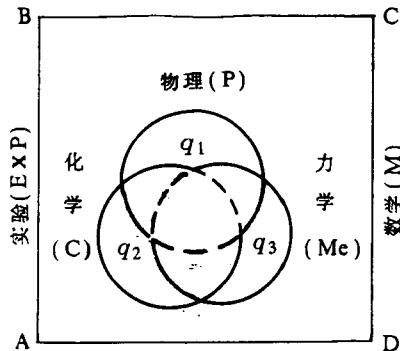
《PPCM》是一个“进展”型的“跨学科”或“交叠学科”的不定期出版物。什么叫“交叠”？怎么个“交叠”法呢？

学科的数目很多，内中的各色各样的自然科学系统内的科技问题的数目更多到难以数计！那么，这许多学科、系统与问题如何“交叠”呢？原来学科、系统与问题虽多，要解决这许多问题，只涉及五“层”基础：

一平面代表“实验”
一平面代表“数学”
一平面代表“物理学”
一平面代表“化学”
一平面代表“力学”

使五层交叠于一个平面内：
（五者交叠出）三角形 ($q_1 q_2 q_3$)
= (五层交叠学科) …… (甲)

三中心在一等边三角形的顶点



如图所示，它与（甲）式的内容已经发表了 15 年之久（刘叔仪，一门基本的交叉科学，贵州科技报，1981. 5. 25），1985 年创始的《PPCM》在（甲）式的方向上到底走了好远？

今回首，《进展》祈审焉：

- 有蓉城布鲁塞尔派之最大信息热力学理论体系；
- 有厦门哥本哈根学派的有限时间热力学创论；
- 有湘师大派的（理论物理）统一场论之宏论；
- 有（沈、湘、湘、蓉、京）五派之材料科学独创；
- 有齐鲁派之基本粒子创论；
- 有筑派之地球化学新进展；
- 有大连化学物理学派之化学动力学新进展；
- 有编委获诺贝尔奖（1992，化学），第一次；
- 还有北京热力学状态场论学派的新创学科：“热力学状态场论（S-F.TOT）”新创热力学第二定律，耦合律（LOC）”，这包括“（克劳休斯-卡诺）的热力学第二定律”作为特

况！而且还证明了古今热力学界所未能证明的耗散现象的热力学存在！（S-F·TOT）□
(LOC) 已经在古今科学前沿各大领域（如宇宙论，环境科学，低温核聚变，经典与非经典的非平衡过程等等）造成了“各向大突破”！

兹值《PPCM》卷4问世之际，编委会全体同仁谨凝诚向天涯比邻之学人高士致敬，希不吝赐教赐稿。

果园秋实桂开花，
投向高楼小木瓜。
遐迩来鸿若坠玉，
燕山有雁到君家。

《PPCM》编委会
1997年3月于北京

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本刊顾问主编 R. A. 马库斯教授

荣获 1992 年诺贝尔化学奖



鲁道夫·马库斯教授是国际著名的科学家，化学反应速率理论的权威学者。在此领域里他作出了许多杰出贡献。他的创造性的工作和活跃的开拓性思想启迪了无数理论家和实验家。由于在分子间电子转移方面的基础理论的突出成就，他荣膺 1992 年诺贝尔化学奖。

电子转移反应的“马库斯理论”成了解释许多实验结果的奠基石，包括复杂过程的反应速率，马库斯交叉反应关系，马库斯倒置区，分子几何效应，剂效应，反应的标准自由能，电化学过程和生物电子转移。马库斯的工作提供了一种

数学模式用以计算在不破坏化学键的前提下电子在分子间跃迁时的快慢和方向。

马库斯还将电子转移的思想推广到质子、原子和基团的转移。这些工作开拓了有机和生化中有关原子和基团转移反应的理论研究。

标志着现代单分子反应理论的 RRKM 是由马库斯基于 RRK 理论而发展的。这一理论现今为实验学家广泛地用以解释包括诸如从热裂到异构化，从光激发到活化的化学过程或束过程等单分子速率现象。总之，这一单分子反应速度理论几乎是无所不包的。RRKM 理论的胜利推进了非 RRKM 现象的理论研究。马库斯教授本人也是非 RRKM 现象的研究的先驱。

马库斯在非弹性和反应性碰撞以及束缚态的半经典理论方面的开创性研究值得人们可以理解应用广泛的经典轨迹计算的优点和局限性，而这种计算方法常用于研究分子束、红外化学萤光等有关现象。

马库斯还作了许多其它颇具影响的贡献。诸如提出“自然碰撞坐标”的概念，处理原子转移的反应哈密顿算符，“马库斯—柯尔钦路径”，以及最近的将人工智能方法引入分子内动力学，特别是分子内的能量转移的研究。

Professor Rudolph A. Marcus

Prof. Rudy Marcus is internationally well-known and the leading scientist in theories of chemical reaction rates. He has widely been acclaimed for his many outstanding contributions to this field. His creative works and active original ideas have stimulated numerous subsequent experimental and theoretical researches by various scholars. He won the Nobel Prize in chemistry in 1992 for his fundamental theories of how electrons transfer between molecules.

"Marcus Theory" of electron transfer reactions established the cornerstone for understanding experimental data in many aspects, including the calculation of reaction rates for these complex processes, the "Marcus cross-reaction relation", the "Marcus inverted region", the effect of molecular geometry, solvent, and standard free energy of reaction, electrochemical processes and biological electron transfers. The work provides a mathematical way to determine how fast or slow, or in what direction, electrons jump between molecules without breaking chemical bonds.

Marcus has also generalized the electron transfer idea to other transfers of proton, atoms and groups. This work pioneers the path of theoretical study of atom transfer and group transfer reaction in organic chemistry and biochemistry.

"The RRKM theory" developed by Rudy Marcus, based on the earlier RRK theory, represents the advent of the modern theory of unimolecular reactions. This theory is widely used today by experimentalists to interpret measurements of all kinds of unimolecular rate phenomena, from thermal dissociation to isomerization, from photoexcitation to activation, both chemically and in beams. In summary, it is nearly all-inclusive. The success of RRKM theory has encouraged extensive studies for "non-RRKM" behavior. Marcus himself has been in the forefront of exploring the non-statistical behavior.

Marcus pioneering research on semiclassical theory of inelastic and reactive collision and bound states provided a basis for understanding the merits and limitations of the wide and practical use of classical trajectory calculations to investigate molecular beam, infrared chemiluminescence and relevant phenomena.

Marcus has also made many other influential contributions, including the introduction of the concept of "natural collision coordinates", a reaction Hamiltonian for treating atom transfer, the "Marcus-Coltrin path", and most recently, the introduction of Artificial Intelligence searches to the study of intramolecular dynamics, particularly, the study of energy transfer within molecules.

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Abstract and brief introduction

In the period(1979 ~ 1991), A NEW DISCIPLINE(S-F. TOT)Was Established by the authors of this paper [1], [2], ..., [8]; In this paper, We BEGIN to ESTABLISH Another NEW DISCIPLINE((OEOE)(S-F. TOT))BY APPLICATION of the (OLD(1st and 2nd) Laws OT TREATED By(S-F. TOT)), TO DISSIPATIONLESS System WITHOUT Using the New(2nd-Law)OT, the Law of Coupling(LOC).

In § 1, (S-F. TOT) FOUNDATION was given with complete Details of Derivations SO THAT Beginners MAY HAVE Enough theoretical preparation to ENTER into the Research Work without going thru the Articles[1], [2], ..., [8];

In § 2, Interesting Experiments were done to Measure Atmospheric Temperature AT Two Stations(1 and 2);

In § 3, IMPORTANT Theories Were Set up to INTERPRETE the Experimental Results of this paper and to PROVIDE more FOUNDATION for the DEVELOPMENT of ((OEOE)(S-F. TOT)).

A MORE Detailed SUMMARY of this paper is given in the CONCLUSIONS at the end of

the paper, the readers are suggested to go thru these CONCLUSIONS.

§ 1(S-F. TOT)FOUNDATION for Open Environment Of Earth(OEOE)

(1) What is State-Field Theory of Thermodynamics(S-F. TOT)

I(1-1)What is (S-F. TOT)? |(A), (B)|^①

(A)[In the Period(1979 ~ 1991), A NEW DISCIPLINE refered as State-Field Theory of Thermodynamics(S-F. TOT), ACROSS Physics, Chemistry and Mechanics, was established by the authors[1], [2], ..., [8]. Many Poly-directional Break-up Along Various Frontiers of Modern Science and Technology Have Been Made by(S-F. TOT)] I(1-1)(A)

(B)STATE-FIELD:[Classic Field in Geometrical Space of Coordinates(x, y, z) is Material Field such as Magnetic Field with Non-Intersecting FAMILY of Field-Lines; Different from Material Field, State-Field is ABSTRACT Field in State Space of Thermodynamic Coordinates such as

$(y_1, y_2) = (V, P); (P, T); (T, V)$. $(V, P, T) = (\text{Volume, Pressure, Temperature})$. For Example: The Free Energy(Z) is a function of(T, P):

$[Z(T, P) = C] = [\text{A Field Line in}(T, P)\text{plane}]; \text{When the Constant } (C) \text{ takes all possible continuous values, there appear a Non-Intersecting Family of (Free Energy) CONTOURS as Field-lines}] I(1-1)(B)$

(2) 3 Kinds of Thermodynamic STATES

I(1-2)Equilibrium States(E. States):Definitons and Principles|(A), (B), (C)| :

(A)Definitions about(E.State):

[IF: In FINITE time interval(Δt), the(experimentally) MEASURABLE macroscopic properties($y_1, y_2, \dots, y_f, \dots, y_N; V, P, T$) OF The[(Thermodynamic SYSTEM of macroscopic materials) = System] and the INMEASURABLE macroscopic properties($\Phi_1, \Phi_2, \dots, \Phi_e$) DONOT CHANGE WITH TIME(t), (A)Condition

THEN:

(a) The Sytem IS in(E.State)WITHIN(Δt); (A)_a

① I(1-1)⋯|(A), (B)| is A MASTER FORMULA of [Paper I, Section § 1, Subsection(1)], Which CONTAINS EQUATIONS|(A), (B)| Designated AS:
 [Paper I, Section § 1, Subsection(1)]; I(1-1)(A)
 [Paper I, Section § 1, Subsection(1)]. I(1-1)(B)
 In later Papers(II , III , IV , V ⋯), the above type of master formula and its equations WILL BE REFERED AS SUCH.

(b) $(\Phi_1, \Phi_2, \dots, \Phi_e)$ are (E.State) Functions; (A)_b

(c) $[(y_1, y_2, \dots, y_f, \dots, y_N; V, P, T) \text{ and } (\Phi_1, \Phi_2, \dots, \Phi_e)]$ ARE ALL referred AS [(E.State) VARIABLES, and (EACH of them) is a Single-Valued Continuous and Differentiable (S.V.C.D) Function of Certain INDEPENDENT Variables (y_1, y_2, \dots, y_f) :
 (EACH) = $f(y_1, y_2, \dots, y_f) \dots$ (S.V.C.D)] I(1-2)(A)

(B) (E.State) Equation:

[@ Any Equation of Type (A)_c Above is Referred as An (E.State) Equation:

$$y_{fti} = f_i(y_1, y_2, \dots, y_f) \dots \text{(S.V.C.D)} \dots \text{(B)}_a$$

⑤ (E.State) Equation of Hydrostatic System (V, P, T) :

$$T = f(V, P) \dots \text{(S.V.C.D)} \dots \text{(B)}_b$$

⑥ (E.State) Equation of Equilibrium Ideal Gas (E.IG):

$$T = R^{-1}(PV) \dots \text{(B)}_c \dots \text{I (1-2)(B)}$$

(C) [Surface of (E.States)] (SES) and Surface Representation:

[of Thermodynamics:

⑦ {The Geometric Figure of (E.State) Equation [$T = f(V, P)$] in the 3-dimensional Coordinate System} is a SURFACE Known as (SES) (C).

⑧ Each Point in (SES) Represents An (E.State) of the System and Each Point Outside (SES) Represents A Non-Equilibrium State (N-E.State) of the System; And Thermodynamic (Concepts, Relations, ...) Can be Represented By (SES) ... (C)_b] I(1-2)(C)

(3) 3 Kinds of States: (E.States), (Quasi-Equilibrium States) (Q-E.States) and (N-E.States):

I(1-3) 3 Kinds of States and Plane Representation of Thermodynamics {(A), (B), (C), (D)}:

(A) Plane Representation of Thermodynamics:

⑨ In the Cartesian Coordinate System $(y_1, y_2) = (V, P)$; OR (P, T) ; OR (T, V) , Each Point (y_1, y_2) Represents An (E.State) of The Material System; (A)_a

⑩ Thus the POSITION Vector r of the Point (y_1, y_2) Represents The Same (E.State):

$$r = [y_1, y_2] = (\text{E.State}) \dots \text{(A)}_b$$

⑪ Example: $r = [V, P] = (\text{E.State})$ of the System (A)_c

⑫ Thermodynamic (Concepts, Relations) Can Also Be Represented in The PLANE (y_1, y_2) ... (A)_d] (1-3)(A)

(B) Quasi-Equilibrium State (Q-E.State):

⑬ IF: The State-Distance (ξ) Between A State (I) and Its Neighbouring (E.State) (i) is Infinitesimal

$$0 < \xi \rightarrow 0,$$

THEN: State (I) is termed as (Q-E.State) in the Neighbourhood of (E.State) (i) (B)_a

⑭ (Q-E.State) Does Change With Time (t), But Its Rate of Change is Infinitely SLOW!

..... (B)_b

② But, in EVALUATION of (Q-E. State) Properties,

$\because (0 < \zeta \rightarrow 0)$ has NO VALUE to be taken definitely,

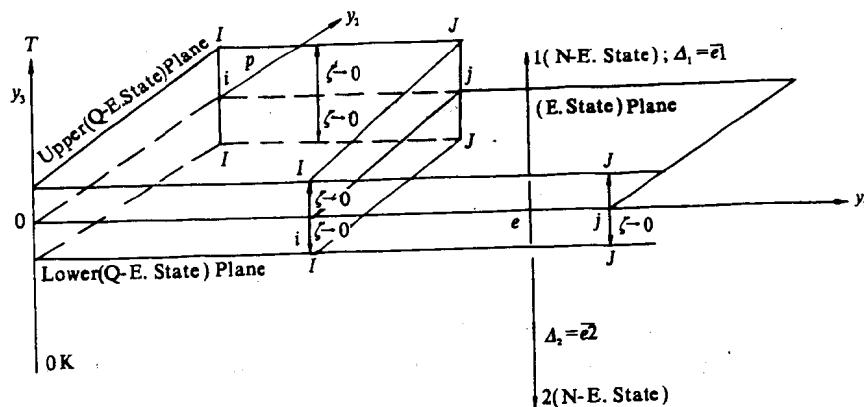
\therefore VALUE OF [(Q-E. State) Property = (E. State) Property]

Such as (Q-E. State) Equation = (E. State) Equation $f(V, P, T) = 0$ (B)_c

③ But PHYSICALLY:

(Q-E. State) \neq (E. State) ... (B)_d] I(1-3)(B)

(C) Non-Equilibrium State (N-E. State):



FigI(1-3) Plane representation of 3 kinds of states

[④ Plane Representation of 3 Kinds of States FigI(1-3):

(E. States) (Such as i, j) Are IN The (E. State) Plane — The Middle Plane (V, P) in Fig (1-3) From WHICH The State-Distances (ζ, Δ) Are Measured (C)_a

⑤ The (Upper and Lower) (Q-E. State) Plane Contain ALL (Q-E. states) (Such as I, J) In the Neighbourhood of the (E. State) Plane with:

$0 < \zeta \rightarrow 0$ (C)_b

⑥ Any State (Such as 1, 2) Separated From the (E. state) Plane By FINITE Distance (Δ) (Such as Δ_1 and Δ_2) is A (N-E. State):

$\Delta \geq (\zeta \rightarrow 0) \dots \{\} \text{c}]$ I(1-3)(C)

(D) Independent NUMBER of State-Variables of

[(Hydrostatic and Hydrodynamic) Systems:

⑦ The RATE of Change of state: TableI(1-3):

State:	(E. State)	(Q-E. State)	(N-E. State)
Rate of State Change	0	$0 < (\text{Rate}) \rightarrow 0$	The Rate Varies in The Following Enormous Range:
	(Finite minute rate such as $\frac{dV}{dt} = \dot{V} = 10^{-100} \text{ ml/s} \rightarrow$ (relativistic speed))		

② Hydравстic System has ONLY 2(State-Variables):

$$(y_1, y_2) = (V, P); \text{or} (P, T); \text{or} (T, V) \dots \dots \dots \quad (D)_b$$

③ But, For (N-E) Hydrodynamic system, the NUMBER of Independent Variables is NOT YET KNOWN Completely, They are:

$$(V, P, T; \dot{V}, \dot{P}, \dot{T}; \dots \dots \dots) \dots \dots \dots \quad (D)_c$$

④ Thermodynamics of (N-E. states) is Not Matured in Many Respects! (D)_d] $\dots \dots \dots \quad (1-4)(D)$

End I(1-3){(A), (B)(C), (D)}
End[Theory of states(TOS)]

Theory Of Processes(TOP)

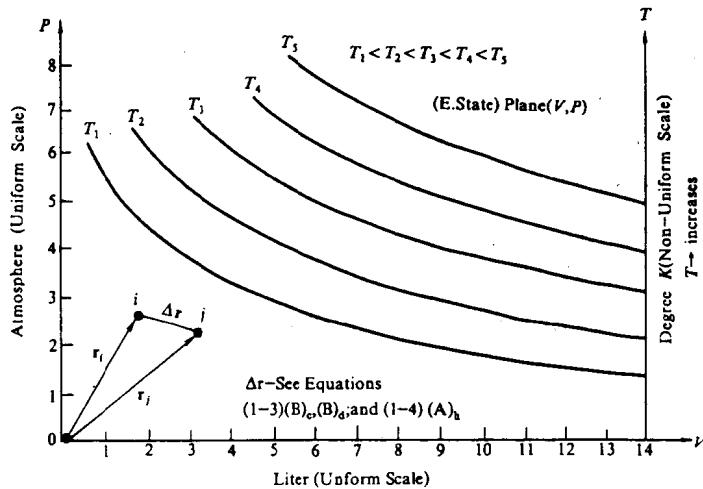
(4) Definitions of 2 Kinds of Thermodynamic Processes, and Their Properties:

I(1-4) Classic Processes{(A), (B), (C)}:

(A) 3 Kinds of States and Classic Processes:

[@] (E.State) Curve is NOT LOCUS of Process:

An (E.State) Curve is An 1-dimensional Continuous Collection of (E. States), Such as Isothermal Curves in FigI(1-4)(I) $\dots \dots \dots \quad (A)_a$



FigI(1-4)(I) The isothermal(E.state) curves

⑥ By Definition I(1-2)(A)_a, Any (E.state) on an Isothermal (E.state) Curve Can NOT change With Time(t) —— (Rate) = 0, NO Process! So, An (E.state) Curve is NOT the Locus of