Does Entropy Play a Role in Biology?

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Embryo Physics Course, April 3, 2013

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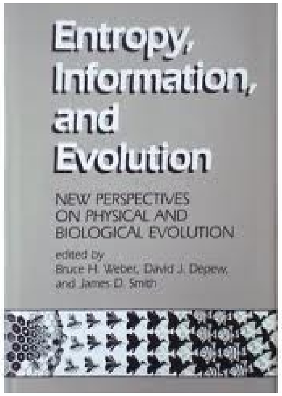
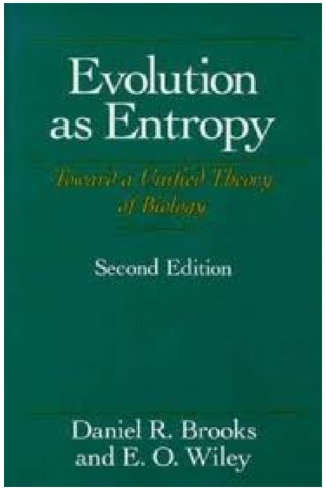
Introduction

- I used to be a thermodynamicist:
  - http://evgenii.rudnyi.ru/publications.html
  - Practical applications of entropy in chemical thermodynamics
- Biology:
  - Entropy is related to information
  - Entropy is related to evolution





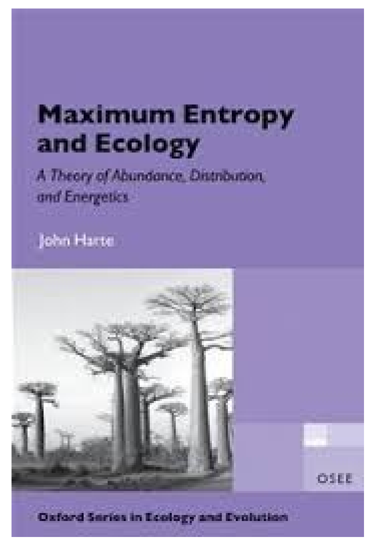
- The entropy as I know it is different from entropy in biology.

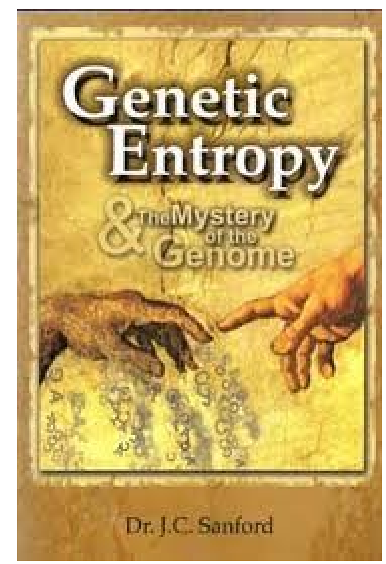
Outline

- Short introduction to entropy in (chemical) thermodynamics
  - Practical science to solve practical problems

- Entropy and information

- Entropy and evolution





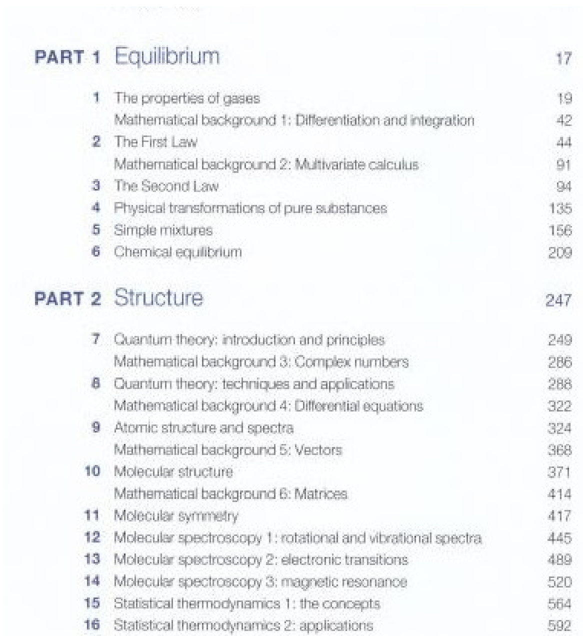
Does Thermodynamics have Foundations?

- See for example MIT's Teaching the Second Law
  - http://video.mit.edu/watch/teaching-the-second-law-9283/

- It would be a bad idea to start learning thermodynamics by discussing its foundations.

Where to Start

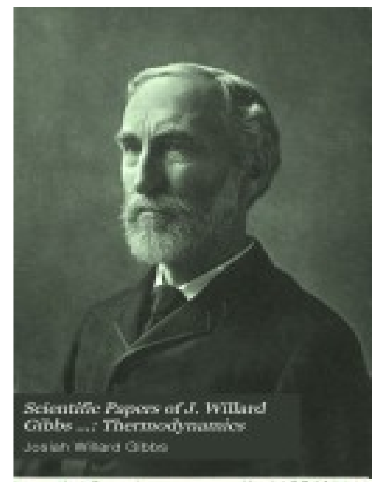
Peter Atkins, Physical Chemistry



Josiah Willard Gibbs

"On the Equilibrium of Heterogeneous Substances"

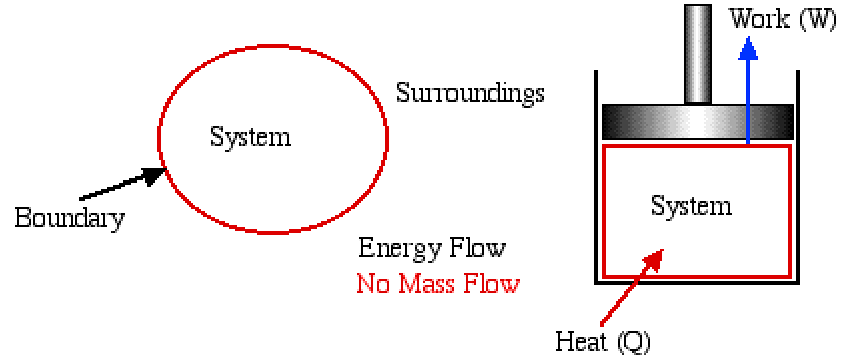
1875–1878



IMPORTANT: First learn classical thermodynamics

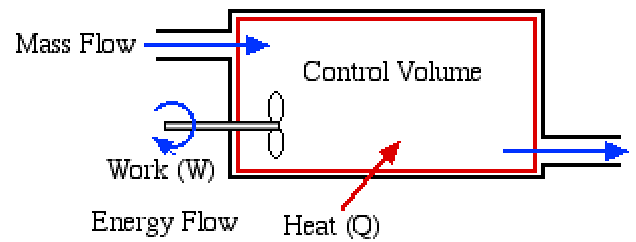
Thermodynamic System

- Isolated system
- Closed system
- Open system



http://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter1.html

- There is no "just entropy"
- Entropy must be of something



Typical Fallacy in Biology

- E. Calvin Beisner, Mutation Fixation: A Dead End for Macro-evolution: http://www.icr.org/article/270/
  - “and that the idea of their improving rather than harming organisms is contrary to the Second Law of Thermodynamics, which tells us that matter and energy naturally tend toward greater randomness rather than greater order and complexity.”

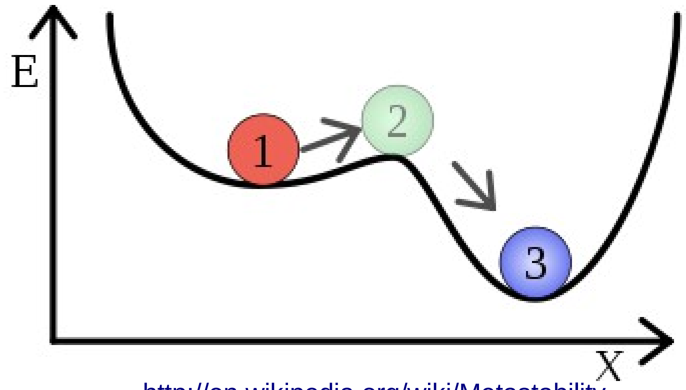
- Potential meaning: the entropy of an isolated system is maximal at equilibrium?
  - The Earth (biosphere) is not an isolated system though.

Equilibrium

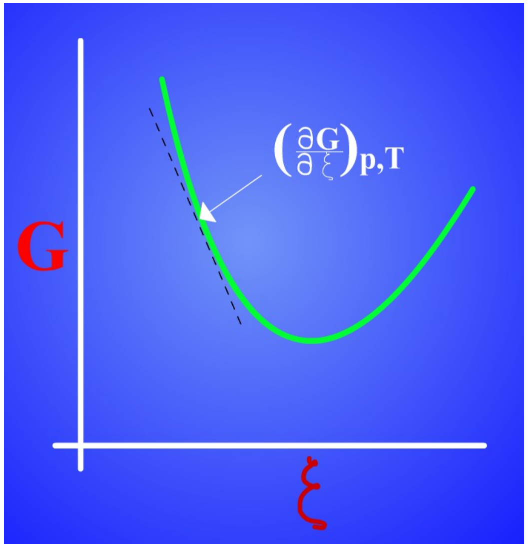
- Zeroth Law of Thermodynamics:
  - Two systems in equilibrium have the same temperature
- Thermodynamics goal: equilibrium criterion
  - Computing equilibrium composition
- Thermostatics or thermodynamics?
- Thermodynamics does not replace kinetics
  - There is no explicit time in thermodynamics
  - Time could be implicit though
    - Local equilibrium

Stable, Metastable and Frozen Equilibrium

- Nonequilibrium state
  - Thermodynamics can deal with it as well
- Example: $N_2 + 3H_2 = 2NH_3$
  - Consider the mixture with and without a catalyst
  - Frozen equilibrium

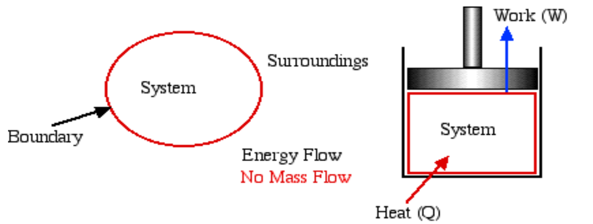


http://en.wikipedia.org/wiki/Metastability



http://www.unomaha.edu/tiskochem/Flash_Files/Gibbs.swf

Function of State: Physics



- The First Law
- The Second Law

$$dU = \delta Q - \delta W \qquad dS \geqslant \delta Q / T \qquad (1)$$

$$\int_a^b dU = U_b - U_a = \Delta U \qquad (2)$$

- Function of State
  - Does not depend on path
- Function of Change
  - Depends on path

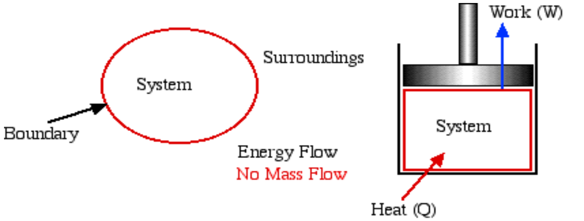
$$\int_a^b \delta Q = Q \qquad (3)$$

- The way to proceed:
  - We do not need inequality in this equation.

$$dU = TdS - pdV \qquad (4)$$

$$U(S,V) \quad T(S,V) \quad p(S,V)$$

Function of State: Mathematics



- A closed system at equilibrium:
  - two independent variables.
- Chemists' choice:
  - temperature and pressure.
- There are other options:
  - There are many equations.

$$G = U - TS + pv$$

$$dG = -SdT + Vdp$$

$$U(T, p) \quad G(T, p)$$

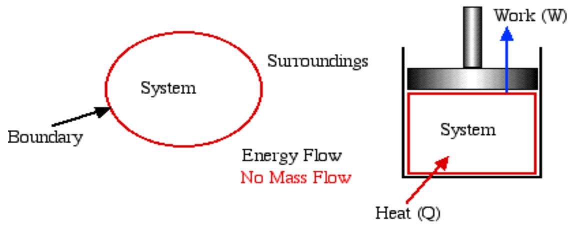
$$S(T, p) \quad V(T, p)$$

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

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$$

Function of State: Mathematics



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Experimental Thermodynamics

- The Third Law
  - Entropy is absolute
- Enthalpy (internal energy)
  - Only change can be measured;
  - Enthalpy of formation

Journal of
Physical and Chemical Reference Data

Monograph No. 9

NIST-JANAF Thermochemical Tables
Fourth Edition
Part I, Al-Co

Malcolm W. Chase, Jr.

National Institute of Standards and Technology
Gaithersburg, Maryland 20899-0001

- JANAF Thermochemical Tables (Joint Army-Naval-Air Force Thermochemical Tables)

Chloroborane (BCl) $B_1Cl_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.862	138.362	138.362	INFINITE
100	29.117	180.668	240.206	−5.954	139.790	131.204	−68.534
200	29.874	200.994	216.081	−3.017	140.875	122.156	−31.904
250	30.748	207.751	213.761	−1.502	141.209	117.435	−24.537
298.15	31.659	213.245	213.245	0.	141.419	112.835	−19.768
300	31.693	213.441	213.245	0.059	141.425	112.658	−19.615
350	32.572	218.394	213.635	1.666	141.546	107.852	−16.096
400	33.335	222.794	214.510	3.314	141.583	103.036	−13.455
450	33.976	226.759	215.654	4.997	141.551	98.219	−11.401
500	34.510	230.367	216.948	6.710	141.462	93.408	−9.758
600	35.322	236.735	219.729	10.204	141.159	83.823	−7.297
700	35.892	242.225	222.560	13.766	140.730	74.300	−5.544
800	36.307	247.046	225.325	17.377	140.209	64.844	−4.234
900	36.619	251.342	227.982	21.024	139.614	55.459	−3.219
1000	36.861	255.213	230.514	24.698	138.958	46.143	−2.410

http://www.nist.gov/data/PDFfiles/jpcrdM9.pdf

NIST Webbook: http://webbook.nist.gov/

Water - Mozilla Firefox

File Edit View History Bookmarks Tools Help

NIST Water

webbook.nist.gov/cgi/cbook.cgi?Formula=h2o&NoIon=on&Units=SI&cTC=on

Condensed phase thermochemistry data

Go To: Top, References, Notes / Error Report

Quantity	Value	Units	Method	Reference	Comment
$\Delta_f H^\circ_{liquid}$	-285.830 ± 0.040	kJ/mol	Review	Cox, Wagman, et al., 1984	CODATA Review value
$\Delta_f H^\circ_{liquid}$	-285.83	kJ/mol	Review	Chase, 1998	Data last reviewed in March, 1979
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
S°_{liquid}	69.95 ± 0.03	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
$S^\circ_{liquid,1\ bar}$	69.95	J/mol*K	Review	Chase, 1998	Data last reviewed in March, 1979

Liquid Phase Heat Capacity (Shomate Equation)

$C_p^\circ = A + B*t + C*t^2 + D*t^3 + E/t^2$

$H^\circ - H^\circ_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$

$S^\circ = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$

C_p = heat capacity (J/mol*K)
H° = standard enthalpy (kJ/mol)
S° = standard entropy (J/mol*K)
t = temperature (K) / 1000.

View plot Requires a Java capable browser.

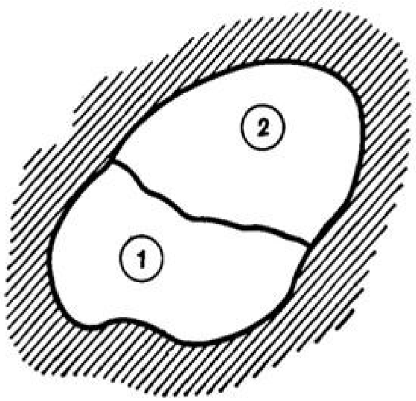
View table.

Open Systems

- Isolated system

$$U = const$$
$$V = const$$
$$m = const$$
$$S = max$$

- A subsystem in the isolated system



- New variables in a function of state

$$U(S, V, n_1, n_2, \ldots)$$

$$G(T, p, n_1, n_2, \ldots)$$

- Chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_{j \neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}}$$

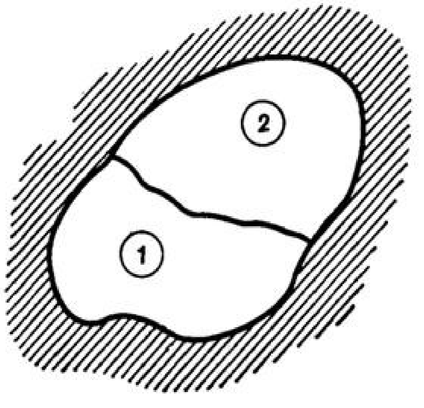
$$dG = -TdS + pdV + \Sigma \mu_i dn_i$$

Variational Principle

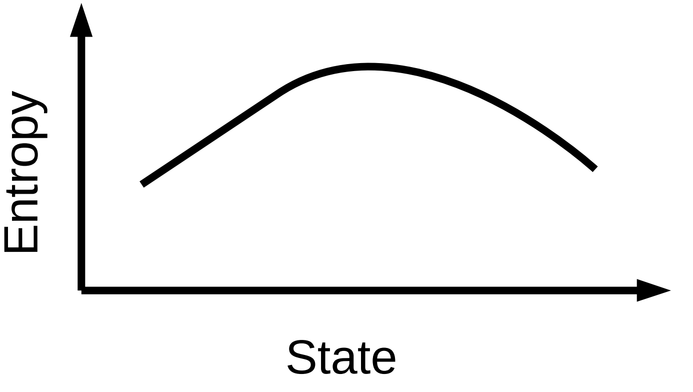
- Isolated system

$$U = U_1 + U_2$$
$$V = V_1 + V_2$$
$$m = m_1 + m_2$$
$$S = max$$

- A subsystem in the isolated system



- Virtual change



- Equilibrium Criterion

$$T_1 = T_2$$
$$p_1 = p_2$$
$$\mu_1 = \mu_2$$

http://twt.mpei.ac.ru/TTHB/2/KiSyShe/eng/Chapter5/5-3-Conditions-of-stability-and-equilibrium-for-an-isolated-homogeneous-system.html

Example 1: A mixture of N_2, H_2, NH_3, N_2H_4

- Given: a closed system at constant T, P, b_H, b_N
- Find: equilibrium number of moles

$$\min_{n_i} \quad G = \mu_{H_2} n_{H_2} + \mu_{N_2} n_{N_2} + \mu_{NH_3} n_{NH_3} + \mu_{N_2H_4} n_{N_2H_4}$$

$$2n_{H_2} + 3n_{NH_3} + 4n_{N_2H_4} = b_H$$

$$2n_{N_2} + n_{NH_3} + 2n_{N_2H_4} = b_N \qquad (1)$$

$$n_i > 0$$

$$N_2 + 3H_2 = 2NH_3$$

$$N_2 + 2H_2 = N_2H_4$$

$$\min_{\xi_j} G = \mu_{H_2} n_{o,H_2} + \mu_{N_2} n_{o,N_2} + \mu_{NH_3} n_{o,NH_3} + \mu_{N_2H_4} n_{o,N_2H_4} + $$

$$+ \xi_1 \left(2\mu_{NH_3} - 3\mu_{H_2} - \mu_{N_2}\right) + \xi_2 \left(\mu_{N_2H_4} - 2\mu_{H_2} - \mu_{N_2}\right) \qquad (2)$$

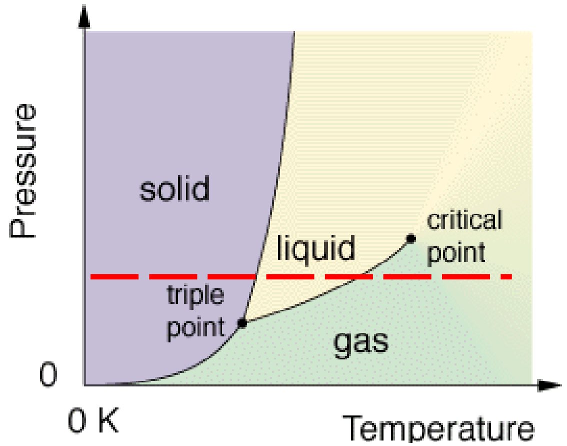
$$2\mu^*_{NH_3} - 3\mu^*_{H_2} - \mu^*_{N_2} = -RT \ln K_{x,1} =$$

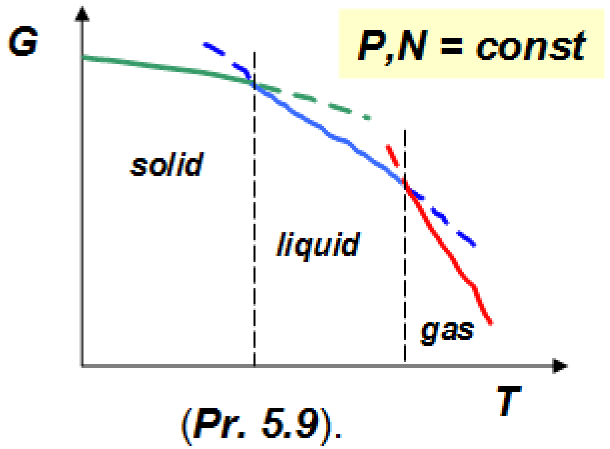
$$= -RT \ln \frac{\left(n_{o,NH_3} + 2\xi_1\right)^2 \left(n_o - 2\xi_1 - 2\xi_2\right)^2}{\left(n_{o,H_2} - 3\xi_1 - 2\xi_2\right)^3 \left(n_{o,N_2} - \xi_1 - \xi_2\right)} \qquad (3)$$

Example 2: One component phase diagram

- Given: a closed system at constant T, P
  - Mole Gibbs Energies
    - Solid $G_S(T, p)$
    - Liquid $G_L(T, p)$
    - Gas $G_G(T, p)$
- Find equilibrium composition

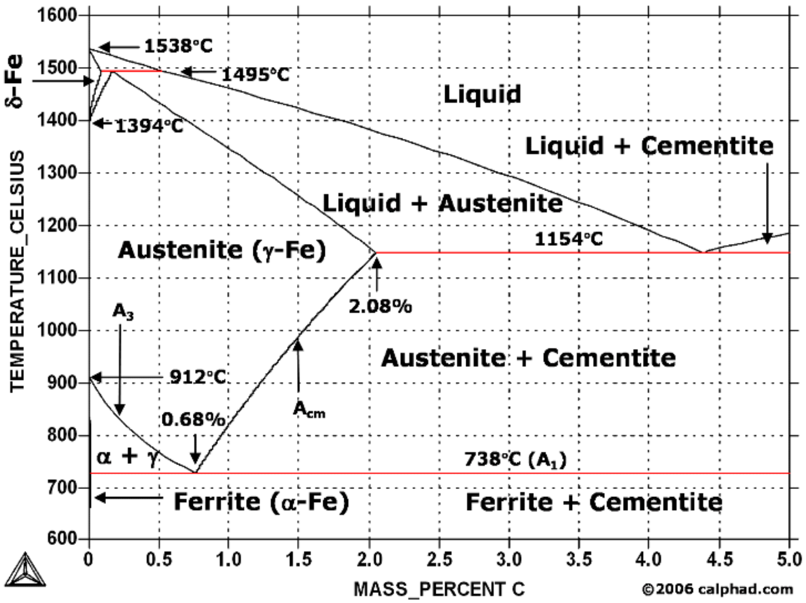
$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

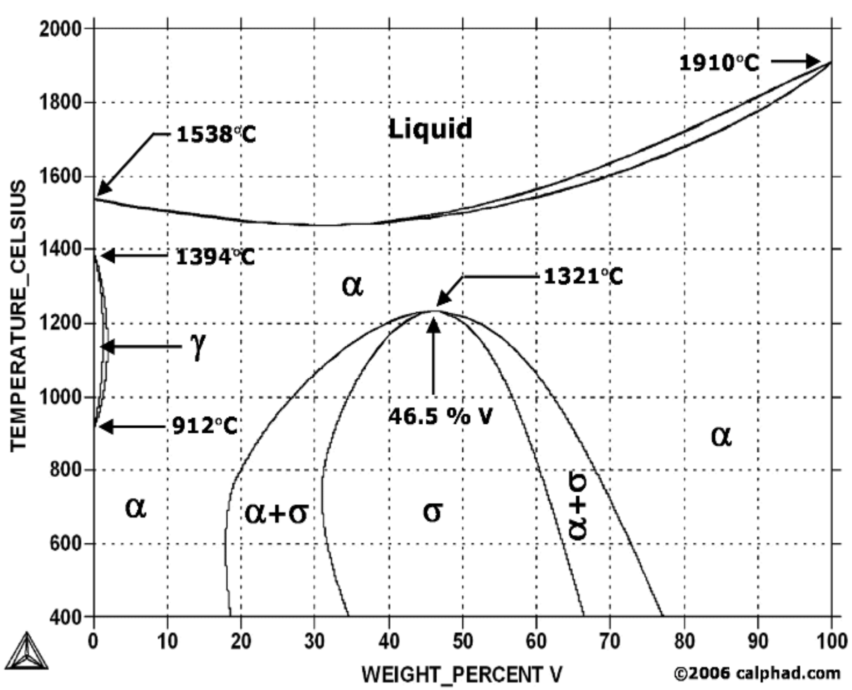




http://www.physics.rutgers.edu/~wdwu/351/Lecture15.ppt

CALPHAD: CALculation of PHAse Diagrams

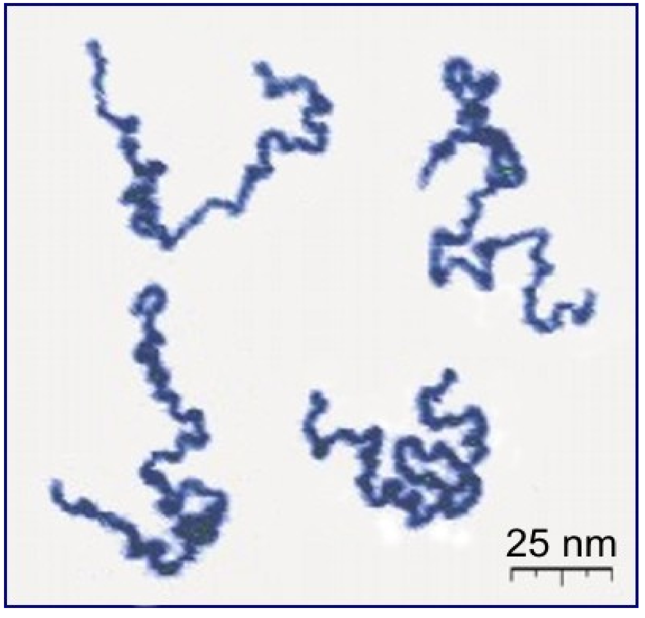




http://www.calphad.com/

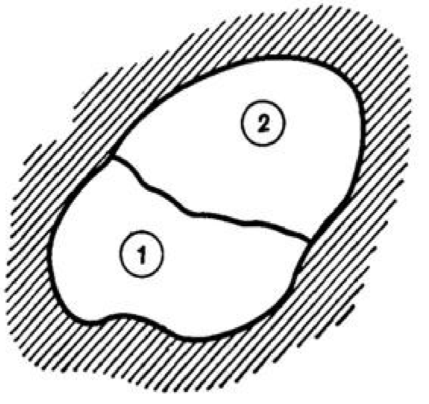
Problems with Extension of Thermodynamics

- Thermodynamics of polymers
  - How to define state?



http://en.wikipedia.org/wiki/Polymer

- Thermodynamics is additive $U = U_1 + U_2$

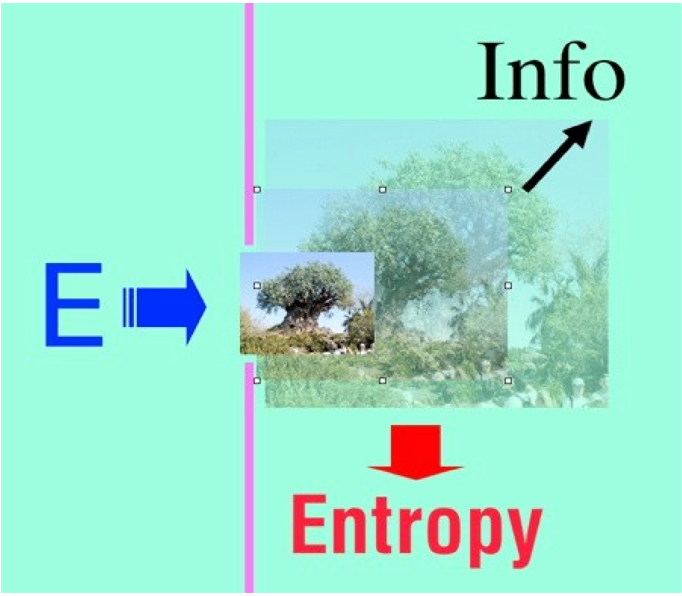


- Interfaces
  - Gibbs' excess properties
- Long range forces
  - Another thermodynamics to treat the Universe

Biology, Entropy, and Information

- Brenner, S. (2012). The Revolution in the Life Sciences. Recognition of DNA as the carrier of information created a new fundamental dimension for viewing the natural world. Science 338(6113), 1427-1428.

- Entropy = Information?



http://www.kk.org/thetechnium/archives/2009/01/the_cosmic_gene.php

P.S. My comment on the paper:
http://blog.rudnyi.ru/2012/12/dna-as-the-carrier-of-information.html

Short History on Entropy and Information, 1

- Ludwig Boltzmann, Statistical Thermodynamics
  - 1877, Entropy and the number of potential microstates
- Claude E. Shannon, Information Theory
  - 1948, A Mathematical Theory of Communication

The Bell System Technical Journal

Vol. XXVII July, 1948 No. 3

A Mathematical Theory of Communication

By C. E. SHANNON

Quantities of the form $H = -\Sigma\, p_i \log p_i$ (the constant K merely amounts to a choice of a unit of measure) play a central role in information theory as measures of information, choice and uncertainty. The form of H will be recognized as that of entropy as defined in certain formulations of statistical mechanics[8] where p_i is the probability of a system being in cell i of its phase space. H is then, for example, the H in Boltzmann's famous H theorem. We shall call $H = -\Sigma\, p_i \log p_i$ the entropy of the set of probabilities

[8] See, for example, R. C. Tolman, "Principles of Statistical Mechanics," Oxford, Clarendon, 1938.

Information Entropy

Short History on Entropy and Information, 2

- 1957, Edwin Thompson Jaynes
  - Entropy is Information!
  - Over 6000 citations in Google Scholar

Information Theory and Statistical Mechanics

E. T. Jaynes
Department of Physics, Stanford University, Stanford, California
(Received September 4, 1956; revised manuscript received March 4, 1957)

"With such an interpretation the expression "irreversible process" represents a semantic confusion; it is not the physical process that is irreversible, but rather our ability to follow it. The second law of thermodynamics then becomes merely the statement that although our information as to the state of a system may be lost in a variety of ways, the only way in which it can be gained is by carrying out further measurements."

"It is important to realize that the tendency of entropy to increase is not a consequence of the laws of physics as such, … . An entropy increase may occur unavoidably, due to our incomplete knowledge of the forces acting on a system, or it may be entirely voluntary act on our part."

My Discussion on Entropy vs. Information

- Everything-list, http://groups.google.com/group/everything-list
- Summary at http://blog.rudnyi.ru/2012/02/entropy-and-information.html
- A number of practical problems to think it over

- 1.1) From CODATA [14] tables
- S ° (298.15 K) J K-1 mol-1

- Ag cr 42.55 ± 0.20
- Al cr 28.30 ± 0.10

- What these values tell us about information?

Non-Equilibrium Thermodynamics

- For example: Course at TU Delft
  - http://ocw.tudelft.nl/courses/sustainable-processes-and-energy-technologies/non-equilibrium-thermodynamics/lectures/

$$\Delta S + \Delta S_0 \geq 0$$

$$\frac{dS_{irr}}{dt}\Delta t = \Delta S + \Delta S_0$$

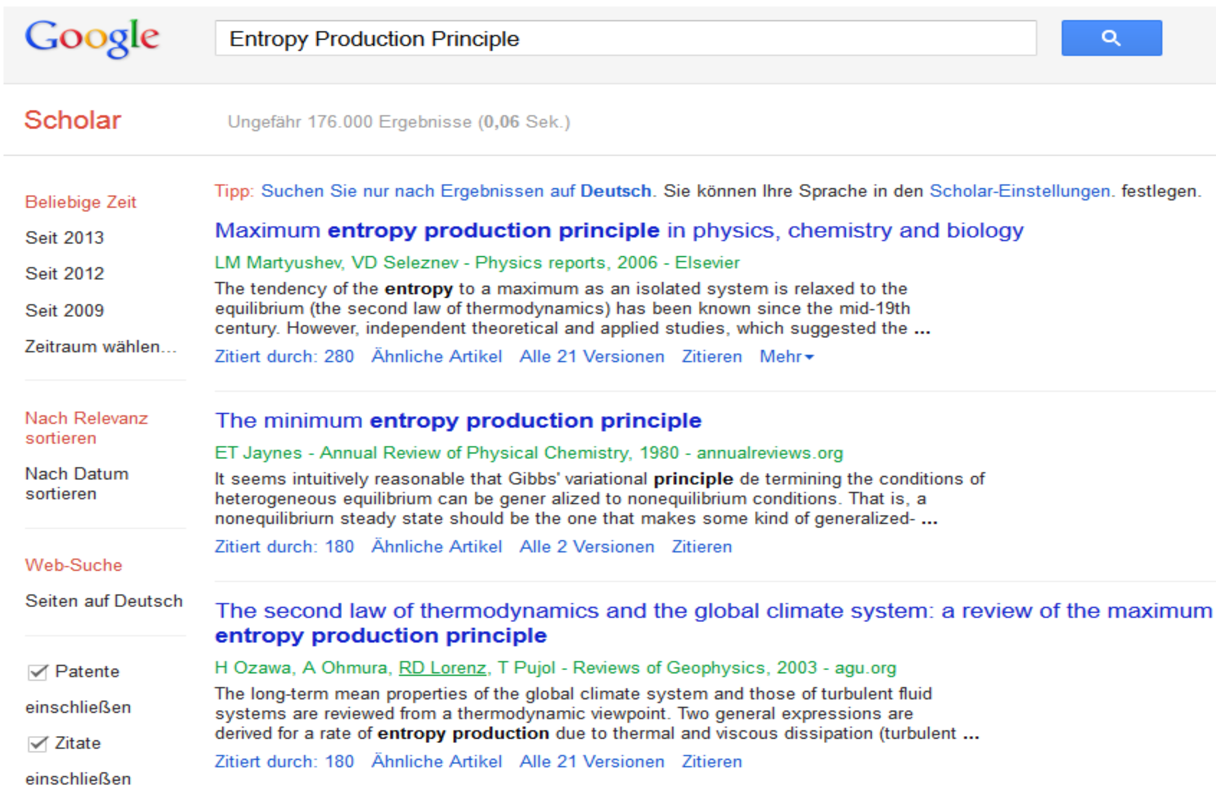
$$\frac{dS_{irr}}{dt} = \Omega \int_L \sigma(x)dx$$

$$\sigma = \sum_i J_i X_i \geq 0$$

- Entropy production is not a function of state.
- What is thermodynamic flux and thermodynamic force?

Extremum Principles for Entropy Production

- Prigogine: Minimum Entropy Production
  - Linear systems
- Now: Maximum Entropy Production Principle



Entropy and Evolution, 1

- Annila, A. & S.N. Salthe (2010) Physical foundations of evolutionary theory. Journal of Non-Equilibrium Thermodynamics 35: 301-321
  - My review at http://blog.rudnyi.ru/2013/02/physical-foundations-of-evolutionary-theory.html
- p. 303 “A chemical reaction mixture is an example of an open system that will naturally progress toward the most probable, i.e., the maximum entropy, state.”

- Put a glass with hot water on a table. The entropy of the glass will spontaneously decrease
  - The statement in the paper is factually wrong.

Entropy and Evolution, 2

- MAXIMUM ENTROPY PRODUCTION
- p. 307 “The 2nd law of thermodynamics in this form, as an equation of motion, is conceptually simple. It says: energy flows from heights to lows as soon as possible.”

- Diamond at normal conditions is thermodynamically unstable. Yet, people still buy diamonds as investment for future hard times.
  - The statement in the paper is factually wrong.

My Personal Notes on MEPP

ELSEVIER

Physics Reports 426 (2006) 1–45

www.elsevier.com/locate/physrep

Maximum entropy production principle in physics, chemistry and biology

L.M. Martyushev[a, b, *], V.D. Seleznev[b]

$$\delta_J \left[\sigma(J_k) - \mu \left(\sigma(J_k) - \sum_i X_i J_i \right) \right]_X = 0$$

- There are no simple examples:
  - Climate system; Crystal growth; Evolution in biology.
  - The simple problems have not been worked out.
- Relationship between minimum and maximum entropy production is puzzling:
  - "Thus, some hierarchy of the processes is observed. If the time is short, the system maximizes entropy production at preset fixed forces at a given moment. … If the time is long, the system changes free thermodynamic forces so as to decrease entropy production."

Conclusion: Nice example on entropy and biology

http://www.facebook.com/photo.php?fbid=10151498176469589

- *Ille Gebeshuber*: Not just Gold and magnets, but also ice is produced by bacteria: The bacterium *Pseudomonas syringae* produces proteins which cause water to freeze at fairly high temperatures.