

# Does Entropy Play a Role in Biology?

Evgenii Rudnyi

CADFEM GmbH

Rosenheim, Germany

<http://blog.rudnyi.ru>, [evgenii@rudnyi.ru](mailto:evgenii@rudnyi.ru)

Embryo Physics Course, April 3, 2013





# Does Entropy Play a Role in Biology?

Evgenii Rudnyi, Embryo Physics Course

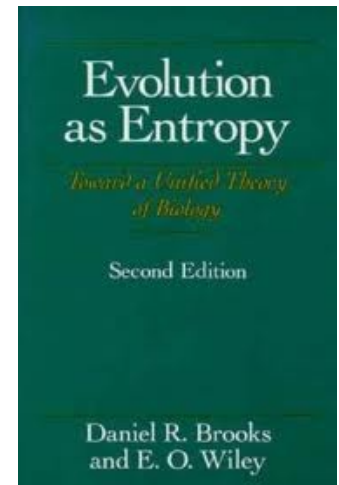
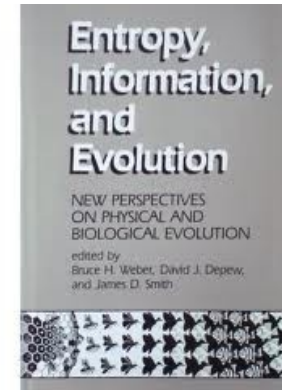
3 April 2013

<http://blog.rudnyi.ru>, [evgenii@rudnyi.ru](mailto:evgenii@rudnyi.ru)

# Introduction

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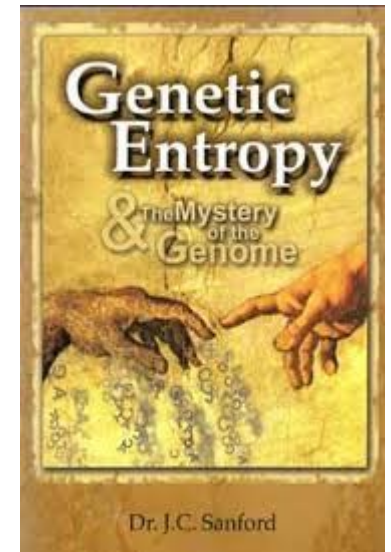
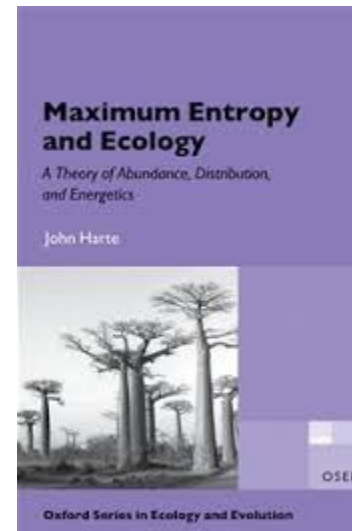
- ▶ I used to be a thermodynamicist:
  - ▶ <http://evgenii.rudnyi.ru/publications.html>
  - ▶ Practical applications of entropy in chemical thermodynamics
- ▶ Biology:
  - ▶ Entropy is related to information
  - ▶ Entropy is related to evolution
- ▶ The entropy as I know it is different from entropy in biology.



# Outline

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- ▶ Short introduction to entropy in (chemical) thermodynamics
  - ▶ Practical science to solve practical problems
- ▶ Entropy and information
- ▶ Entropy and evolution



# Does Thermodynamics have Foundations?

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- ▶ 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.

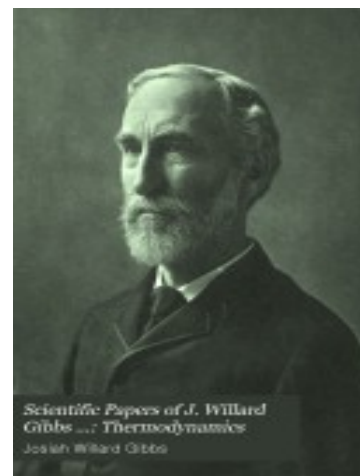
# Where to Start

## Peter Atkins, Physical Chemistry

<b>PART 1</b>	<b>Equilibrium</b>	<b>17</b>
1	The properties of gases	19
	Mathematical background 1: Differentiation and integration	42
2	The First Law	44
	Mathematical background 2: Multivariate calculus	91
3	The Second Law	94
4	Physical transformations of pure substances	135
5	Simple mixtures	156
6	Chemical equilibrium	209
<b>PART 2</b>	<b>Structure</b>	<b>247</b>
7	Quantum theory: introduction and principles	249
	Mathematical background 3: Complex numbers	286
8	Quantum theory: techniques and applications	288
	Mathematical background 4: Differential equations	322
9	Atomic structure and spectra	324
	Mathematical background 5: Vectors	368
10	Molecular structure	371
	Mathematical background 6: Matrices	414
11	Molecular symmetry	417
12	Molecular spectroscopy 1: rotational and vibrational spectra	445
13	Molecular spectroscopy 2: electronic transitions	489
14	Molecular spectroscopy 3: magnetic resonance	520
15	Statistical thermodynamics 1: the concepts	564
16	Statistical thermodynamics 2: applications	592

## Josiah Willard Gibbs

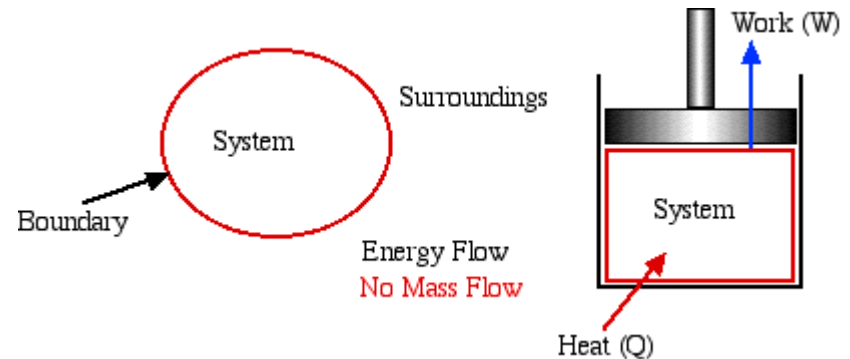
### "On the Equilibrium of Heterogeneous Substances" 1875–1878



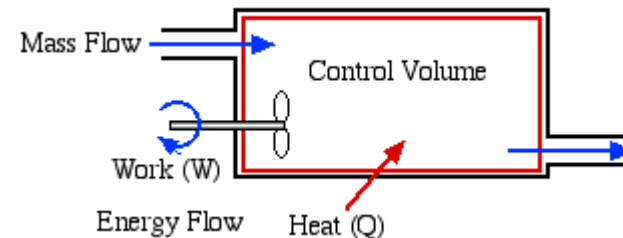
IMPORTANT: First learn classical thermodynamics

# Thermodynamic System

- ▶ Isolated system
- ▶ Closed system
- ▶ Open system
- ▶ There is no “just entropy”
- ▶ Entropy must be of something



[http://www.ohio.edu/mechanical/thermo/Intro/Chapt.1\\_6/Chapter1.html](http://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter1.html)



# Typical Fallacy in Biology

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- ▶ 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.



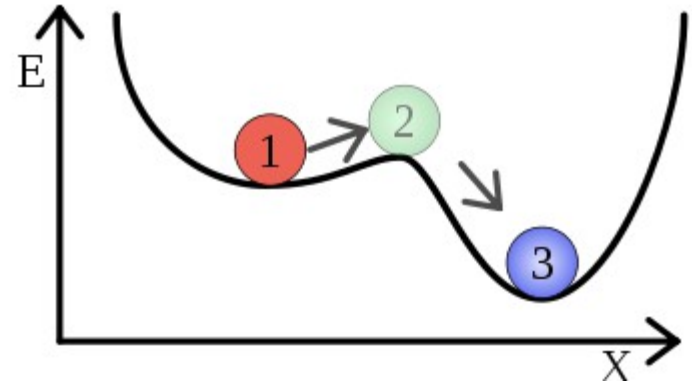
# Equilibrium

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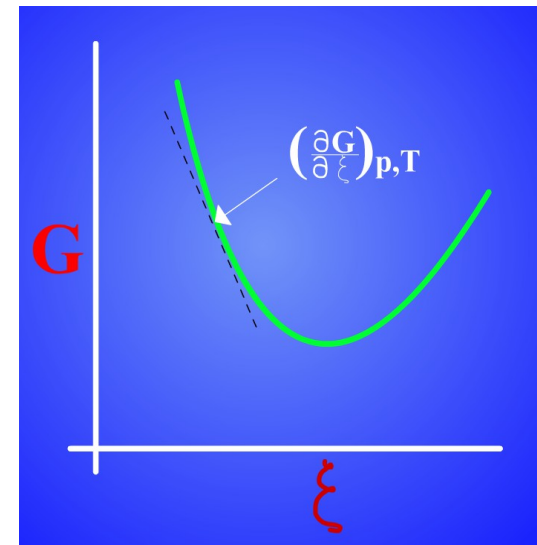
- ▶ Zeroth Law of Thermodynamics:
  - ▶ Two systems in equilibrium have the same temperature
- ▶ Thermodynamics goal: equilibrium criterion
  - ▶ Computing equilibrium composition
- ▶ Thermostatics or thermodynamics?
- ▶ Thermodynamics does not replace kinetics
  - ▶ There is no explicit time in thermodynamics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

# Stable, Metastable and Frozen Equilibrium

- ▶ Nonequilibrium state
  - ▶ Thermodynamics can deal with it as well
- ▶ Example:  
$$\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$$
  - ▶ Consider the mixture with and without a catalyst
  - ▶ Frozen equilibrium

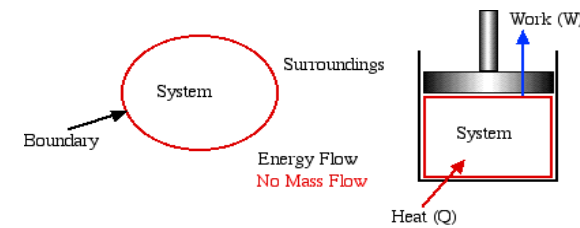


<http://en.wikipedia.org/wiki/Metastability>



[http://www.unomaha.edu/tiskochem/Flash\\_Files/Gibbs.swf](http://www.unomaha.edu/tiskochem/Flash_Files/Gibbs.swf)

# Function of State: Physics



- ▶ The First Law

$$dU = \delta Q - \delta W \quad dS \geq \delta Q/T \quad (1)$$

- ▶ The Second Law

- ▶ Function of State

- ▶ Does not depend on path

- ▶ Function of Change

- ▶ Depends on path

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

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

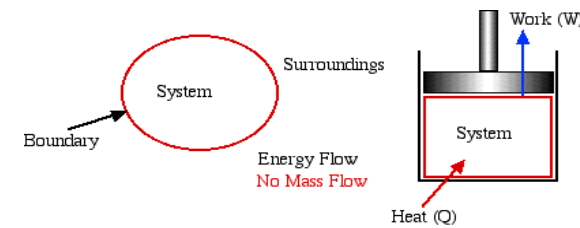
- ▶ The way to proceed:

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

- ▶ We do not need inequality in this equation.

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

# 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.

$$G = U - TS + pv$$

$$dG = -SdT + Vdp$$

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

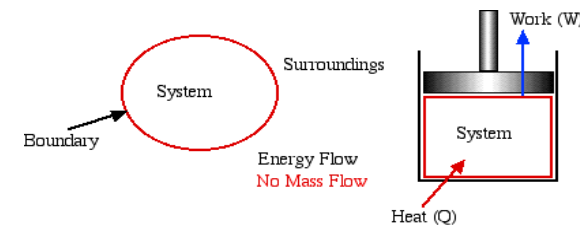
$$S(T, p) \quad V(T, p)$$

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

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

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

# Function of State: Mathematics



- ▶ A closed system at equilibrium:
  - ▶ two independent variables.
- ▶ Chemists' choice:
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$$\left( \frac{\partial C_p}{\partial p} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_p$$

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

# Experimental Thermodynamics

- ▶ The Third Law
  - ▶ Entropy is absolute
- ▶ Enthalpy (internal energy)
  - ▶ Only change can be measured;
  - ▶ Enthalpy of formation
- ▶ JANAF Thermochemical Tables (Joint Army-Naval-Air Force Thermochemical Tables)

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*

Chloroborane (BCl)

$\text{B}_1\text{Cl}_1(\text{g})$

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$				Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$			
$T/\text{K}$	$C_p^\circ$	$S^\circ$	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_r$
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&Nomencl=on&Units=SI&cTC=on

## Condensed phase thermochemistry data

Go To: [Top](#), [References](#), [Notes](#) / [Error Report](#)

Data compilation [copyright](#) by the U.S. Secretary of Commerce on behalf of the U.S.A. All rights reserved.

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

### Liquid Phase Heat Capacity (Shomate Equation)

$$C_p^\circ = A + B \cdot t + C \cdot t^2 + D \cdot t^3 + E/t^2$$
$$H^\circ - H^\circ_{298.15} = A \cdot t + B \cdot t^2/2 + C \cdot t^3/3 + D \cdot t^4/4 - E/t + F - H$$
$$S^\circ = A \cdot \ln(t) + B \cdot t + C \cdot t^2/2 + D \cdot t^3/3 - E/(2 \cdot t^2) + G$$

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

[View plot](#) Requires a Java capable browser.

[View table.](#)

# Open Systems

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- ▶ Isolated system

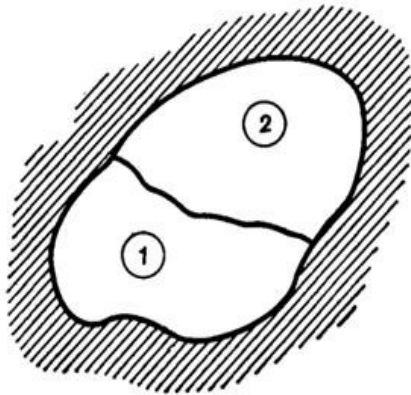
$$U = \text{const}$$

$$V = \text{const}$$

$$m = \text{const}$$

$$S = \text{max}$$

- ▶ A subsystem in the isolated system



- ▶ New variables in a function of state

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

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

- ▶ Chemical potential

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

$$dG = -Tds + pdV + \sum \mu_i dn_i$$



# Variational Principle

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- ▶ Isolated system

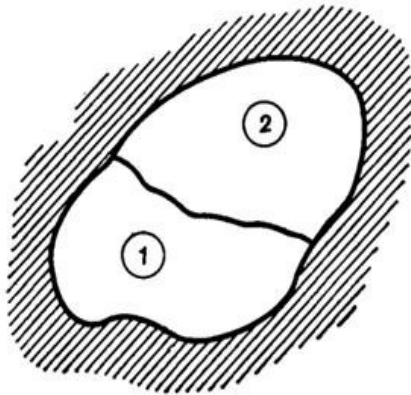
$$U = U_1 + U_2$$

$$V = V_1 + V_2$$

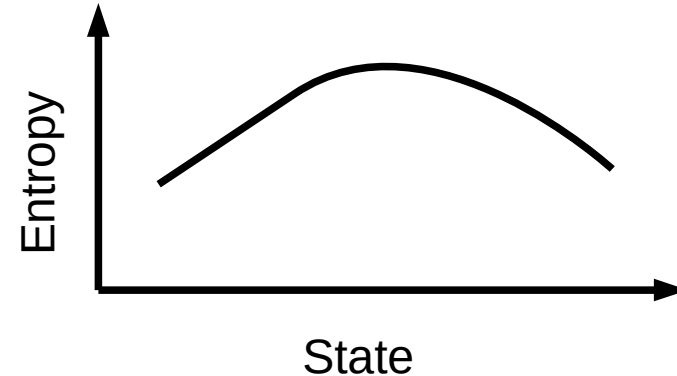
$$m = m_1 + m_2$$

$$S = \max$$

- ▶ A subsystem in the isolated system



- ▶ Virtual change



- ▶ Equilibrium Criterion

$$T_1 = T_2$$

$$p_1 = p_2$$

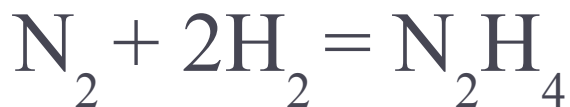
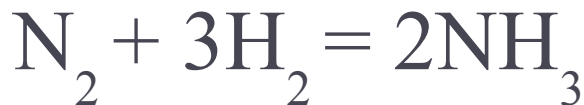
$$\mu_1 = \mu_2$$

## 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

$$\begin{aligned} \min_{n_i} G &= \mu_{H_2} n_{H_2} + \mu_{N_2} n_{N_2} + \mu_{NH_3} n_{NH_3} + \mu_{N_2H_4} n_{N_2H_4} \\ 2n_{H_2} + 3n_{NH_3} + 4n_{N_2H_4} &= b_H \\ 2n_{N_2} + n_{NH_3} + 2n_{N_2H_4} &= b_N \\ n_i &> 0 \end{aligned} \quad (1)$$

$$\begin{aligned} \min_{\xi_j} G &= \mu_{H_2} n_{o,H_2} + \mu_{N_2} n_{o,N_2} + \mu_{NH_3} n_{o,NH_3} + \mu_{N_2H_4} n_{o,N_2H_4} + \\ &+ \xi_1 (2\mu_{NH_3} - 3\mu_{H_2} - \mu_{N_2}) + \xi_2 (\mu_{N_2H_4} - 2\mu_{H_2} - \mu_{N_2}) \end{aligned} \quad (2)$$

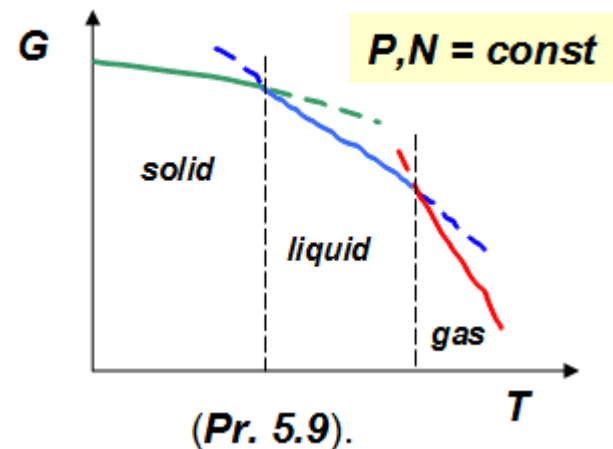
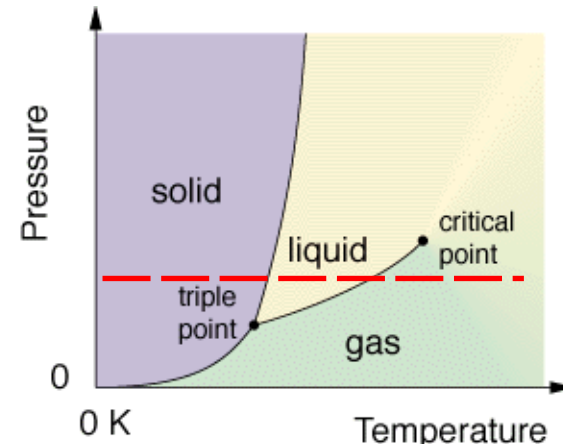


$$\begin{aligned} 2\mu_{NH_3}^* - 3\mu_{H_2}^* - \mu_{N_2}^* &= -RT \ln K_{x,1} = \\ &= -RT \ln \frac{(n_{o,NH_3} + 2\xi_1)^2 (n_o - 2\xi_1 - 2\xi_2)^2}{(n_{o,H_2} - 3\xi_1 - 2\xi_2)^3 (n_{o,N_2} - \xi_1 - \xi_2)} \end{aligned} \quad (3)$$

## Example 2: One component phase diagram

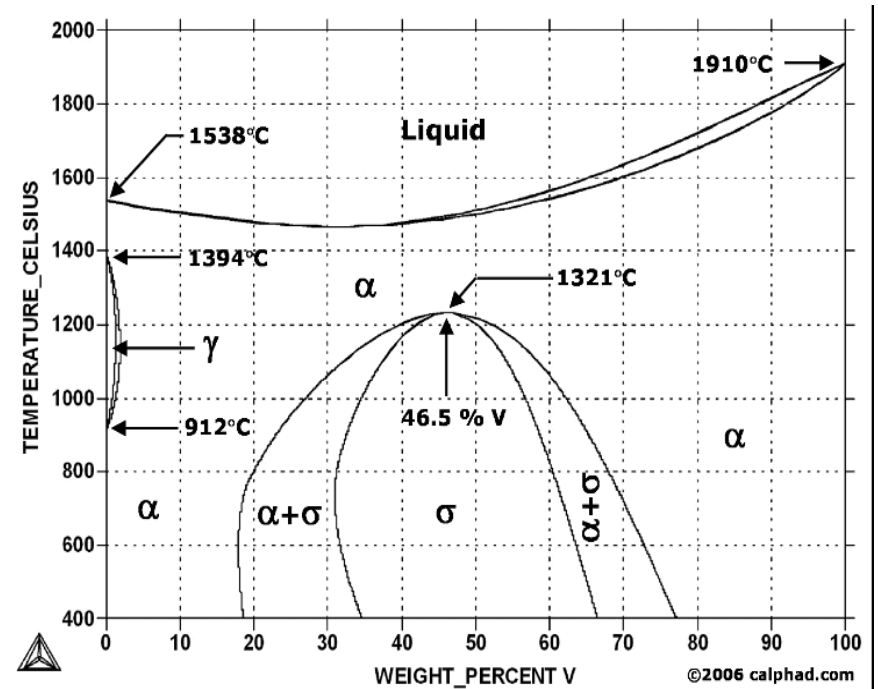
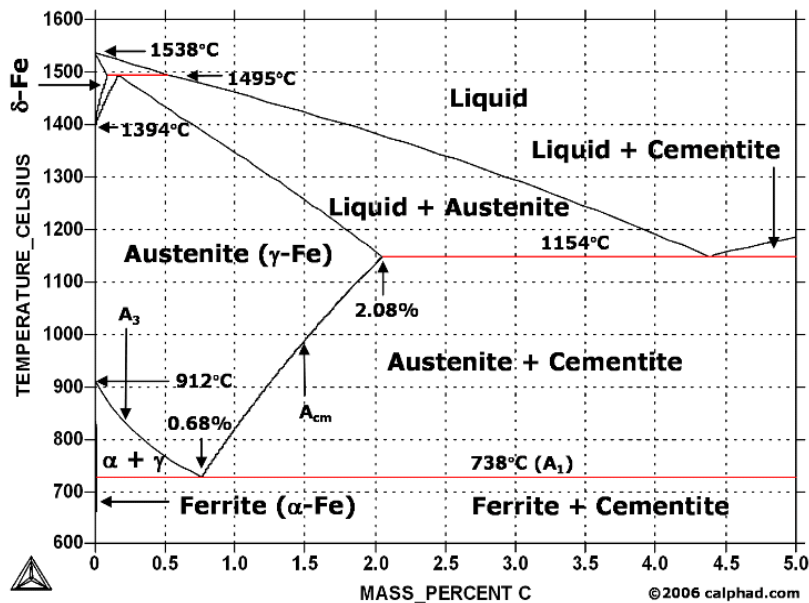
- ▶ Given: a closed system at constant  $T, P$ 
  - ▶ Mole Gibbs Energies
    - ▶ Solid  $G_S(T, p)$
    - ▶ Liquid  $G_L(T, p)$
    - ▶ Gas  $G_G(T, p)$
- ▶ Find equilibrium composition

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



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

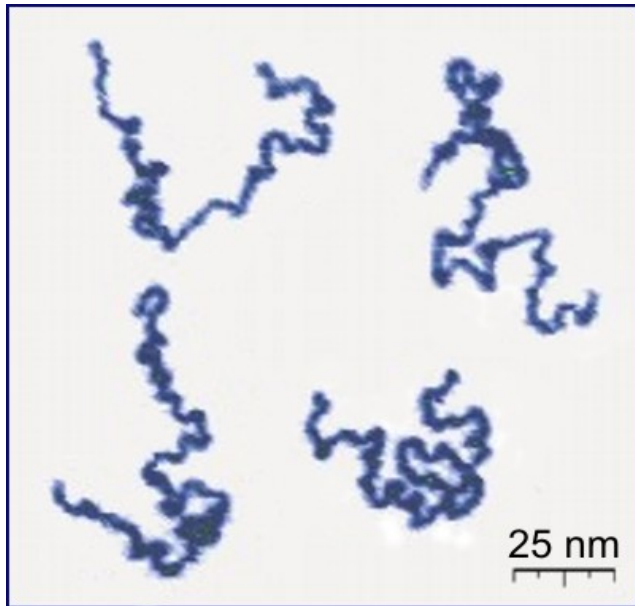
# CALPHAD: CALculation of PHAse Diagrams



<http://www.calphad.com/>

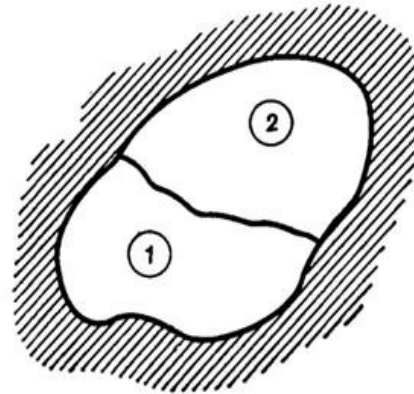
# Problems with Extension of Thermodynamics

- ▶ Thermodynamics of polymers
  - ▶ How to define state?



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

- ▶ Thermodynamics is additive  $U = U_1 + U_2$



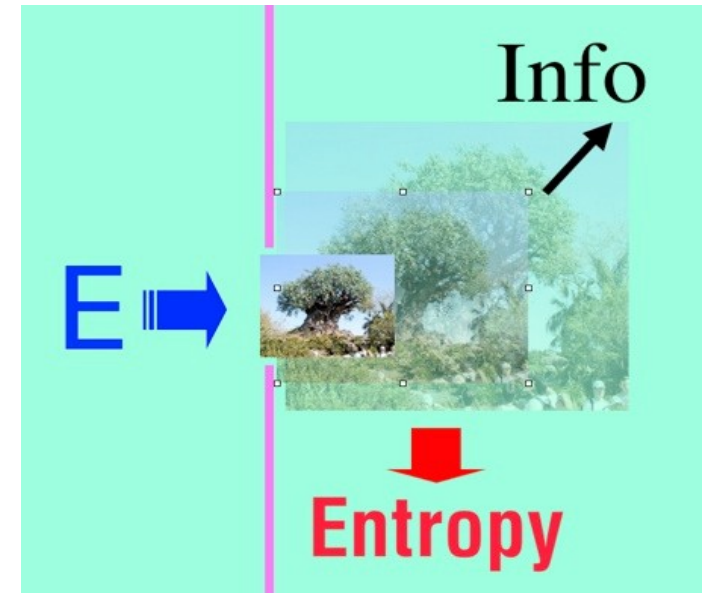
- ▶ Interfaces
  - ▶ Gibbs' excess properties
- ▶ Long range forces
  - ▶ Another thermodynamics to treat the Universe

# 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?

P.S. My comment on the paper:

<http://blog.rudnyi.ru/2012/12/dna-as-the-carrier-of-information.html>



[http://www.kk.org/thetechnium/archives/2009/01/the\\_cosmic\\_gene.php](http://www.kk.org/thetechnium/archives/2009/01/the_cosmic_gene.php)

# 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

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### A Mathematical Theory of Communication

By C. E. SHANNON

Quantities of the form  $H = -\sum p_i \log p_i$  (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<sup>8</sup> 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  $H = -\sum p_i \log p_i$  the entropy of the set of probabilities

<sup>8</sup> 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
- ▶  $S^\circ (298.15 \text{ K}) \text{ J K}^{-1} \text{ mol}^{-1}$
- ▶ Ag cr  $42.55 \pm 0.20$
- ▶ Al cr  $28.30 \pm 0.10$
- ▶ What these values tell us about information?

# Non-Equilibrium Thermodynamics

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- ▶ 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

The screenshot shows a Google Scholar search interface. At the top, the Google logo is on the left, and a search bar contains the text 'Entropy Production Principle' with a magnifying glass icon on the right. Below the search bar, the word 'Scholar' is displayed in red, followed by the text 'Ungefähr 176.000 Ergebnisse (0,06 Sek.)'. The main content area lists search results. The first result is titled 'Maximum entropy production principle in physics, chemistry and biology' by LM Martyushev and VD Seleznev, published in Physics reports in 2006. The second result is 'The minimum entropy production principle' by ET Jaynes, from the Annual Review of Physical Chemistry in 1980. The third result is 'The second law of thermodynamics and the global climate system: a review of the maximum entropy production principle' by H Ozawa, A Ohmura, RD Lorenz, and T Pujol, from Reviews of Geophysics in 2003. On the left side of the results, there are filters: 'Beliebige Zeit' with a list of years (2013, 2012, 2009) and a 'Zeitraum wählen...' option; 'Nach Relevanz sortieren'; 'Nach Datum sortieren'; 'Web-Suche'; 'Seiten auf Deutsch'; and checkboxes for 'Patente' and 'Zitate', each with an 'einschließen' option.

Google Entropy Production Principle

Scholar Ungefähr 176.000 Ergebnisse (0,06 Sek.)

Beliebige Zeit  
Seit 2013  
Seit 2012  
Seit 2009  
Zeitraum wählen...

Nach Relevanz sortieren  
Nach Datum sortieren

Web-Suche  
Seiten auf Deutsch

☒ Patente einschließen  
☒ Zitate einschließen

Tipp: Suchen Sie nur nach Ergebnissen auf Deutsch. Sie können Ihre Sprache in den Scholar-Einstellungen festlegen.

**Maximum entropy production principle in physics, chemistry and biology**  
LM Martyushev, VD Seleznev - Physics reports, 2006 - Elsevier  
The tendency of the **entropy** to a maximum as an isolated system is relaxed to the equilibrium (the second law of thermodynamics) has been known since the mid-19th century. However, independent theoretical and applied studies, which suggested the ...  
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**The minimum entropy production principle**  
ET Jaynes - Annual Review of Physical Chemistry, 1980 - annualreviews.org  
It seems intuitively reasonable that Gibbs' variational **principle** determining the conditions of heterogeneous equilibrium can be generalized to nonequilibrium conditions. That is, a nonequilibrium steady state should be the one that makes some kind of generalized- ...  
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**The second law of thermodynamics and the global climate system: a review of the maximum entropy production principle**  
H Ozawa, A Ohmura, RD Lorenz, T Pujol - Reviews of Geophysics, 2003 - agu.org  
The long-term mean properties of the global climate system and those of turbulent fluid systems are reviewed from a thermodynamic viewpoint. Two general expressions are derived for a rate of **entropy production** due to thermal and viscous dissipation (turbulent ...  
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# Entropy and Evolution, 1

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- ▶ Annala, 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

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- ▶ 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.

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Physics Reports 426 (2006) 1–45

[www.elsevier.com/locate/physrep](http://www.elsevier.com/locate/physrep)

## Maximum entropy production principle in physics, chemistry and biology

L.M. Martyushev<sup>a, b, \*</sup>, V.D. Seleznev<sup>b</sup>

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

- ▶ 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>

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- ▶ *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.