

BC3252: Part IV
The Second Law of
Thermodynamics



The need for a new law:
Which way will something go?

Many processes occur **spontaneously**
(the reverse never happens unaided):

- Balloons pop (and don't unpop)
- Iron rusts (and doesn't unrust)
- Rivers flow downhill (never uphill)
- Socks get unpaired in the dryer (don't form pairs)
- Heat flows from a hotter object to a colder one
(never in the opposite direction)

The reverse of all these **conserve energy** so
the first law is of no use in predicting direction.

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Both endothermic and exothermic reactions
can occur spontaneously



Rusting of iron is **exothermic**: $\Delta_r H < 0$



Vaporization is **endothermic**: $\Delta_r H > 0$

But **iron rusts**
and **acetone (nail polish remover) evaporates**:
both are **spontaneous processes**.

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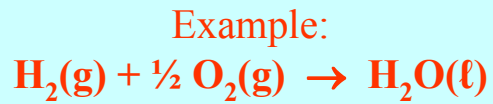
Observations about the unidirectionality
of all naturally occurring processes

The direction of spontaneous change is always
towards a state of equilibrium.

In order to drive a spontaneous process in the
opposite direction (away from equilibrium)
some external action is needed.

The method used to drive a process in the
non-spontaneous direction always involves
utilizing a different spontaneous process.
The combined process is spontaneous.

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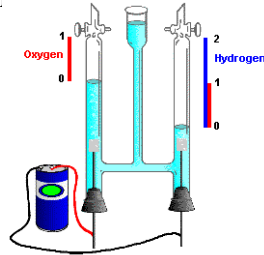


Spontaneous (explosively so) as written.

The reverse can be done (electrolysis of water), but requires **electricity**, which comes from some *other* spontaneous process (waterfall, battery, coal-fired power plant).

Spontaneous processes can be harnessed to do useful work.

A hydrogen powered automobile?



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The conversion of heat into work

Heat engines convert **heat** into **work**.

Major role in industrial revolution!

Analysis in 19th C. led to much of modern thermodynamics

The Second Law says there are precise limitations on how much heat can be utilized to do work.



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The impossibility of **Perpetual Motion Machines of the Second Kind**

It is impossible to construct a machine, functioning in cycles, that converts heat completely into an equivalent amount of work, without producing changes elsewhere.

Such a machine would not violate the first law (energy is conserved) but would violate the second.

Can't power a ship by extracting heat from the ocean!

Analyzing these is sometimes subtle.

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The second law and entropy

Definition: $dS \equiv dq_{\text{rev}}/T$

If T is constant, $\Delta S = (1/T) \int dq_{\text{rev}} = q_{\text{rev}}/T$

One version of Second Law:

Entropy S is a state function.

Analogy with first law:

Definition: $dU \equiv dq + dw$

One version of First Law:

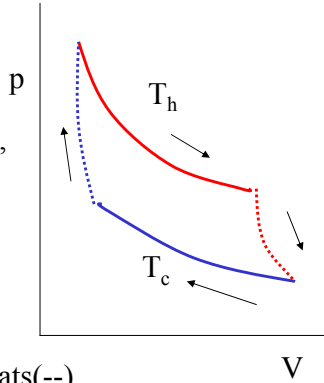
Energy U is a state function.

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Steam engines and the Second Law: The Carnot Cycle

Gas in engine

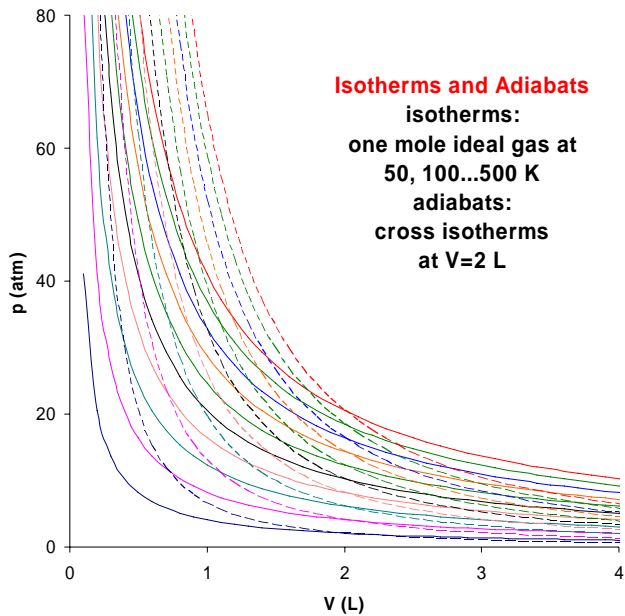
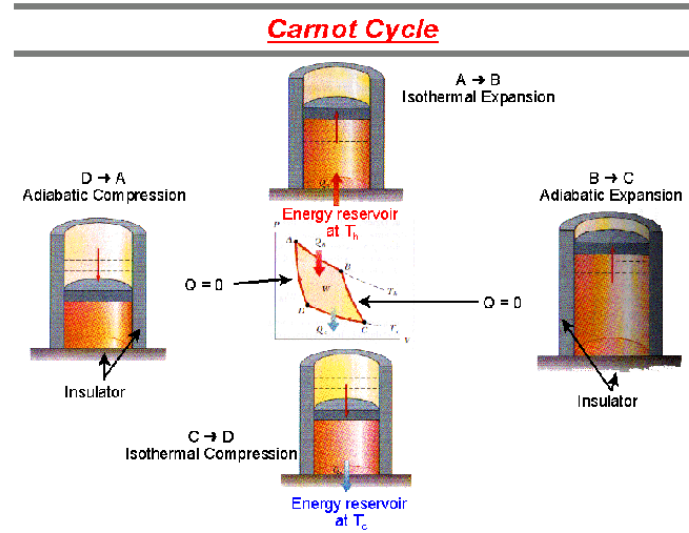
- (a) expands isothermally [drawing heat from hot (T_h) bath],
- (b) expands adiabatically [cools to T_c], doing work (red);
- (c) is compressed isothermally [dumping heat to cold (T_c) bath],
- (d) compressed adiabatically [warming to T_h], work is done (blue).



Analyze with isotherms (—) and adiabats(--)

Net work: area bounded by curves.

All steps are reversible.



Isotherms and Adiabats
 isotherms:
 one mole ideal gas at
 50, 100...500 K
 adiabats:
 cross isotherms
 at $V=2$ L

**Carnot cycle:
 is it realistic?**
 In principle,
 any path can be
 constructed as
 a sequence of
 reversible
 isothermal and
 adiabatic steps.

Heat Engines and The Carnot Cycle

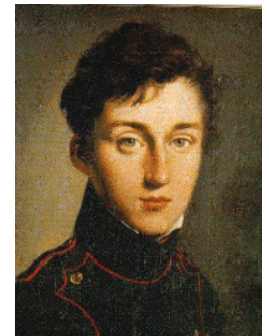
Net work is being done, while heat is transferred from hot (T_h) to cold (T_c) reservoir.

Efficiency of engine (ratio of work done to heat absorbed at T_2) depends on temperatures.

Maximum efficiency:

$$f = w/q_h = (T_h - T_c)/T_h$$

100% only if $T_c = 0$ K



Sadi Carnot en 1814

Entropy changes in isolated systems

$$dS \equiv dq_{\text{rev}}/T$$

In isolated systems, $dq = 0$

So if the process is reversible $\Delta S = 0$

The second law says that if a process is spontaneous (not reversible) $\Delta S > 0$.

If $\Delta S < 0$, the process will not occur spontaneously (but the reverse process will occur.)

Clausius: The energy of the universe is constant.

The entropy of the universe increases.

Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu.

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Calculating Entropy Changes: phase transitions

$$dS \equiv dq_{\text{rev}}/T \quad (\text{always start with definitions!})$$

For isothermal processes: $\Delta S = q_{\text{rev}}/T$

Phase transitions are reversible if they occur at the equilibrium transition temperature:

A(l) [at T_{bp} and 1 atm] \rightarrow A(g) [at T_{bp} and 1 atm]

$$\Delta_{\text{vap}}S = S_{\text{gas}}(T_{\text{bp}}, 1 \text{ atm}) - S_{\text{liquid}}(T_{\text{bp}}, 1 \text{ atm})$$

If p is constant, $q = \Delta_{\text{vap}}H$ so $\Delta_{\text{vap}}S = \Delta_{\text{vap}}H / T_{\text{bp}}$

Since $\Delta_{\text{vap}}H$ is always positive $\Delta_{\text{vap}}S$ is always positive

Thus $S_{\text{gas}} > S_{\text{liquid}}$

Similarly, $S_{\text{liq}} > S_{\text{solid}}$ (for the same substance)

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Trouton's Rule (a handy generalization)

For many substances:

$$\Delta_{\text{vap}}S = 88 \pm 5 \text{ J/mol-K.}$$

Exceptions:

liquids that dissociate upon vaporization,

liquids with very low boiling points

hydrogen bonded liquids.

See problem set.

$\Delta_{\text{vap}}S$ vs. ΔS_{vap} Atkins uses former, many texts latter

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Calculating ΔS : isothermal expansion/compression of an ideal gas

For isothermal processes $\Delta S = q_{\text{rev}}/T$

We must consider the reversible path (even if the actual process is not reversible!)

Since ideal gas, when T is constant, U is constant

$$\Delta U = 0 = q + w, \text{ so } q_{\text{rev}} = -w_{\text{rev}}$$

$$\text{But } w_{\text{rev}} = -nRT \ln(V_2/V_1) = nRT \ln(p_2/p_1)$$

$$\Delta S = q_{\text{rev}}/T = nR \ln(V_2/V_1) = -nR \ln(p_2/p_1)$$

When gases expand, entropy increases:

$$\text{If ideal, } \Delta S_m = R \ln(V_2/V_1) = -R \ln(p_2/p_1)$$

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Deriving some more entropy equations

$$dU = dq + dw \text{ so } dU = dq_{\text{rev}} + dw_{\text{rev}}$$

$$dS = dq_{\text{rev}}/T \text{ so } dq_{\text{rev}} = TdS$$

If the only work is pV work, $dw_{\text{rev}} = -pdV$

So for **reversible changes, pV work only**:

$$dU = TdS - pdV$$

This is sometimes known as

“the fundamental equation for dU”.

Used as the starting point for many derivations.

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Fundamental equations reversible changes, pV work only

$$dU = TdS - pdV$$

But $H = U + pV$

$$dH = dU + pdV + Vdp$$

$$dH = TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp$$

The first relates variations in U, S, and V

the second relates variations in H, S, and p.

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How does Entropy vary with temperature at constant **volume**?

$$dU = TdS - pdV. \text{ If } V \text{ is constant, } dU = T dS$$

Focus on U as a function of T and V, $U(T, V)$:

$$\begin{aligned} dU &= (\partial U/\partial T)_V dT + (\partial U/\partial V)_T dV \\ &= C_V dT + (\partial U/\partial V)_T dV \end{aligned}$$

If volume is constant, $dV = 0$, so $dU = C_V dT$

Therefore $C_V dT = T dS$, so $dS = C_V dT/T$

$$\Delta S = \int C_V dT/T$$

If C_V is constant, $\Delta S = C_V \ln(T_2/T_1)$

Entropy increases with temperature

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How does Entropy vary with temperature (if **pressure** is constant)?

$$dH = TdS + Vdp. \text{ If } p \text{ is constant, } dH = TdS$$

Focus on H as a function of T and p: $H(T, p)$

$$\begin{aligned} dH &= (\partial H/\partial T)_p dT + (\partial H/\partial p)_T dp \\ &= C_p dT + (\partial H/\partial p)_T dp \end{aligned}$$

So if $dp = 0$, $dH = C_p dT$

Therefore $C_p dT = TdS$, so $dS = C_p dT/T$

$$\Delta S = \int C_p dT/T$$

If C_p is constant, $\Delta S = C_p \ln(T_2/T_1)$

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How does Entropy of an **ideal gas** change when temperature **and** volume are changing?

$$dU = TdS - pdV$$

$$dS = dU/T + p/T dV$$

For ideal gas: $dU = C_V dT$ and $p/T = nR/V$

$$dS = nC_{V,m} dT/T + nR dV/V$$

$$dS_m = C_{V,m} dT/T + R dV/V$$

If C_V is constant (ok for small ΔT)

$$\Delta S_m = C_{V,m} \ln(T_2/T_1) + R \ln(V_2/V_1)$$

$$\text{or } \Delta S = C_V \ln(T_2/T_1) + nR \ln(V_2/V_1)$$

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Entropy change for an **ideal gas** when **both** temperature and pressure are changing

$$dH = TdS + Vdp$$

$$dS = dH/T - V/T dp$$

Ideal gas: $dH = C_p dT$ and $V/T = nR/p$

$$dS = C_p dT/T - nR dp/p$$

$$dS = nC_{p,m} dT/T - nR dp/p$$

$$dS_m = C_{p,m} dT/T - R dp/p$$

If C_p is constant (ok for small ΔT)

$$\Delta S_m = C_{p,m} \ln(T_2/T_1) - R \ln(p_2/p_1)$$

$$\text{or } \Delta S = C_p \ln(T_2/T_1) - nR \ln(p_2/p_1)$$

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Are these two equations consistent?

$$dS_m = C_{p,m} dT/T - R dp/p$$

$$C_{p,m} = C_{V,m} + R, \text{ so}$$

$$dS_m = (C_{V,m} + R) dT/T - R dp/p$$

$$dS_m = C_{p,m} dT/T + R (dT/T - dp/p)$$

$$pV = nRT \text{ so } pdV + Vdp = nRdT$$

Divide by pV (or nRT): $dV/V + dp/p = dT/T$

$$dT/T - dp/p = dV/V$$

$$dS_m = C_{V,m} dT/T + R dV/V \quad \text{Yes!}$$

Use whichever one is convenient for the data.

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Adiabatic reversible
expansion of an ideal gas

Reversible: $dq = dq_{\text{rev}} = 0 \rightarrow dS = 0 \rightarrow \Delta S = 0$.

If C_V is constant,

$$\Delta S = C_V \ln(T_2/T_1) + nR \ln(V_2/V_1)$$

$$C_V \ln(T_2/T_1) = -nR \ln(V_2/V_1)$$

$$\ln(T_2/T_1)^{C_V/nR} = \ln(V_1/V_2)$$

$$\rightarrow (T_2/T_1)^{C_V/nR} = (V_1/V_2)$$

Same result as derived previously.

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Calculating ΔS for phase transitions away from the transition temperature

Freezing at $T \neq T_{\text{mp}}$ is **not** reversible

Cannot use $\Delta S = q/T$ or $\Delta S = \Delta H/T$

Invent a reversible way to effect the change

Example: freeze water at -10°C ($p = 1 \text{ atm}$)
(*supercooled water*)

- warm the liquid reversibly from -10°C to 0°C
- freeze at 0°C , where $\Delta S_{\text{fus}} = q/T = \Delta H_{\text{fus}}/T$
- cool the solid reversibly from 0°C to -10°C .

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Results: Freeze water at -10°C ($p = 1 \text{ atm}$) fusion = melting = reverse of freezing

a) Warm liquid reversibly from -10°C to 0°C :

$$\Delta S_{\text{m}} = C_{\text{p,m}} \ln(T_2/T_1); C_{\text{p,m}}(\text{water}) = 76 \text{ J/K-mol}$$

$$\Delta S_{\text{m}} = (76 \text{ J/K-mol}) \ln(273/263) = 2.83 \text{ J/K-mole}$$

b) Freeze at 0°C : $\Delta_{\text{frz}}S^\circ = \Delta_{\text{frz}}H^\circ/T_{\text{fp}}$

$$T_{\text{fp}} = 0^\circ\text{C}, \Delta_{\text{fus}}H_{\text{m}}^\circ = 6008 \text{ J/mole}$$

$$\Delta_{\text{frz}}S_{\text{m}}^\circ = -6008/273.15 = \rightarrow -22.00 \text{ J/K-mole}$$

c) Cool ice reversibly from 0°C to -10°C :

$$\Delta S_{\text{m}} = C_{\text{p}} \ln(T_2/T_1); C_{\text{p,m}}(\text{ice}) = 37 \text{ J/K-mol}$$

$$\Delta S_{\text{m}} = (37 \text{ J/K-mol}) \ln(263/273) = -1.38 \text{ J/K-mole}$$

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ΔS_{m} for freezing water at -10°C

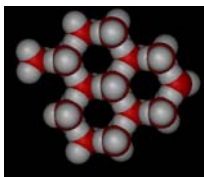
$$\Delta S_{\text{m}} = (2.83 - 22.00 - 1.38) = -20.55 \text{ J/K-mole}$$

So at -10°C , $\Delta_{\text{frz}}S_{\text{m}} = -20.55 \text{ J/K-mole}$

Whereas at 0°C , $\Delta_{\text{frz}}S_{\text{m}} = -22.00 \text{ J/K-mole}$

Both are negative:

ice is more ordered than liquid water.



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What happens to the surroundings?

Use the same three steps to find q_{sys}

(since we don't know $\Delta_{\text{frz}}H_{\text{m}}^\circ$ at -10°C)

One mole of water is freezing in the system:

a) warming: $q = C_{\text{p,m}}\Delta T = 760 \text{ J}$

b) freezing: $q = \Delta_{\text{frz}}H_{\text{m}}^\circ = -6008 \text{ J}$

c) cooling: $q = C_{\text{p,m}}\Delta T = -370 \text{ J}$

$$q_{\text{sys}} = -5618 \text{ J}, \text{ so } q_{\text{surr}} = +5618 \text{ J}$$

Imagine a path such that surroundings absorb

5618 J of heat reversibly at **fixed** $T = -10^\circ\text{C}$, so:

$$\Delta S_{\text{surr}} = 5618/263 = 21.35 \text{ J/K.}$$

(always ok to assume that the q_{surr} is reversible.)

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What is ΔS_{total} ?

When one mole of ice freezes at -10°C

$$\Delta S_{\text{sys}} = -20.55 \text{ J/K}, \quad \Delta S_{\text{surr}} = 21.35 \text{ J/K},$$

$$\Delta S_{\text{tot}} = +0.80 \text{ J/K}$$

Process is **spontaneous** (not reversible) and $\Delta S_{\text{tot}} > 0$

Compare: when one mole of ice freezes at 0°C

$$\Delta S_{\text{sys}} = -6008/273 = -22.00 \text{ J/K},$$

$$\Delta S_{\text{surr}} = +6008/273 = +22.00 \text{ J/K},$$

$$\Delta S_{\text{tot}} = 0 \text{ J/K}$$

Process is **reversible** and $\Delta S_{\text{tot}} = 0$

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The inequality of Clausius



Start with the definition $dw = -p_{\text{ex}}dV$

Expansion: $dV > 0$, so work is negative.

If reversible $p_{\text{ex}} = p$; reversible work is $-\int pdV$

If not reversible, p_{ex} is **less** than p :

size of (negative) work is smaller. Thus $dw_{\text{rev}} \leq dw$

Compression: $dV < 0$, so work is positive.

If not reversible, p_{ex} is **greater** than p :

size of (positive) work is larger. Thus $dw_{\text{rev}} \leq dw$

So it is always true that $dw_{\text{rev}} \leq dw$

$$dU = dq + dw.$$

Since dU is independent of path, $dq \leq dq_{\text{rev}}$

But $dq_{\text{rev}} = TdS$, so **$dq - TdS \leq 0$**

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The inequality of Clausius: $dq - TdS \leq 0$

$dq - TdS < 0$ for any spontaneous processes

$dq - TdS = 0$ for reversible processes

Very useful for derivations!

Example: isolated system.

$dq = 0$, so $-TdS < 0$ for spontaneous processes.

Divide by T (which is always positive):

$dS > 0 \rightarrow \Delta S > 0$ for spontaneous processes
in isolated systems

Entropy increases in spontaneous processes in isolated systems (asserted earlier, but now proved).

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Using $dq - TdS \leq 0$ to decide which way things will go

$$dU = dq + dw \rightarrow dq = dU - dw$$

$$dq - TdS = dU - dw - TdS \leq 0.$$

If we have pV work only and $p_{\text{ex}} = p$

$$dU + pdV - TdS \leq 0$$

If V and S are constant $dU \leq 0$

$\rightarrow \Delta U < 0$ for spontaneous processes
at constant V and S

Internal Energy decreases in spontaneous processes when V and S are constant. **Sleds go downhill.**

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Using $dq - TdS \leq 0$ to decide which way things will go: **enthalpy**

$$H = U + pV \rightarrow dH = dU + pdV + Vdp$$

$$dU = dH - pdV - Vdp.$$

For pV work only with $p_{\text{ex}} = p$, $dU + pdV - TdS \leq 0$

$$dH - pdV - Vdp + pdV - TdS \leq 0$$

$$dH - Vdp - TdS \leq 0$$

If p and S are constant, $dH \leq 0$

$\Delta H < 0$ for spontaneous processes at constant p and S

Enthalpy decreases in spontaneous processes if p and S are constant.

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Legendre Transformations

$$dU = TdS - pdV$$

From $H = U + pV$ we got $dH = TdS + Vdp$

Definition of H swapped roles of p and V (with sign change).

one example of a Legendre transformation.

Let's do the same thing with T and S!

Define $A \equiv U - TS$ (Helmholtz Free Energy)

$$dA = dU - TdS - SdT = TdS - pdV - TdS - SdT$$

$$dA = -SdT - pdV$$



Legendre



Helmholtz

One more Legendre Transformation:
Gibbs Free Energy

$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

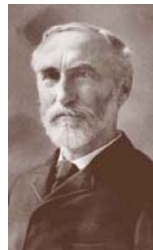
$$dA = -SdT - pdV$$

Define $G \equiv H - TS$ (Gibbs Free Energy)

$$dG = dH - TdS - SdT = TdS + Vdp - TdS - SdT$$

$$dG = -SdT + Vdp$$

These four fundamental equations apply to reversible changes in closed systems, with pV work only.



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$A \equiv U - TS$ (Helmholtz Free Energy)
 $G \equiv H - TS$ (Gibbs Free Energy)

Both A and G have units of energy.

Both are extensive.

But why do we need two more forms of energy, when we already have U and H?

Answer:

U and H tell you which way processes will proceed spontaneously at constant S, while A and G do so at constant T

much more practical: it is hard to control S!

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Using $dq - TdS \leq 0$ to decide
which way things will go (for A)

For pV work only and $p_{\text{ex}} = p$, $dU + pdV - TdS \leq 0$

$A \equiv U - TS$, so $dA = dU - TdS - SdT$

$dA + TdS + SdT + pdV - TdS \leq 0$

$dA + pdV + SdT \leq 0$

If V and T are constant, $dA \leq 0$

$\Delta A < 0$ for spontaneous processes at constant (V, T)

Helmholtz free energy will decrease in spontaneous processes if V and T are constant.

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Using $dq - TdS \leq 0$ to decide
which way things will go (for G)

For pV work only $p_{\text{ex}} = p$, $dH - Vdp - TdS \leq 0$

$G \equiv H - TS$, so $dG = dH - TdS - SdT$

$dG + TdS + SdT - Vdp - TdS \leq 0$

$dG - Vdp + SdT \leq 0$

If p and T are constant, $dG \leq 0$

$\Delta G < 0$ for spontaneous processes at fixed (T, p)

Gibbs free energy will always decrease in spontaneous processes when p and T are constant.

That is why ΔG is usually our focus in chemistry.

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Helmholtz Free energy
and maximum work

$A \equiv U - TS \rightarrow$

$dA = dU - TdS - SdT = dq + dw - TdS - SdT$

$dq - TdS = (dA - dw + SdT) \leq 0$

this time not restricted to pV work only!

If $dT = 0$, then $dA \leq dw$, so $\Delta A \leq w$.

Multiply by -1: $-w \leq -\Delta A$

-w is the work done by the system

$-\Delta A$ is the maximum work a system can do in any isothermal process (Arbeit = work)

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Gibbs Free energy
and maximum non-pV work

$G \equiv H - TS = U + pV - TS$

$dG = dq + dw + pdV + Vdp - TdS - SdT$

$dq - TdS = (dG - dw - pdV - Vdp + SdT) \leq 0$

Let $dw = -pdV + dw'$ where $dw' = \text{non-pV work}$

$dq - TdS = (dG - dw' - Vdp + SdT) \leq 0$

If p and T are constant, then $dG \leq dw'$, $\Delta G \leq w'$

Multiply by -1: $-w' \leq -\Delta G$

-w' is the non-pV work done by the system

$-\Delta G$ is the maximum non-pV work a system can do at constant T and p. "Free energy"

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The Fundamental equations for **closed** systems,
reversible changes, **pV work only**

$$dU = + TdS - pdV \quad U(S, V)$$

$$dH = + TdS + Vdp \quad H(S, p)$$

$$dA = - SdT - pdV \quad A(T, V)$$

$$dG = - SdT + Vdp \quad G(T, p)$$

Closed systems have **fixed n**, so there are two independent state variables. For example, two from (T, p, V_m) with one equation linking them.

Each energy depends on any pair on independent variables, but the fundamental equations indicate which are the most convenient.

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Using The Fundamental equations:
Example: how does G vary with T?

$$dG = - SdT + Vdp$$

$$\text{but } dG = (\partial G/\partial p)_T dp + (\partial G/\partial T)_p dT$$

Equate coefficients

$$V = (\partial G/\partial p)_T \quad \text{and} \quad -S = (\partial G/\partial T)_p$$

Slope of a graph of G vs. T at fixed p is $-S$

Same for molar quantities: $-S_m = (\partial G_m/\partial T)_p$

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How G varies with T: $(\partial G_m/\partial T)_p = -S_m$

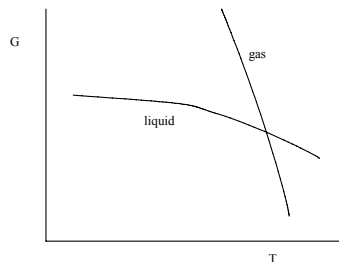
We know some facts about S_m values:

S_m 's are **positive**, increase with T.

$S_m(\text{gas}) \gg S_m(\text{liquid}) > S_m(\text{solid})$

We can sketch G vs. T
for any substance \rightarrow

Intersection at
phase transition T



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How G varies with p: $(\partial G_m/\partial p)_T = V_m$

V_m 's are always positive

small for condensed phases

large for gases

Thus G_m increases with p

slowly for condensed phases,

steeply for gases

Later we will derive and use an important equation for $G_m(p)$ for gases

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Maxwell Relations



$$dG = (\partial G/\partial p)_T dp + (\partial G/\partial T)_p dT$$

$dG = V dp - S dT$ now **equate coefficients**:

$$V = (\partial G/\partial p)_T \text{ and } -S = (\partial G/\partial T)_p$$

Take derivatives:

first with respect to **T**: $(\partial V/\partial T)_p = (\partial^2 G/\partial T \partial p)$

second with respect to **p**: $-(\partial S/\partial p)_T = (\partial^2 G/\partial p \partial T)$

$$(\partial^2 G/\partial T \partial p) = (\partial^2 G/\partial p \partial T) \text{ (Euler reciprocity theorem),}$$

so $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$ Maxwell relation from dG

The slope of V vs. T is the same as
the slope of S vs. p!

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Using a Maxwell relation:

$$(\partial V/\partial T)_p = -(\partial S/\partial p)_T$$

For an ideal gas $V = nRT/p$,

$$\text{so } (\partial V/\partial T)_p = nR/p = -(\partial S/\partial p)_T$$

If T is constant $dS = -(nR/p) dp$

$$\text{Integrate: } \Delta S = -nR \ln(p_2/p_1)$$

Familiar result, obtained differently.

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Using Maxwell Relations

$dU = +TdS - pdV$. Divide by dV, with T constant:

$$(\partial U/\partial V)_T = T (\partial S/\partial V)_T - p$$

Maxwell relation from $dA = -SdT - pdV$:

$$(\partial S/\partial V)_T = (\partial p/\partial T)_V$$

Substitute: $(\partial U/\partial V)_T = T (\partial p/\partial T)_V - p$

with an equation of state, we can evaluate RHS!

For ideal gas: $(\partial p/\partial T)_V = nR/V$, so $(\partial U/\partial V)_T = 0$

We asserted this earlier without proof

(if T is constant, U is constant for an ideal gas),

but now (finally!) a formal proof.

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Comments: derivations and proofs

Lots of derivations and proofs in this section!

Some lead to equations used for calculations, many lead to equations used for further derivations.

Memorizing each result (along with the specific conditions) is not a fruitful way to learn thermodynamics: understanding how to get there is.

Start with definitions and basic equations.

There are often several ways to get to a result.

Be logical. Show clearly how each line follows from the one above.

Sometimes it is helpful to work backwards to figure out how to get there, but proofs must be presented forwards: from definitions to the desired result.

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