Chemistry BC3252y
Part V: The Third Law

The Laws of Thermodynamics:

I. You cannot win. The best you can do is break even.

II. You can break even only at absolute zero

III. You cannot get to absolute zero.

The Third Law

As the temperature approaches 0°K, it is observed that ΔS for all transformations between pure perfectly crystalline substances approaches zero.

Example: $\mathbf{C(s) + O_2(s) \rightarrow CO_2(s)}$

At 0°K, $\mathbf{\Delta_r S = 0}$ *All have same entropy*!

For convenience, and since the zero of the scale is arbitrary, we may say that **all pure perfectly crystalline substances have zero entropy at 0°K**.

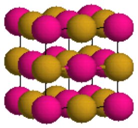
This defines a **third law entropy** scale: **S°**

S° values are always > 0 when T > 0 K.

introduced (1907) as **Nernst Heat Theorem**

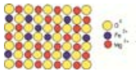
solved important problem: how to use thermal measurements to determine free energy (the missing constant of integration).

Why "**pure perfectly crystalline**"?

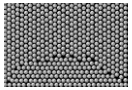


At absolute zero, there is no thermal excitation: atoms or molecules occupy the most stable locations in the perfectly ordered crystal lattice. There is no disorder.

All motion does NOT cease: QM prohibits that.



But for a **mixture**, entropy of mixing remains: does not decrease upon cooling (e.g.: $Fe_xMg_{1-x}O$).



If the crystal is **flawed**, some entropy is associated with the defects.

There are some other special substances that have a **residual entropy** at absolute zero:

e.g. CO orients randomly on the lattice.

The Third Law: consequences

As the temperature approaches 0°K, ΔS for all transformations between pure perfectly crystalline substances approaches zero.

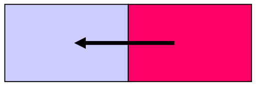
Because of this, **you cannot get to 0°K**.

Why not? ***How do we make things cold?***

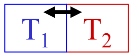
Method I:

Place object in contact with something colder.

Heat always flows from hotter to colder. Why?



Heat flows from hotter to colder object. Why? **Entropy!**



Object **1** is at T_1 and object **2** is at T_2

If $T_2 > T_1$ **what is sign of** $\mathbf{dq_1}$? [***can we show it is +*** ?]

$dq_1 = -dq_2$ Allow process to occur reversibly.

$dS_1 = dq_1/T_1$ and $dS_2 = dq_2/T_2 = -dq_1/T_2$.

$dS_{tot} = dS_1 + dS_2 = dq_1/T_1 - dq_1/T_2$

$dS_{tot} = dq_1(1/T_1 - 1/T_2) = dq_1[(T_2 - T_1)/T_1T_2]$

But if the process is spontaneous, $dS_{tot} > 0$.

T_1T_2 is > 0, so $\mathbf{dq_1}$ and $\mathbf{(T_2 - T_1)}$ have the same sign

If object 2 is hotter [$T_2 > T_1$] then $dq_1 > 0$

2nd law requires that **heat flows into object 1.**

Refrigeration when no colder object is available

Method II. **Boil under reduced pressure**.

For all substances, $\Delta_{vap}H > 0$

If part of a sample evaporates (boils), but the system is insulated so no heat can flow in, the remaining liquid cools.

The energy required for vaporization comes from the thermal energy in the liquid.

If we reduce the pressure, it continues to boil: the remaining liquid gets even cooler.

Water in a vacuum trap!

Boiling under reduced pressure

What drives this process? $\mathbf{\Delta_{vap}S > 0}$

The liquid vaporizes because entropy is higher in the gas.

But the entropy in the liquid that remains becomes lower, as its temperature falls.

The cooling of the liquid depends on the entropy difference between the liquid and the gas

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Other methods of refrigeration

Method III: **Joule-Thompson Expansion**

As a real gas expands, it cools.

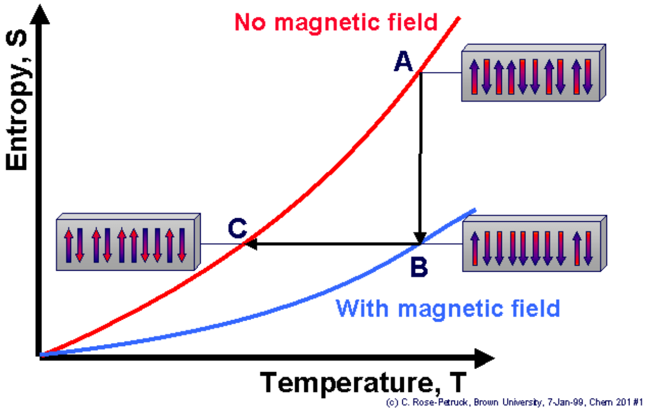
Why does it expand? Entropy increases!

Method IV: **Adiabatic Demagnetization**

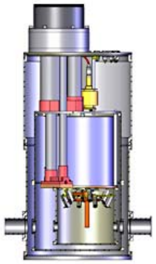
1) Magnetic substance: turn on field isothermally (e.g. in contact with thermal bath): the spins align.

2) Remove the bath (→ adiabatic) and turn off field: the magnetic dipoles become disordered, $\Delta_{mag}S > 0$. since q=0, the energy needed to create disorder must be taken from system's thermal energy: it cools.

Adiabatic Demagnetization

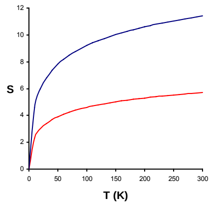


(c) C. Rose-Petruck, Brown University, 7-Jan-99, Chem 201 #1



Vericold® apparatus

The bottom line…



All methods of refrigeration rely on some process in which ΔS > 0.

But as T approaches absolute zero, ΔS values get smaller and smaller.

So it is harder and harder to cool things as T approaches absolute zero.

Result: **you cannot get to absolute zero**.

We saw earlier that for solid elements $C_p \rightarrow 0$ as $T \rightarrow 0$

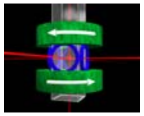
True for compounds too. Show using the 3rd law:

If p is constant, $dS = (C_p/T)\,dT$.

So if $dS \rightarrow 0$ as $T \rightarrow 0$, then $C_p \rightarrow 0$

Why? QM: quantum states inaccessible at small RT.

"Laser cooling"



Coldest temperatures obtained to date use lasers to cool gas-phase molecules:

photons collide with the molecules, reducing their speed.

Phenomenon occurs called **Bose-Einstein condensation**

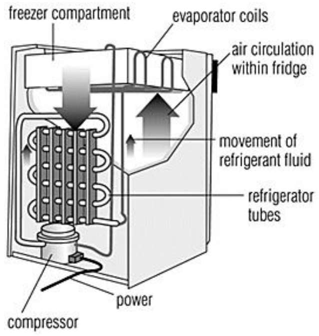
"Cooling rubidium atoms to less than 170 billionths of a degree above absolute zero [1.7×10^{-7} K] caused the individual atoms to condense into a 'superatom' behaving as a single entity"

1995 quote from Eric Cornell and Carl Wieman

2000 Nobel Prize in Physics

But the third law still applies!….

Household Refrigerators also air conditioners, heat pumps…



Refrigerator

Coolant cycles through sealed coils

Repeated **expansion/compression** *and* **evaporation/condensation**.

Heat transferred into room:
use electricity to pump heat
from inside (colder)
to outside (warmer).

Heat pumps can heat houses on same principle.

Coolant: *used* to be Freon, CF_2Cl_2

Third Law Entropy

S° ≡ 0 for all pure perfectly crystalline substances at absolute zero.

How do we determine S° for substances at other temperatures (e.g. 25°C)?

$dS = dq_{rev}/T$

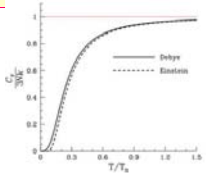
Warm reversibly at constant pressure:

$dq = C_p\,dT$, so **$dS = (C_p/T)\,dT$**

Integrate from **0 K** to desired **T**.

Must include ΔS for any phase transition.

Calculating Third Law Entropy beginning of integral (0 to ~25 K)



$dS = (C_p/T)\,dT$

Integrate from 0 K to desired T.

Data for C_p does not go to 0 K.

Debye theory says that **$C_p = a\,T^3$** at very low T.

Suppose T′ is the lowest T where C_p known

Then $C_p(T') = aT'^3$ determines constant **a.** Integrate to T′:

$$\int_0^{T'} \frac{C_p dT}{T} = \int_0^{T'} \frac{aT^3 dT}{T} = \int_0^{T'} aT^2 dT = \left.\frac{aT^3}{3}\right|_0^{T'} = \frac{aT'^3}{3} = \frac{C_p(T')}{3}$$

Result: integral below lowest T (=T′) is (1/3) lowest C_p value

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Calculating Third Law Entropy

Sometimes can use equation **$C_p = a + bT + c/T^2$**

But often $C_p(T)$ data is in tabular form, without a good analytical fit for the desired complete range of T.

Perform numerical integration of $(C_p/T)\,dT$.

1. Fine ruled paper, count boxes, or
2. Cut and weigh integral, or
3. Piecewise fit and integrate analytically (on computer)

Example: $O_2(g)$:

$$S°(O_2(g)\text{ at }25°C) = \int_0^{T_{fp}} \frac{C_{p,s}dT}{T} + \frac{\Delta H_{fus}}{T_{fp}} + \int_{T_{fp}}^{T_{bp}} \frac{C_{p,l}dT}{T} + \frac{\Delta H_{vap}}{T_{bp}} + \int_{T_{bp}}^{298.15} \frac{C_{p,g}dT}{T}$$

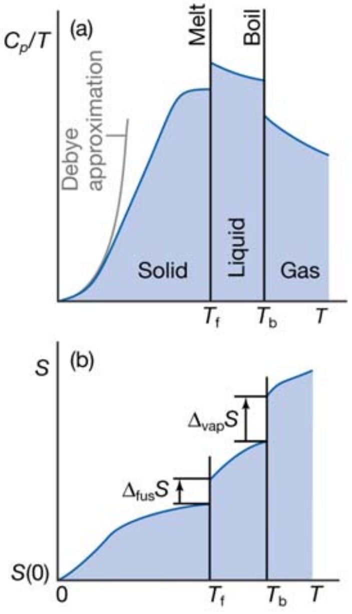
Two phase transitions…

C_p changes discontinuously at phase transitions.

This is the **integrand**:

Calculating Third Law Entropy of $O_2(g)$

Atkins
Fig. 4.12 (7/E)
Figure 3.14 (8/E)



The resulting **integral**:

Molecular interlude II: **What is Entropy?**

Definition: **$dS = dq_{rev} / T$** What does this mean?

Expanding ideal gas: $\Delta S = nR \ln (V_2/V_1)$
entropy increases… but what *is* entropy?

We have said that entropy is related to disorder

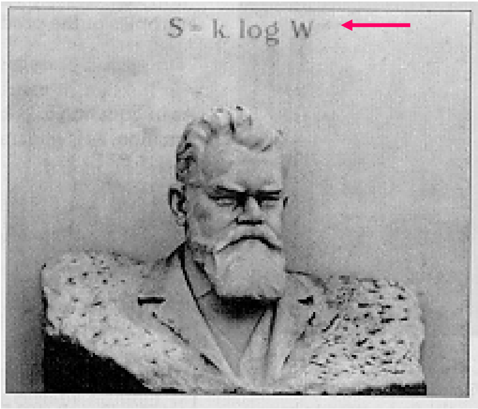
Where does this idea come from, and
what does disorder have to do with (dq_{rev} /T)?

Statistical thermodynamics provides insight.

Ludwig Boltzmann's epitaph: **$S = k \ln W$**

$k = k_B = R/N_A$ and W = partition function.
W counts all possible arrangements.

Boltzmann's tombstone



Molecular interpretation of Entropy

$S = k \ln W$

$\Delta S = S_2 - S_1 = k \ln W_2 - k \ln W_1 = k \ln (W_2/W_1)$

How do we obtain W? use Statistical Mechanics

For now, use fact that $W_2/W_1 = f_2/f_1$
where f_k is the probability of a particular outcome
(*not p_k to avoid confusing with partial pressure*).

Example: three cards (1, 2, 3) arranged at random.

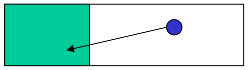
probability first card is 1: $f_1 = 1/3$; probability not 1: $f_{not} = 2/3$

$W_1 = 2$ (123, 132);

$W_{not\ 1} = 4$ (231, 213, 312, 321)

$f_{not}/f_1 = 2$ and $W_{not}/W_1 = 2$.

Molecular interpretation of Entropy



Imagine box with total volume V_2,
a portion of it has volume V_1.

Molecule **a** moves freely, randomly, around the box.

What is probability that **a** is somewhere in the box
(i.e. in V_2)? answer: one! $f_{2a} = 1$

What is probability that **a** is in V_1?
answer: $f_{1a} = (V_1/V_2)$.
true for a, b, c… (total of **m** molecules)

What is probability that all **m** molecules are in V_1?

Probabilities multiply, so $f_{1,tot} = (V_1/V_2)^m$

Probability that all molecules are in V_2 , $f_{2,tot} = 1^m = 1$

Isothermal expansion of an ideal gas

ΔS for process (all gas in V_1) to (all in V_2)?

$\Delta S = k \ln (W_2/W_1) = k \ln (f_2/f_1) = k \ln f_2 - k \ln f_1$

$\Delta S = k \ln(1) - k \ln (V_1/V_2)^m = 0 - mk \ln(V_1/V_2)$

$n = m/N_A \rightarrow m = N_A n$ and $k = R/N_A \rightarrow mk = nR$

$\Delta S = -n(N_A k) \ln (V_1/V_2) = \mathbf{+nR \ln (V_2/V_1)}$

Boltzmann's equation $S = k \ln W$ gives the same result for isothermal expansion of an ideal gas as we found earlier using $dS = dq_{rev}/T$

Entropy is smaller when the molecules are in V_1 because there are fewer such arrangements.
Larger volume provides more possibilities for molecules.

Residual entropy of ice at absolute zero

Two ways to determine **S° for water at 25°C**:

(1) integrate heat capacity data, plus $\Delta_{fus}H°/T_{mp}$

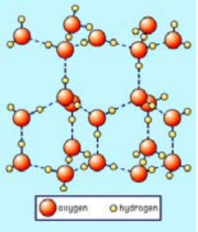
(2) measure $\Delta S°$ at 25°C for the reaction
$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(\ell)$, and
combine with S° values for H_2 and O_2

Very precise results **differ by ~ 3.4 J/K-mole**

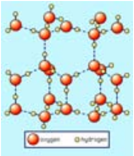
Conclusion: ice at 0 K has **S° = 3.4 J/K-mole**. **Why?**

Look at crystal structure of ice:

O atoms at tetrahedral sites,
H (yellow) *between* each O (red),
but not halfway!



Residual entropy of ice: S°(0 K) = 3.4 J/K-mole



How may ways can we arrange H atoms on lattice?

Each H has two possible positions along O─O axis

What if $W = 2^{2N}$?

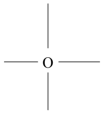
$S = k \ln W = 2N\, k \ln 2 = 2R \ln 2 = 11.53$ J/K-mole

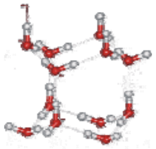
Too big! Ignores formula H_2O:

each O must have exactly 2 H atoms closer to it.

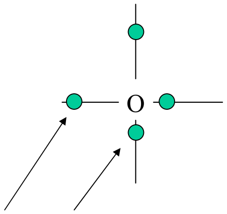
Not ok to position H's randomly

Need a recount!





Residual entropy of water: S°(0 K) = 3.4 J/K-mole



Previous count included a total of $2^4 = 16$ arrangements around each O (H atom *out* or *in*)

1 has all H's *in* (H_4O); 1 has no H *in* (O)

4 have 3 H's *in* (H_3O); 4 have 1 H *in* (HO)

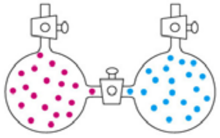
16–10 = **6** have 2 H's *in* (H_2O) these are correct

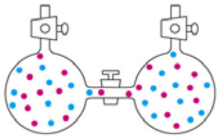
6/16 = 3/8 of total arrangements at each O are ok.

$W = 2^{2N}(3/8)^N = 4^N(3/8)^N = (3/2)^N$.

$S = k \ln W = kN_A \ln (3/2) = R \ln (3/2)$
= 3.37 J/K-mole. Agrees with experiment.

Entropy of Mixing


(a) Before mixing


(b) After mixing

• Gas A • Gas B

Two ideal gases, same T, p, initially separate.

Open stopcock: what happens? They mix.

Come back later: they don't unmix!

No energetic driving force: $\Delta_{mix}U = 0$.

Entropy drives process. What is $\boldsymbol{\Delta_{mix}S}$?

Gas A starts in V_A, ends in V_A+V_B

$\Delta S_A = n_A R \ln([V_A+V_B]/V_A)$

If $n_A = n_B = n$ and $V_A = V_B = V$: then $\Delta S_{A \text{ or } B} = nR \ln 2$

$\Delta_{mix}S = \Delta S_A + \Delta S_B = 2\, nR \ln 2$

$\Delta_{mix}S = 11.53$ J/K for one mole of each gas. $\Delta_{mix}S > 0$

Entropy of Mixing of ideal gases, arbitrary amounts

n_A moles A: start in $V_A = n_ART/p$, end in V_A+V_B

$\Delta S_A = n_A\, R \ln([V_A+V_B]/V_A)$ similar for B

$\Delta_{mix}S = n_A\, R \ln([V_A+V_B]/V_A) + n_B\, R \ln([V_A+V_B]/V_B)$

$[V_A+V_B]/V_A = [(RT/p)(n_A+n_B)]/[(RT/p)n_A] = n_{tot}/n_A$

Define $X_i = n_i/n_{tot}$: then $n_{tot}/n_A = 1/X_A$.

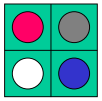
$\Delta_{mix}S = R\{n_A \ln(1/X_A) + n_B \ln(1/X_B)\}$

$$\boldsymbol{\Delta_{mix}S = -n_{tot}\, R\, \{X_A \ln X_A + X_B \ln X_B\}}$$

all $X_k < 1 \rightarrow (\ln X_k) < 0 \rightarrow \boldsymbol{\Delta_{mix}S > 0}$

Ideal gases mix spontaneously, due to entropy.

Entropy of mixing of ideal gases: statistical derivation, small sample



4 balls in a box with 4 sites (like egg carton)

How many arrangements? W = 4! = 24

8 balls, 4 white and 4 black, box with 8 sites

How many arrangements?

$W = 8! = 40320 = W_{tot}$

All black on L, all white on R?

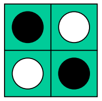
$24 \times 24 = 576 = W_{sep}$

$\Delta S_{mix} = k_B \ln W_{mix} - k_B \ln W_{sep} = k_B \ln(W_{mix}/W_{sep})$

approximation: $W_{mix} = W_{tot} - W_{sep} \sim W_{tot}$

$\Delta S_{mix} = k_B \ln(40320/576) = k_B \ln(70) = 4.25\, k_B$

Entropy of mixing of ideal gases: statistical derivation ($n_A = n_B$)



m atoms of each color (B/W), 2m sites.

$W_{tot} = (2m)!$ and $W_{sep} = (m!)^2$

$\Delta S_{mix} = k_B \ln(W_{mix}/W_{sep}) = k_B \ln\{(2m)!/(m!)^2\}$

Stirling's approximation **ln N! = N ln N – N**

$50! = 3.0 \times 10^{64}$. $\ln 50! =$ **148.477**

$50 \ln 50 - 50 = 195.6 - 50 =$ **145.6** (**1.9%** error)

$100! = 9.3 \times 10^{157}$ $\ln 100! = 363.739$

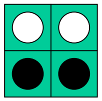
$100 \ln 100 - 100 = 460.5 - 100 = 360.5$ (0.9% error)

$200! = 7.9 \times 10^{374}$ $\ln 200! = 863.2$

$200 \ln 200 - 200 = 1059.7 - 200 = 859.7$ (0.4 % error)

gets better as N increases; exact with molar quantities.

Entropy of mixing of equal amounts of two ideal gases: Classical result: $\Delta_{mix}S = 2\ nR\ \ln 2$



$\Delta S_{mix} = k_B \ln (W_{mix}/W_{sep}) = k_B \ln \{(2m)!/(m!)^2\}$
$= k_B \ln (2m)! - 2 \ln (m!)$

Stirling's approximation: $\ln N! = N \ln N - N$

$\Delta S_{mix} = k_B \{2m \ln (2m) - 2m - 2m \ln m + 2m\}$

$\Delta S_{mix} = 2m\ k_B \ln 2$

$m = nN_A$, so $\Delta S_{mix} = 2\ nR \ln 2$

Agrees with the classical result.

Conclusion: statistical thermodynamics can be used to derive all equations of classical thermodynamics. Our understanding of entropy as disorder comes from this.

The Gibbs-Helmholtz equation
The dependence of G on T

From calculus:

$[\partial(G/T)/\partial T]_p = (1/T)(\partial G/\partial T)_p - (G/T^2)(\partial T/\partial T)_p$
$= (1/T)(\partial G/\partial T)_p - G/T^2$

But $(\partial G/\partial T)_p = -S$, so

$[\partial(G/T)/\partial T]_p = -S/T - G/T^2$
$= -(G + TS)/T^2 = -H/T^2$

$\mathbf{[\partial(G/T)/\partial T]_p = -H/T^2}$ Gibbs-Helmholtz equation

so for reactions $\mathbf{[\partial(\Delta_r G/T)/\partial T]_p = -\Delta_r H/T^2}$

$(\Delta_r G/T)$ vs. T: curve. Slope of tangent is $-\Delta_r H/T^2$

The Gibbs-Helmholtz equation: alternate form

Consider f(x). What is $df/d(1/x)$?

Change variables. Let $u = 1/x$

$df/dx = (df/du)(du/dx)$, so $df/du = (df/dx)/(du/dx)$, .

But $du/dx = -1/x^2$, so $df/du = df/d(1/x) = -x^2(df/dx)$

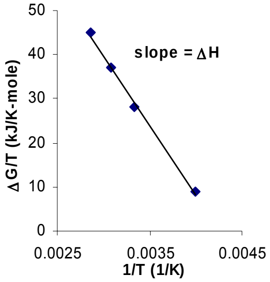
Therefore $[\partial(G/T)/\partial(1/T)]_p = -T^2\ [\partial(G/T)/\partial T]_p$

But $[\partial(G/T)/\partial T]_p = -H/T^2$ so

$\mathbf{[\partial(G/T)/\partial(1/T)]_p = H}$

Gibbs-Helmholtz equation

Plot $\mathbf{(\Delta_r G_m°/T)}$ vs. $\mathbf{(1/T)}$,
slope is $\mathbf{\Delta_r H_m°}$ (often linear) →



Is it ok simply to insert Δ's into an equation?

Example: $\mathbf{(\partial G/\partial T)_p = -S}$

$(\partial G_2/\partial T)_p = -S_2$ and $(\partial G_1/\partial T)_p = -S_1$

Since $\Delta G = G_2 - G_1$,

$(\partial \Delta G/\partial T)_p = (\partial[G_2 - G_1]/\partial T)_p$
$= (\partial G_2/\partial T) - (\partial G_1/\partial T)_p = -(S_2 - S_1) = -\Delta S$

so $\mathbf{(\partial \Delta G/\partial T)_p = -\Delta S}$

Yes, one can (with care) "simply insert Δ's"

Since G and S are both extensive, divide by n:

$\mathbf{(\partial \Delta G_m/\partial T)_p = -\Delta S_m}$

When both are at standard pressure, may also add °

$\mathbf{(\partial \Delta G_m°/\partial T)_p = -\Delta S_m°}$

Dependence of G on p: General Equation? No! Consider special cases: (1) an **ideal gas**

$(\partial G_m/\partial p)_T = V_m = RT/p$

At constant T: $dG_m = RT\,dp/p = RT\,d\ln p$

$\Delta G_m = RT\ln(p_2/p_1)$.

Define $p_1 = p° = 1$ as the standard state (°)

either one atmosphere, or if following IUPAC recommendations, one bar, [1 atm = 1.01325 bar]

reminder: standard state says nothing about T!

At standard state : $G_m = G_m°$ when $p = 1$ atm,

$\Delta G_m = (G_m - G_m°) = RT\ln(p/p°) = RT\ln(p/1)$

$\mathbf{G_m = G_m° + RT\ln p}$ <<< Very important!

(p must be in atmospheres)

The dependence of **G** on **p:** (2) Vaporization of a liquid

$(\partial G/\partial p)_T = V$ or $(\partial \Delta_r G/\partial p)_T = \Delta_r V$

$\Delta_r V$ is small for condensed phases, larger for gases

Vaporization (gas ideal): $\Delta_{vap}V = V_{gas} - V_{liq} \approx V_{gas} = nRT/p$.

Thus $(\partial \Delta_{vap}G/\partial p)_T = nRT/p$.

If temperature is constant: $d\,\Delta_{vap}G = (nRT/p)\,dp$

Integrate: $\Delta_{vap}G(\text{at } p_2) - \Delta_{vap}G(\text{at } p_1) = nRT\ln(p_2/p_1)$

Define $\Delta_{vap}G° = \Delta_{vap}G$ when $p_1 = p° = 1$ atm.

What is $\Delta_{vap}G$ at some other p? (let $p_2 = p'$)

$\Delta_{vap}G(p') - \Delta_{vap}G° = nRT\ln(p'/p°) = nRT\ln p'$

$\Delta_{vap}G(p') = \Delta_{vap}G° + nRT\ln p'$

divide by n: $\mathbf{\Delta_{vap}G_m(p') = \Delta_{vap}G_m° + RT\ln p'}$

Application: Vaporization of water at 25°C

from Atkins at 25°C	$\Delta_f H_m°$ (kJ/mole)	$S_m°$ (J/K-mole)
$H_2O(\ell)$	-285.83	69.91
$H_2O(g)$	-241.82	188.83

$\Delta_{vap}H_m° = 44.01$ kJ/mole endothermic (H increases)

$\Delta_{vap}S_m° = 118.92$ J/K-mole entropy increases

vaporization always increases both H and S.

Is vaporization of water spontaneous at 25°C?

1) Look at entropy of the system plus surroundings:

$\Delta_{vap}S_{surroundings} = -q_{sys}/T = -(44{,}010\text{ J/mole})/(298.15\text{ K}) = -147.61$ J/K-mol

$\Delta_{vap}S_{total} = 118.92\text{ J/K-mole} - 147.61\text{ J/K-mol} = -26.65$ J/K-mol negative: *no*

2) Look at Gibbs free energy of the system:

$\Delta_{vap}G_m° = 44.01 - (298.15)(118.92)/1000 = 8.55$ kJ/mole at 25°C positive: *no*

($\ell \rightarrow g$) for water is not spontaneous at 25°C **and 1 atm (°)**

But what if we change the pressure?

Application: at what pressure will water boil at 25°C?

From two slides earlier... $\mathbf{\Delta_{vap}G_m(p) = \Delta_{vap}G_m° + RT\ln p}$

here $\Delta_{vap}G_m° = 8.55$ kJ/mole at 25°C and 1 atm.

At what value of p will $\mathbf{\Delta_{vap}G_m(p) = 0}$?

$\ln p = -\Delta_{vap}G_m°/RT$

$= -(8550\text{ J/mole}) / (8.31451\text{ J/K-mol})(298.15\text{ K}) = -3.50$

$p = \exp(-3.50) = 0.032$ atm.

The units are atmospheres:

we have actually found $(p/p°) = 0.032$, with p°

The curve of boiling points for water
or vapor pressure as a function of temperature

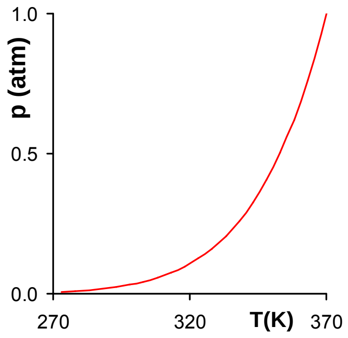
Start with $\Delta_{vap}H_m°$ and $\Delta_{vap}S_m°$ (at 25°C)
Making the approximation that they are constant with T, calculate p for each T:

$\Delta_{vap}G_m° = \Delta_{vap}H_m° - T\Delta_{vap}S_m°$

$p = \exp\{-\Delta_{vap}G_m° /RT\}$

Excel plot of p vs. T:

(We will return to such plots soon, when we study phase equilibria.)



Predicting the normal boiling point

$$\ln p = -\Delta_{vap}G_m° /RT = -\Delta_{vap}H_m° /RT + \Delta_{vap}S_m°/R$$

If we assume that $\Delta_{vap}H_m°$ and $\Delta_{vap}S_m°$ are constant with T, we can use data at 25°C to predict the normal boiling point:
the normal boiling point is at p = **one atm** exactly, so ln p = 0
thus $\Delta_{vap}H_m° /RT = \Delta_{vap}S_m°/R$
(i.e. $\Delta_{vap}G_m° = 0$ at b.p.)
$T_{bp} = (\Delta_{vap}H_m°) / (\Delta_{vap}S_m°)$
For water, this gives
T = (44,010 J/mole)/(118.92 J/K-mole)
= 370.1 K
The correct value is 373.15 K. Not too bad...