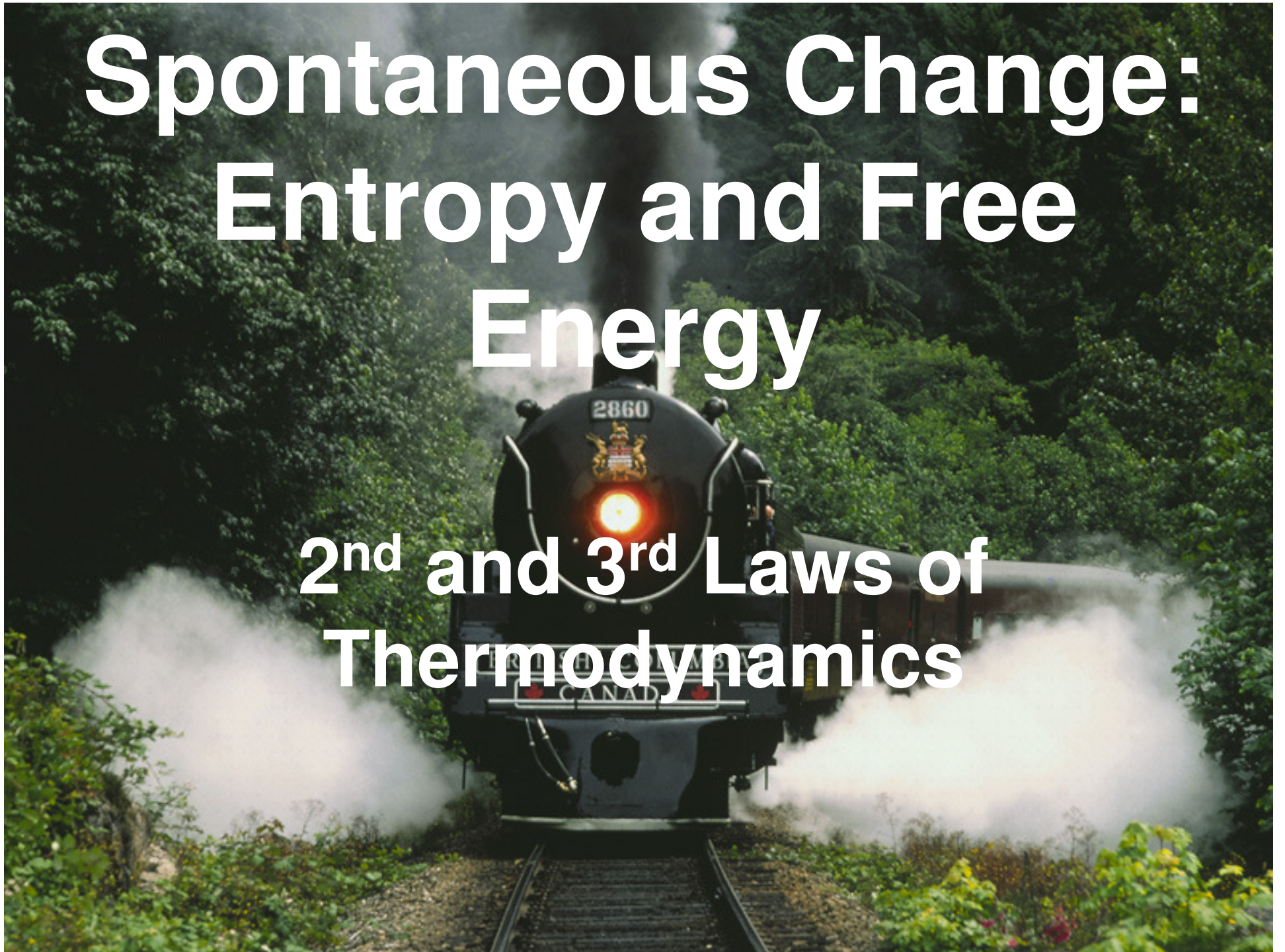


Spontaneous Change: Entropy and Free Energy

2nd and 3rd Laws of
Thermodynamics



Thermodynamics - is a pure science, much like mathematics. It makes very precise definitions of terms and then derives relationships between them. Understanding does not come easily. Fortunately, applications to chemistry are fairly simple.

Three Laws

1. $\Delta U = Q + W$ Conservation of Energy, relates heat and work
U & Q entering system and W done on it are +
U & Q leaving the system and W done by it are –
2. $\Delta S_{\text{univ}} > 0$ criterion for spontaneity or $\Delta G_{\text{SYS}} < 0$
3. $S = 0$ at 0 K for a perfect crystal of a pure substance.

Three State Functions

$\Delta G =$ Gibbs Free Energy $G = H - TS$

$\Delta H =$ Enthalpy, $H = U + PV$

$\Delta S = dQ_{\text{rev}} / T$

Definitions

Heat - a weapon as in “Arnold is packing heat”.

Heat Capacity - the number of heavy weapons Arnold can carry at one time without getting a hernia.

Calorie - the major component of a twinkie.

State Function - Any affair hosted by Jean Chretien.

Work - Something you pay others to do.

electrical work : as in “I having some electrical work done at the cottage.”

Spontaneous process : Anything that goes wrong is spontaneous according to Murphy’s law.

The system : A global geopolitical conspiracy to keep you from getting what you want. The system insures that things don’t work and that they obey Murphy’s law.

2nd Law, The Entropy of the Universe Increases. This extends Murphy’s Law throughout our galaxy and beyond.

Definitions

Heat - Q - energy transferred between system and surroundings as a result of temperature difference. entering Q is +

at constant V : $\Delta U = Q$ at constant P : $\Delta H = Q$

Heat Capacity - amount of energy needed to change the temperature of a substance by $1\text{ }^\circ\text{C}$. $Q = C_p \Delta T$.

Calorie - energy needed to raise 1 gram of water at $25\text{ }^\circ\text{C}$ by 1 degree $^\circ\text{C}$. ($C_p = 1.0\text{ cal./degree}$ for water)

State Function - A property of a system which has a unique value for a specific state of a system (independent of path). $G, H, S,$ and U are. Q and W are not.

Work - chemical reactions can do work on their surroundings

pressure volume work $W = -P_{\text{ext}} \Delta V$

electrical work : out $W = -nEF$ (battery) or in $+nEF$ (electrolysis)

System, Surroundings, Reversibility, Spontaneity

Rather than getting mired in the subtleties of formal thermodynamics (CHEM 2011), we will focus on the state functions G , H , and S and apply them to chemical reactions. We should be aware of the formal thermodynamic concepts underlying chemical equilibria principles.

The major questions are :

1. What is entropy ? What is enthalpy? What is free energy?
2. What determines the direction reactions proceed in and what is the formal criterion for an equilibrium?
3. How do I use Tables of Thermodynamic Data ?

SHORT ANSWERS

1. Entropy is a measure of disorder or increased randomness.
Enthalpy = Q at constant P is a measure of heat changes. It is reflected in bond energy and intramolecular forces.
2. ΔG is negative for a spontaneous process and $\Delta G = 0$ at equilibrium.
3. Phase changes, vapor pressures, redox potentials, bond energies, equilibrium constants & their temperature dependence are all derivable from the data therein.

Microscopic Interpretations

H enthalpy - molecules store energy as:

1. kinetic energy - translational motion $3/2 kT$
2. potential energy - in quantized energy levels involving rotational, vibrational, and electronic energy levels.

Entropy $S = R \ln(W)$ entropy increases with randomness or disorder or with the number of available microstates, W .

Heat Capacity the capacity of molecules to take in energy depends on the availability of energy states roughly within kT of the lowest state.

$\Delta G = \Delta H - T \Delta S$ spontaneity is a compromise between minimizing energy and maximizing entropy.

The macroscopic definition $\Delta S = Q_{rev}/T$ is not especially helpful in understanding entropy. The Microscopic interpretation is simpler.

In molecules internal energy is distributed among rotational, vibrational, and electronic energy levels. Translational energy is not quantized and increases with temperature $KE = 3/2 kT$ per molecule ($3/2 RT$ per mole)

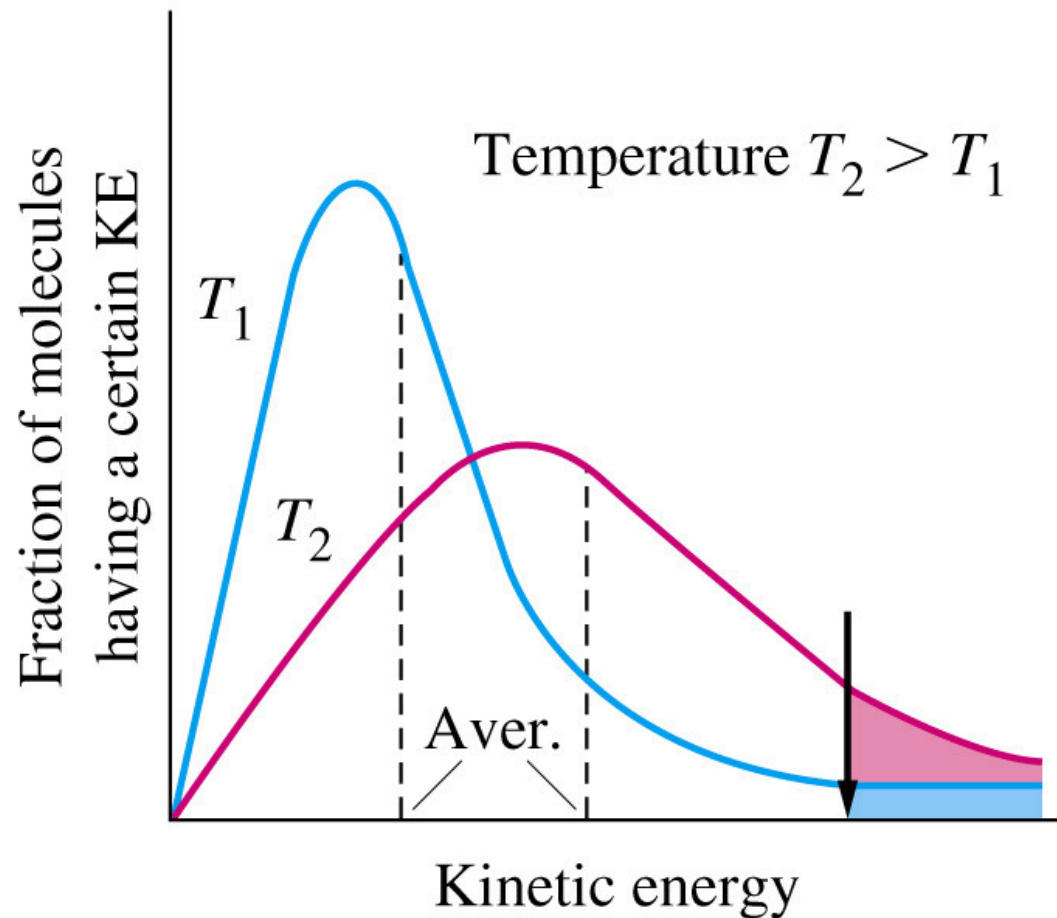
Think of energy levels as underground shelves where molecules store energy. The spacing of levels and the radiation which matches this spacing are as follows :

	rotational	vibrational	electronic	core
ν s ⁻¹	10^{10}	10^{13}	10^{14}	10^{16} 10^{18}
	microwave	infra-red	visible	UV X-ray
$E=N_0h\nu$	4 J/mol	4 kJ/mol	40 kJ/mol	4000 kJ/mol

$3/2RT$ at 298 K = 4 kJ/mol but at 5000 K $3/2RT = 62$ kJ/mol

at 298 K almost all molecules are in their lowest vibrational and electronic states but have a T dependent distribution of rotational energy levels.

Boltzmann Revisited - Energy partitioning



$T_1 = 298\text{K}$ $\text{KE} = 3/2 RT = 3.7 \text{ kJ/mole}$ ROT + some VIB

$T_2 = 1000\text{K}$ $\text{KE} = 3/2 RT = 12.5 \text{ kJ/mole}$ ROT + VIB

$T_3 = 5000\text{K}$ $\text{KE} = 3/2 RT = 62.5 \text{ kJ/mole}$ ROT + VIB + ELEC

What happens when we heat up a substance from 0 K ?

1. At 0 K only 1 microstate is populated. All molecules are in their lowest rot, vib, and electronic state. $S = k \ln(1) = 0$.
2. The heat capacity is related to the availability of energy states. When energy is stored internally the temperature does not rise but as more levels become populated, the entropy increases.

$$\Delta S = Q / T = C_p \Delta T / T$$

The area under the graph of C_p/T vs T is $S = \int C_p / T \, dT$

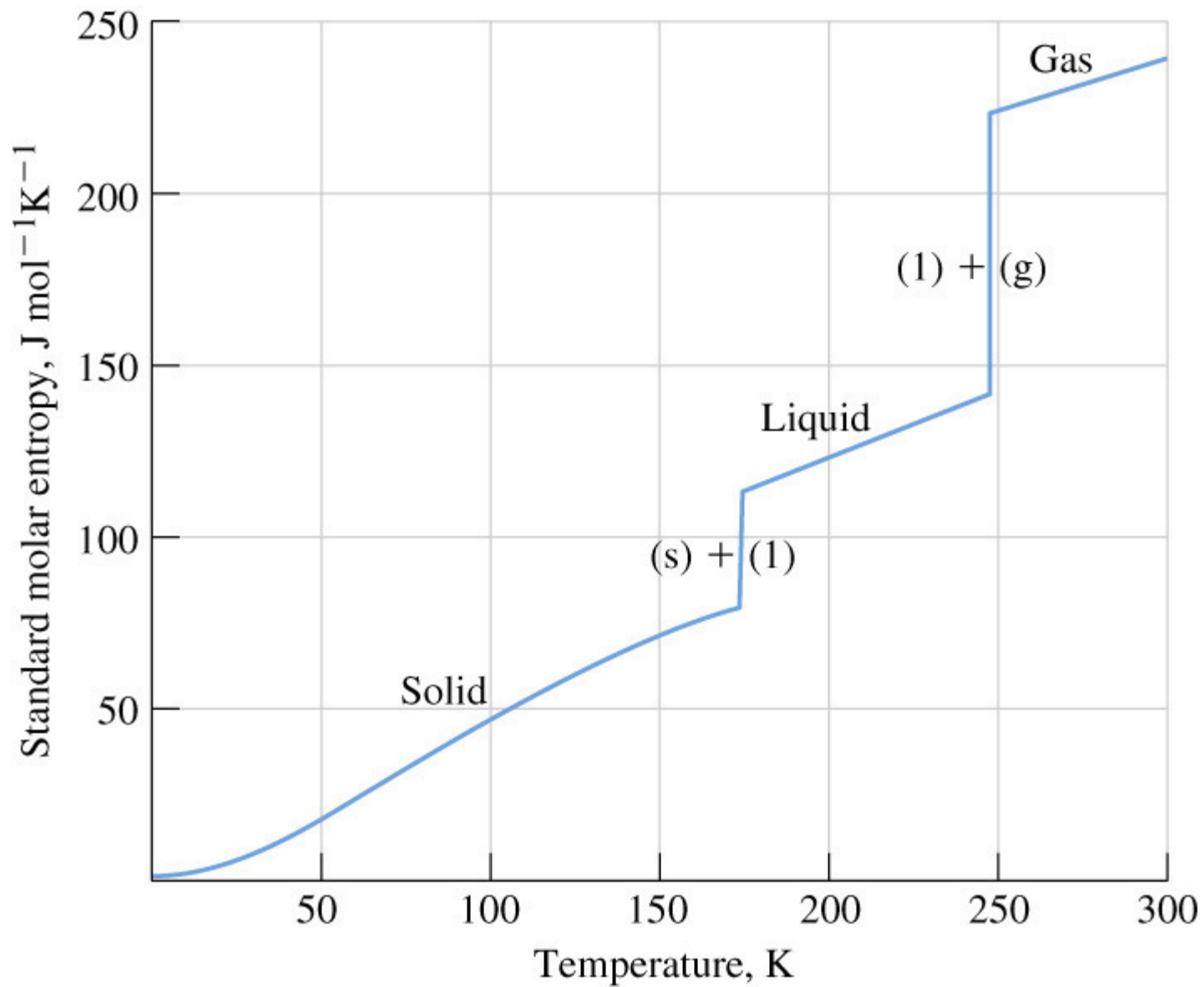
3. Phase changes are accompanied by large increases in translational motion and entropy.

At a phase change $\Delta G = 0$ and thus $\Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T_{\text{BP}}$

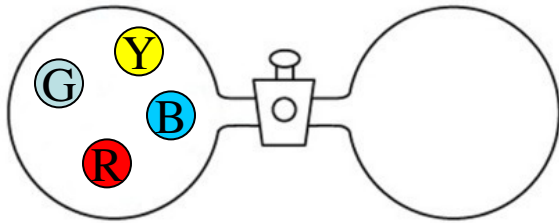
the stored enthalpy is converted into entropy ! The molecules give up some intra-molecular attractive forces for greater freedom. A crystal is more ordered than a liquid.

Trouton's rule is $\Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T_{\text{BP}} = 87 \text{ J mol}^{-1} \text{ K}^{-1}$

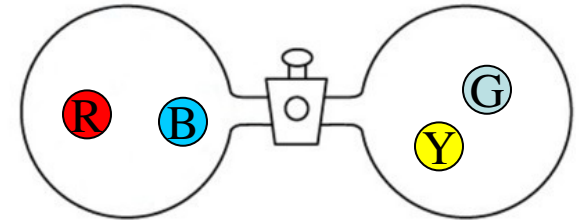
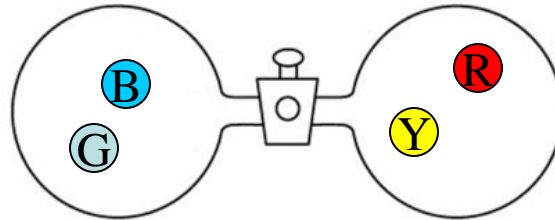
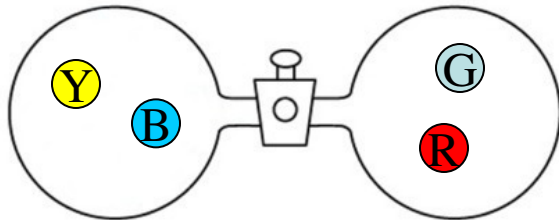
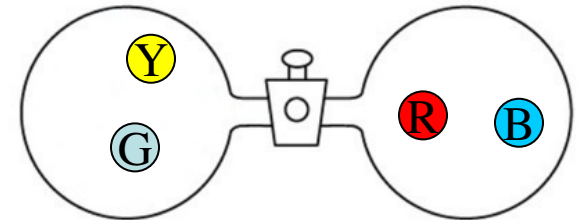
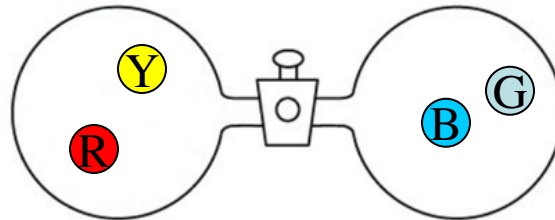
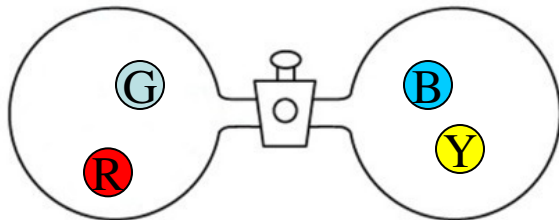
Figure 19-7 S vs T for CH₃Cl (not CHCl₃ as text claims)



Positional Microstates

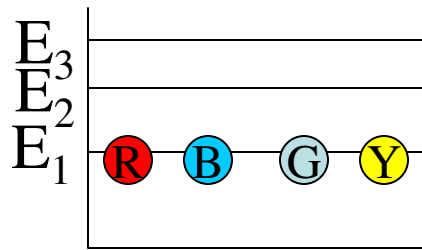


- All 4 particles in the left reservoir.
- Lower number of accessible microstates → Lower Entropy. Probability = $(1/2)^4 = 1/16$

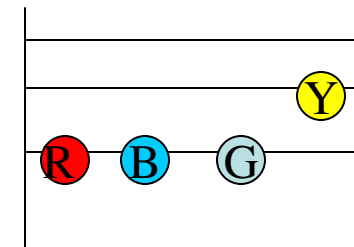
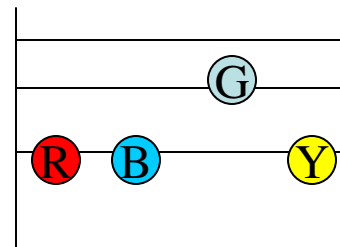
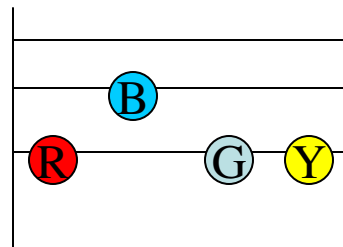
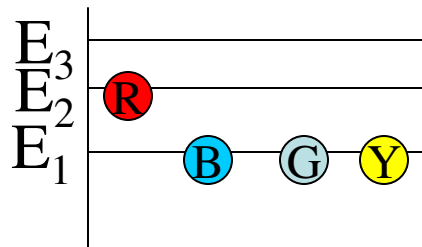


- 2 particles on the left and 2 particles on the right. Higher number of accessible microstates.
- **Conclusion: 1) Entropy increases with increasing the volume that gas system occupies. 2) Entropy increases when the number of molecules of gas increases as a result of a chemical reaction**

Energy Microstates



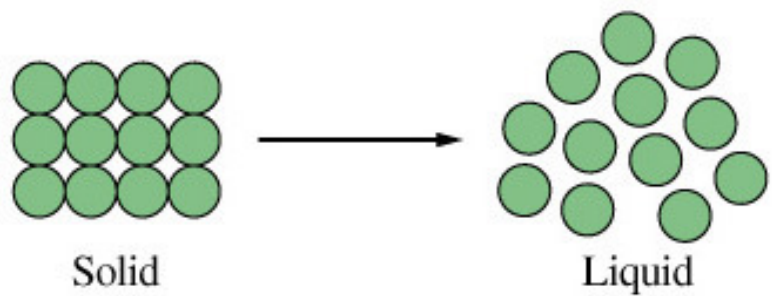
$T = 0$, only one energy level is accessible, one microstate exists. $S = R \ln(1) = 0$



$T > 0$, more energy levels are accessible. There are many microstates. The number of accessible energy microstates, W , increases with temperature.

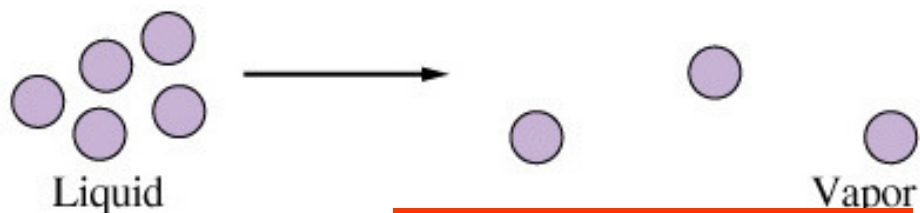
$$S = R \ln(4)$$

Conclusion: Entropy increases with temperature



(a) Melting: $S_{\text{liquid}} > S_{\text{solid}}$

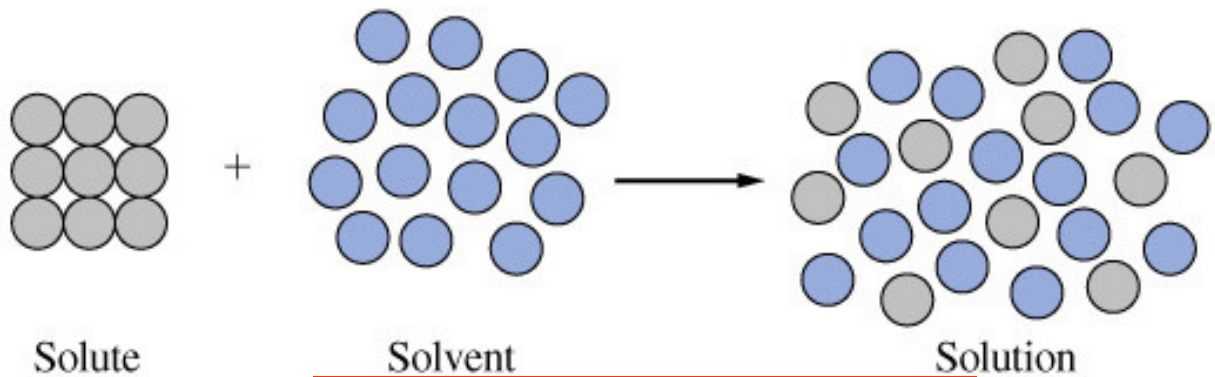
Entropy increases



(b) Vaporization: $S_{\text{vapor}} > S_{\text{liquid}}$

Entropy increases

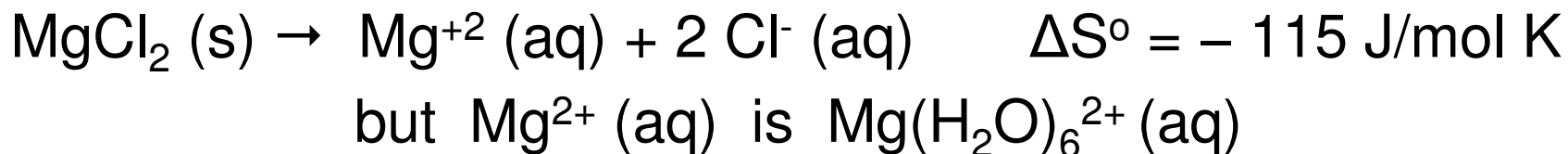
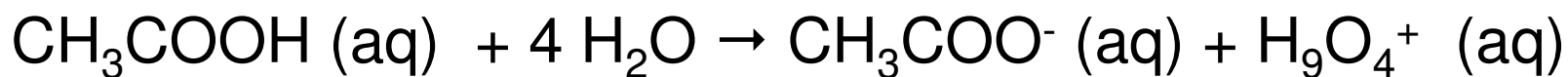
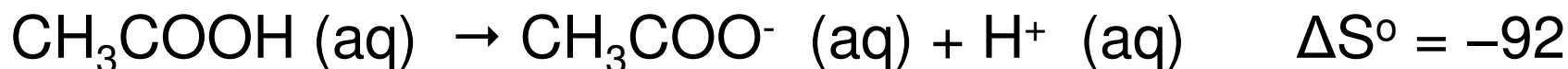
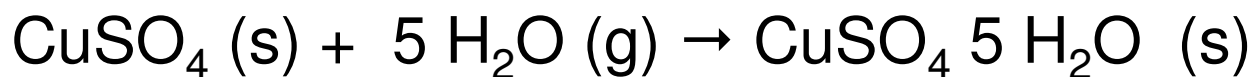
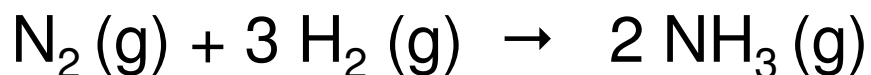
Trouton $\Delta S^{\circ}_{\text{vap}} = 87 \text{ Jmol}^{-1}\text{K}^{-1}$



(c) Dissolving: $S_{\text{soln}} > (S_{\text{solvent}} + S_{\text{solute}})$

Entropy increases

Predict the sign of ΔS° for the following.



Spontaneous Processes. Does G or H rule?

Hypothesis : Exothermic reactions are spontaneous and endothermic ones are not.

1. Freezing of water is **exothermic** ($\Delta H_{\text{sys}} < 0$) but it is **not spontaneous** above 0 °C.
2. Melting of ice is **endothermic** ($\Delta H_{\text{sys}} > 0$) but it is **not spontaneous** below < 0 °C.
3. Gas bulbs containing He and Ne each at 1 atm pressure will spontaneously mix. ($\Delta H_{\text{sys}} = 0$). The reverse is not spontaneous.
4. The reaction $\text{CaCO}_3 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$ is spontaneous at high temp but not at 298 K. { ΔH is + }
5. NH_4NO_3 is very soluble in water yet $\Delta H = + 28$ kJ/mol

Conclusion : ΔH is not the driving force, $\Delta G = \Delta H - T\Delta S$ is.

The submarine Kursk exploded in the ocean. Lots of heat and work with stuff melting, blowing to bits, etc. Clearly not a reversible process.

However the infinitesimal increase in the ocean temperature as a result (the surroundings) is a reversible process.

The system lost heat to the surroundings and did work on them.

$$\Delta Q_{\text{ocean}} = -\Delta H_{\text{sys}} \quad \text{at constant } T \text{ and } P$$

Applying the second law :

$$T\Delta S_{\text{surround}} + T\Delta S_{\text{sys}} = T\Delta S_{\text{univ}} > 0$$

$$\Delta Q_{\text{ocean}} + T\Delta S_{\text{sys}} = T\Delta S_{\text{univ}}$$

$$-\Delta H_{\text{sys}} + T\Delta S_{\text{sys}} = T\Delta S_{\text{univ}}$$

define $\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = -T\Delta S_{\text{univ}}$

G is a criterion for spontaneity at constant T & P which depends ONLY on the system. ΔG strives for a minimum.

If sub explosions are spontaneous why don't they all blow up?

GIBBS EQN IN SOLN

The free energy of each component in a solution may be expressed relative to a 1 Molar reference state.

$$G = G^\circ + RT \ln [C]/[C_{\text{ref}}]$$

For the equilibrium $aA + bB \rightleftharpoons cC + dD$:

$$\Delta G = \sum G (\text{products}) - \sum G (\text{reactants})$$

$$\Delta G = c G_c + d G_d - a G_a - b G_b$$

$$\Delta G = c\{G^\circ_c + RT \ln [C]/[C_o]\} + d \{G^\circ_d + RT \ln [D]/[D_o]\} - a\{G^\circ_a + RT \ln [A]/[A_o]\} - b \{G^\circ_b + RT \ln [B]/[B_o]\}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\text{where } Q = [C/C_o]^c [D/D_o]^d / \{[A/A_o]^a [B/B_o]^b\}$$

and $\Delta G = 0$ and $Q = K$ at equilibrium

$$\Delta G = 0 = \Delta G^\circ + RT \ln K_{\text{eq}} \quad \text{and} \quad \Delta G^\circ = - RT \ln K_{\text{eq}}$$

Derivation of eqn relating S° and S

Reversible Isothermal expansion of 1 mole of an ideal gas

$$\Delta U = 0 = Q + W \quad \text{so } Q = -W$$

$$W = -PdV = -nRT dV/V$$

integrating from V_i to V_f

$$W = -nRT \int dV/V = -RT \ln(V_f/V_i)$$

$$\Delta S = Q_{\text{rev}}/T = -W = RT \ln(V_f/V_i) = -R \ln(V_f/V_i)$$

in terms of pressures $P = nRT/V$, $\Delta S = R \ln(P_i/P_f)$

for $P_i = 1 \text{ atm} = P^\circ$ (standard conditions) where $S_i = S_o$

$$\Delta S = S_f - S_i = R \ln(P_o/P) - S_o = S^\circ - R \ln(P)$$

watch signs and rework this slide.

The naught is not for naught. Do sweat the °

ΔG is not ΔG°

The naught refers to substances in their reference states. For solutes it means 1 M for all reactants and products.

For $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$\Delta G^\circ = +$ says that if all three are at 1 M the reaction goes spontaneously backwards.

$\Delta G^\circ = 0$ has no particular significance. It would apply only if $K_{\text{eq}} = 1$ (not a common occurrence).

$\Delta G = 0$ happens every time a system reaches equilibrium.

Delta, schmelta. - don't sweat the Δ .

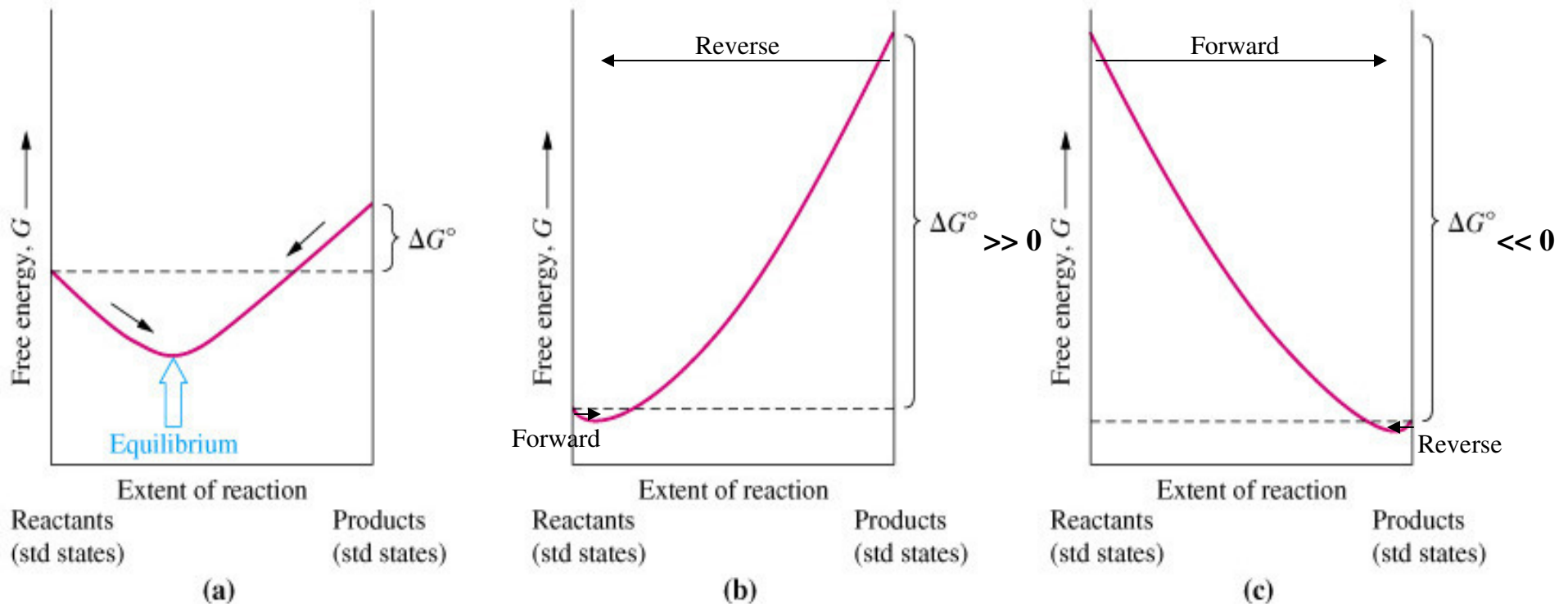
Every G, H, and S is a difference between initial and final states of a system.

S°_{298} for CHCl_3 is the difference in S for CHCl_3 at 0 K and CHCl_3 at 298 K so why isn't there a delta?

ΔG°_f for CHCl_3 IS the difference in G for graphite, $\frac{1}{2} \text{H}_2$ and $\frac{3}{2} \text{Cl}_2$ vs that for CHCl_3 with each in their standard states.

“*G vs Extent of Reaction*” Plot:

$$\Delta G = \Delta G^\circ + RT \ln Q_{eq} \quad \text{and} \quad \Delta G^\circ = -RT \ln K_{eq}$$



1. The equilibrium position is at the minimum in G vs extent of reaction.
2. Spontaneous processes are always in the direction of decreasing G .
3. ΔG° determines the location of the equilibrium.

? Which graph would apply to dissociation of acetic acid, of HCl ?

Significance of the Magnitude of ΔG°

ΔG°	$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$	
+200 kJ/mol	9.1×10^{-36}	No reaction
+100	3.0×10^{-18}	
+50	1.7×10^{-9}	
+10	1.8×10^{-2}	
+1.0	6.7×10^{-1}	
0	1.0	Equilibrium calculation is necessary
-1.0	1.5	
-10	5.6×10^1	Reaction goes to completion
-50	5.8×10^8	
-100	3.3×10^{17}	
-200	1.1×10^{35}	

$$\Delta G = \Delta H - T \Delta S$$

- Spontaneity ($\Delta G < 0$) depends upon the interplay between enthalpy and entropy
- Forming bonds : ΔH is – which favors a negative G
- Increased order : ΔS is – which favors a positive G

What can we say about $\text{Cl}_2 (\text{g}) \rightarrow 2 \text{Cl} (\text{g})$?

Breaking the bond will be unfavorable, $\Delta H +$
but entropy increases. $\Delta S +$

Given a high enough Temp $T \Delta S > \Delta H$ and $\Delta G < 0$

The four possible cases are :

H + & S - : never spontaneous

H + & S + : spontaneous at high temp.

H - & S - : spontaneous at low temp.

H - & S + : spontaneous at any temp

Standard Enthalpy, Free Energies, and Third Law Entropies in Appendix D2.

$$\Delta G^\circ = \sum \Delta G^\circ_f (\text{products}) - \sum \Delta G^\circ_f (\text{reactants})$$

likewise using ΔH°_f or S° .

Reference zeros.

ΔG°_f & ΔH°_f - relative to elements in their most stable form at 298 K. These are zero for elements which are gases : N_2 , O_2 , H_2 , Cl_2 , etc and solids S_{rhombic} , Ni , etc or liquids Br_2 or Hg .

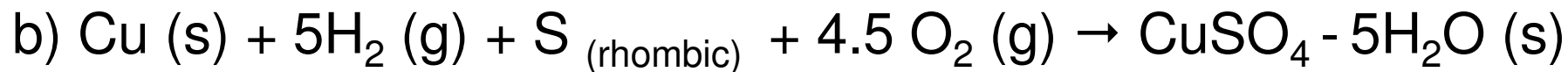
S° - third law entropies are zero for a pure crystal at 0 K !

this applies to all elemental and molecular forms.

Note: every element has its own zero for G & H while every substance is assigned its own zero for S. Values for ions assume $G^\circ_f = 0$ for H^+ (aq).

Tabulations are at 298 K allowing one to compute these state functions for millions of reactions. For other temperatures one may assume H and S are independent of T over a small range but this is increasingly a poor approximation for large extrapolations.

ΔG°_f and ΔH°_f for glycine and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ refer to what chemical reactions?



Entropy of Formation is not normally tabulated and rarely of any interest but we can compute it in two ways. For reaction b using Table D-2:

1) Using ΔG°_f and ΔH°_f for the formation reaction b.

$$S^\circ_f = (\Delta H^\circ_f - \Delta G^\circ_f) / T = \{-2280 - (-1880)\} / 298 = -1342 \text{ J mol}^{-1} \text{ K}^{-1}$$

note that S° for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 300.4$!!

2. From third law entropies at 298 K for the constituents in reaction b.

$$\Delta S^\circ_f = 300.4 - 33.15 - 5 (130.7) - 31.8 - 4.5 (205.1) = -1341$$

Note that S° for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ starts at 0 at 0 K for a perfect crystal and gets to 300.4 at 298 K. It has nothing to do with the reaction above.

ΔS°_f tells us the entropy relative to its elemental parts being 0 at 298 K.

Enthalpy Driven Reaction.

Example 7B



$$\Delta G^\circ_f \text{ kJ/mol} \quad 0 \quad 0 \quad -742.2$$

$$\Delta H^\circ_f \text{ kJ/mol} \quad 0 \quad 0 \quad -824.2$$

$$S^\circ \text{ J/mol K} \quad 27.28 \quad 205.1 \quad 87.40$$

$$\Delta G^\circ = 2(-742.2) - 3(0) - 4(0) = -1485.4 \text{ kJ/mol}$$

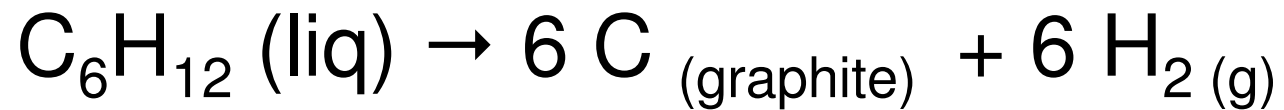
$$\Delta H^\circ_f = 2(-824.2) - 3(0) - 4(0) = -1648.4 \text{ kJ/mol}$$

$$\Delta S^\circ = 2(87.40) - 3(205.1) - 4(27.28) = -549 \text{ J/mol K}$$

note : $\Delta S_{\text{sys}} < 0$ but $\Delta S_{\text{surroundings}} = +1648000 \text{ J} / 298 = +5530 \text{ J/mol K}$

thus $\Delta S_{\text{universe}} = +5530 - 549 = +4981 \text{ J/mol K}$ a spontaneous process
exothermic reactions dump heat to the surroundings

Entropy Driven Reaction



ΔG°_f kJ/mol	+32	0	0
ΔH°_f kJ/mol	-123	0	0
S° J/mol K	+298.4	5.74	130.7

$$\Delta G^\circ = 6(0) + 6(0) - (32) = -32 \text{ kJ/mol}$$

$$\Delta H^\circ = 6(0) + 6(0) - (-123) = +123 \text{ kJ/mol}$$

$$\Delta S^\circ = 6(130.7) + 6(5.74) - (298.4) = 520.2 \text{ J/mol K}$$

$T \Delta S^\circ$ more than offsets unfavorable ΔH° .

Here $\Delta S_{\text{universe}} = 520 - 123000/298 = 520 - 412 = +108 \text{ J/mol K}$
surroundings are more ordered but the system is more disordered.

Cold Packs - ionic salts with endothermic ΔH_{soln}

	NH_4NO_3	(s)	\rightleftharpoons	NH_4^+	(aq)	+	NO_3^-	(aq)	RXN
G	-183.9			-79.3			-108.7		-4.1 kJ/mol
H	-365.6			-132.5			-205		+28.1 kJ/mol
S	151.1			113.4			146.4		+108.7 J/mol K

The + ΔS° is a result of dissociation into 2 ions

$\Delta H^\circ = \Delta H^\circ$ (solvation of ions) - ΔH° (lattice energy of solid)

solubility is obtained from : $\Delta G^\circ = -5.7 \log K$

first obtain $\log K = -(-4.1) / 5.7 = +0.71$

$$K = 10^{0.71} = 5.2 \text{ M}^{-2}$$

let x = solubility then $K = x^2$ and $x = 2.3 \text{ M}$.

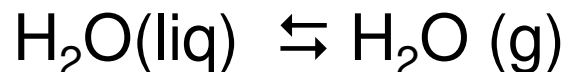
solubility is a trade off between two big numbers

Data mining in Appendix D-2.

$$RT = 2.48 \text{ kJ/mol}$$

1. vapor pressure of water at 25 °C

$$2.303 RT = 5.71 \text{ kJ/mol}$$



$$\Delta G^\circ = -RT \ln(P_{\text{H}_2\text{O}}) = -228.6 - (-237.1) = +8.5 \text{ kJ/mol}$$

$$P = e^{-8500/8.3144(298)} = 0.032 \text{ atm} \quad \text{or} \times 760 \text{ torr/atm} = 24.5 \text{ torr}$$

2. Vapor pressure at 50 °C. assume H & S independent of T.

$$\Delta H^\circ_{\text{VAP}} = \Delta H^\circ_f(\text{gas}) - \Delta H^\circ_f(\text{liq})$$

$$= -241.8 - (-285.8) = +44.0 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{VAP}} = S^\circ(\text{gas}) - S^\circ(\text{liq}) = 188.8 - 69.91 = 119 \text{ J/mol K}$$

$$\Delta G^\circ_{\text{VAP}} = \Delta H^\circ_{\text{VAP}} - T\Delta S^\circ_{\text{VAP}}$$

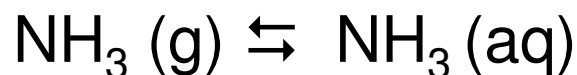
$$= 44.0 - 323(0.119) = +5.56 \text{ kJ/mol}$$

$$P = e^{-5560/\{8.3144(323)\}} = 0.126 \text{ atm} \quad \text{or} \times 760 = 96 \text{ torr}$$

For approx Bp of water, At Bp $\Delta G_{\text{VAP}} = 0$, $T = \Delta H / \Delta S = 44000/119 = 369 \text{ K}$

The real BP is 373. (assuming H & S indep of T isn't too bad)

3. Solubility of ammonia in water at 1 atm



$$\Delta G^\circ = \Delta G^\circ_f (\text{NH}_3 (\text{aq})) - \Delta G^\circ_f (\text{NH}_3 (\text{g}))$$

$$\Delta G^\circ = -RT \ln [\text{NH}_3] = -26.5 - (-16.45) = -10.05$$

$$[\text{NH}_3] = e^{+10.05/RT} = 57 \text{ M}$$

4. K_b for NH_3 $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

$$\Delta G^\circ = \Delta G^\circ_f \{ \text{NH}_4^+ + \text{OH}^- - \text{NH}_3 - \text{H}_2\text{O} \} (\text{aq})$$

$$\Delta G^\circ = -RT \ln K = -79.31 + (-157.20 - (-26.5) - (-237.1))$$

$$\text{p}K_b = -\log K_b = \Delta G^\circ / 2.303RT = 27.09 / 5.7 = 4.74$$

Note. ΔG°_f for water must be included !

5. K_{sp} of AgI $\text{AgI} (\text{s}) \rightleftharpoons \text{Ag}^+ (\text{aq}) + \text{I}^- (\text{aq})$

$$\Delta G^\circ = \Delta G^\circ_f \{ \text{Ag}^+_{(\text{aq})} + \text{I}^-_{(\text{aq})} - \text{AgI}_{(\text{s})} \}$$

$$\log (K_{sp}) = \{ (77.11) + (-51.57) - (-66.19) \} / 5.7$$

$$\log (K_{sp}) = -16 \qquad K_{sp} = 10^{-16}$$

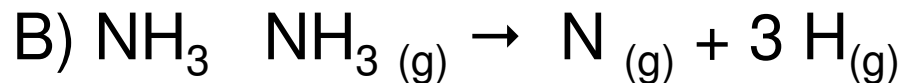
6. Bond Energy

The bond energy is defined as the energy required to break a bond (or the energy released in forming one). This means dissociation into atoms.

Gas phase data must be used. (Why?)



$$\Delta H^\circ = 2 \Delta H^\circ_f (\text{H}) - \Delta H^\circ_f (\text{H}_2) = 2 (218) - 0 = 436 \text{ kJ/mol}$$



$$\Delta H^\circ = 3 \Delta H^\circ_f (\text{H}) + \Delta H^\circ_f (\text{N}) - \Delta H^\circ_f (\text{NH}_3)$$

$$= 3 (218) + 472 - (-46) = 1172 \text{ kJ/mol for 3 N-H bonds}$$

ONE N-H bond energy would be $1172 / 3 = 390 \text{ kJ/mol}$

C) Obtain the C-Cl bond in CCl_4 and C-H bond in methane.

answers should be close to average values in Table 11.3

7. Redox potentials $\Delta G = - n E F$

G is an extensive quantity in kJ/mol

E is an intensive quantity in Volts

Compare Temperature T and Heat Q

1 ml of 50° water vs. 1000 ml of 50° water

ΔG°_f for ions. Taking SHE as a reference, we assign ΔG°_f for $H^+_{(aq)} = 0$

Then for $Zn (s) + 2H^+ \rightarrow Zn^{2+} + H_2$ 1 Coul Volt = Joule

$$\Delta G^\circ = - n E^\circ F = 2 (+ 0.76 V) 94,485 C/mol = 146 kJ/mol$$

$$= G^\circ_f H_2 + G^\circ_f Zn^{2+} - 2 G^\circ_f H^+ - G^\circ_f Zn (s)$$

$$0 + G^\circ_f Zn^{2+} - 0 - 0 = 146 kJ/mol \text{ (see App D)}$$

K_{eq} as Function of Temperature

From the expression:

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

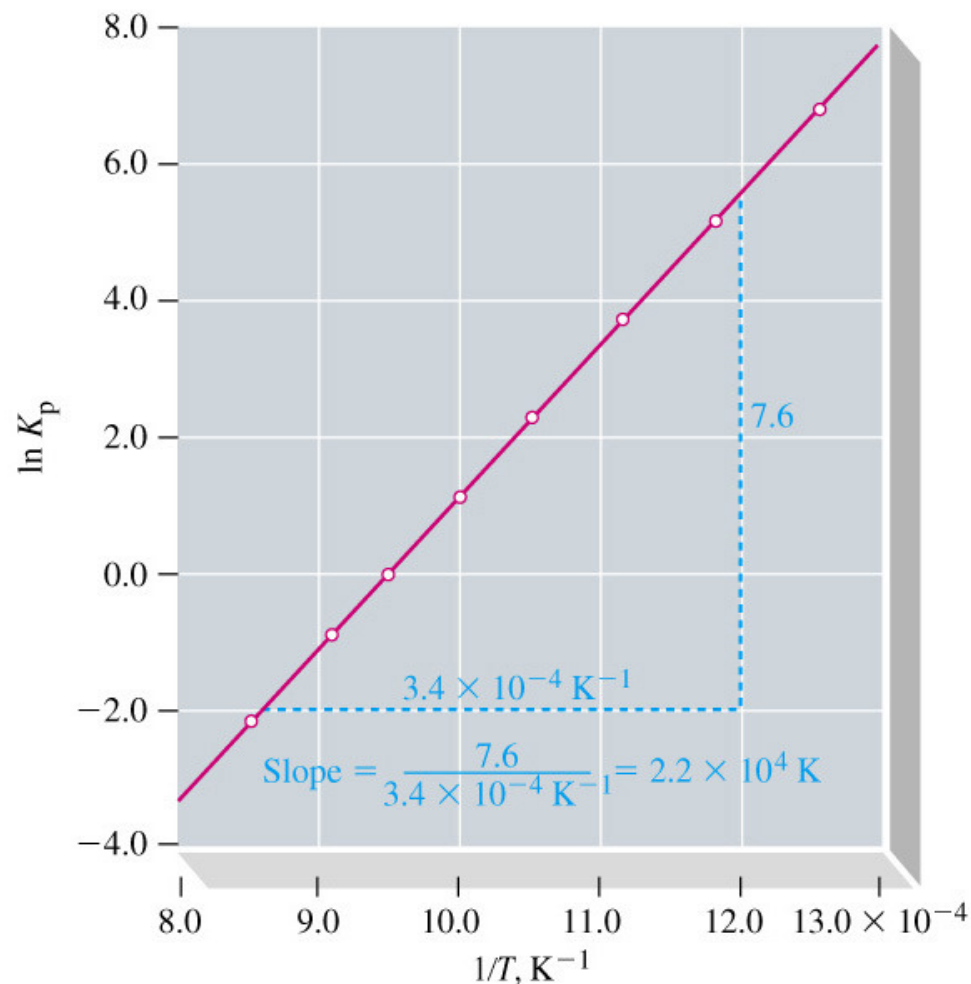
we can obtain the dependence of K_{eq} on T :

$$\ln K_{eq} = -(\Delta H^\circ - T\Delta S^\circ)/RT = -\Delta H^\circ/RT + \Delta S^\circ/R$$

Note: A linear plot of $\ln K_{eq}$ vs. $1/T$ provides ΔH° and ΔS° :

$$\begin{aligned}\Delta H^\circ &= -\text{slope} \times R \\ &= -182.9 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \text{intercept} \times R = -175 \text{ eu} \\ 1 &= 2.2(10) + \text{int} \quad \text{so int} = -21\end{aligned}$$



Dependence of K_p on $1/T$ for:
 $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{SO}_3(\text{g})$

$$\ln K_{\text{eq}} = - \Delta H^{\circ}/RT + \Delta S^{\circ}/R = - \Delta G^{\circ}/RT$$

For two different temperatures T_1 and T_2

$$\ln K_1 = - \Delta H^{\circ}/RT_1 + \Delta S^{\circ}/R$$

$$\ln K_2 = - \Delta H^{\circ}/RT_2 + \Delta S^{\circ}/R$$

Subtracting the first equation from the second adjusting for units (R in J and H in kJ) we obtain the van't Hoff Equation:

$$\ln (K_2/K_1) = +\Delta H^{\circ}/R \{1000/T_1 - 1000/T_2\}$$

The Clausius-Clapyron equation applies the formula to vapor pressure vs T. Simply replace the K's with vapor pressures and ΔH° with $\Delta H^{\circ}_{\text{VAPORIZATION}}$.

This equation is similar to the one used to describe the temperature dependence of rate constants: $\ln (k_2/k_1) = Ea/R \{1/T_1 - 1/T_2\}$

5. Uranium chemistry

	H	G	S
U (S)	0	0	50.21
UF ₆ (g)	-2147	-2064	377.9
UF ₆ (s)	-2197	-2069	227.6
UO ₂ (s)	-1085	-1032	77.03

Is elemental U a solid, liquid, or gas at 298 K ?

Can UF₆ be made from U + F₂ ?

Will U burn in O₂ to form UO₂ ?

Is UF₆ a solid or gas ?

Obtain the heat of sublimation and vapor pressure of UF₆

Assuming Trouton's rule what would S° for UF₆ (liq) be?

Trouton's rule $\Delta S^\circ_{\text{vap}} = 87 \text{ Jmol}^{-1}\text{K}^{-1}$ at the boiling point

(a similar increase in disorder occurs for many liquids on vaporization)