# Absolute Entropies

## Entropy of Mixing

## Appendix A: \( \Delta H_f, \Delta G_f \), BUT S° (no \( \Delta \), no “sub f”)

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_f ) (kJ mol(^{-1} ))</th>
<th>( \Delta G_f ) (kJ mol(^{-1} ))</th>
<th>( S^\circ ) (J mol(^{-1} ) K(^{-1} ))</th>
<th>( C_P ) (J mol(^{-1} ) K(^{-1} ))</th>
<th>Atomic or Molecular Weight (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite()</td>
<td>0</td>
<td>0</td>
<td>5.74</td>
<td>8.52</td>
<td>12.011</td>
</tr>
<tr>
<td>Diamond()</td>
<td>1.89</td>
<td>2.90</td>
<td>2.38</td>
<td>6.12</td>
<td>12.011</td>
</tr>
<tr>
<td>C(_4)(g)</td>
<td>716.7</td>
<td>671.2</td>
<td>158.1</td>
<td>20.8</td>
<td>12.011</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>-110.5</td>
<td>-137.2</td>
<td>197.7</td>
<td>29.1</td>
<td>28.011</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)(g)</td>
<td>0</td>
<td>0</td>
<td>130.7</td>
<td>28.8</td>
<td>2.016</td>
</tr>
<tr>
<td>H(_2)O(g)</td>
<td>-241.8</td>
<td>-228.6</td>
<td>188.8</td>
<td>33.6</td>
<td>18.015</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>-283.8</td>
<td>-237.1</td>
<td>70.0</td>
<td>75.3</td>
<td>18.015</td>
</tr>
<tr>
<td>H(_2)O(s)</td>
<td>-126.3</td>
<td>-155.6</td>
<td>48.0</td>
<td>36.2 (273 K)</td>
<td>18.015</td>
</tr>
<tr>
<td>H(<em>3)O(</em>+)(aq)</td>
<td>-126.3</td>
<td>-155.6</td>
<td>48.0</td>
<td>36.2 (273 K)</td>
<td>18.015</td>
</tr>
<tr>
<td>OH(^-)(aq)</td>
<td>-230.0</td>
<td>-157.24</td>
<td>-10.9</td>
<td>17.01</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(_2)(g)</td>
<td>0</td>
<td>0</td>
<td>255.2</td>
<td>29.4</td>
<td>31.999</td>
</tr>
<tr>
<td>O(_2) (g)</td>
<td>249.2</td>
<td>231.7</td>
<td>163.1</td>
<td>21.9</td>
<td>15.999</td>
</tr>
<tr>
<td>O(_2) (g)</td>
<td>142.7</td>
<td>163.2</td>
<td>238.9</td>
<td>39.2</td>
<td>47.998</td>
</tr>
<tr>
<td>OH(^-)(aq)</td>
<td>39.0</td>
<td>34.22</td>
<td>183.7</td>
<td>29.9</td>
<td>17.01</td>
</tr>
<tr>
<td>OH(^-)(aq)</td>
<td>-230.0</td>
<td>-157.2</td>
<td>-10.9</td>
<td>17.01</td>
<td></td>
</tr>
</tbody>
</table>
**Third Law of Thermodynamics**

The entropy of any perfect crystalline substance approaches 0 as \( T \rightarrow 0K \)

\[ S = k \ln W \]

for perfectly ordered crystalline substance \( W \rightarrow 1 \) as \( T \rightarrow 0K \) \( \Rightarrow S \rightarrow 0 \)

---

\[ S^\text{298,15} = \Delta S_\text{II}+\Delta S_\text{III}+\Delta S_\text{IV}+\Delta S_\text{V}+\Delta S_\text{E} \]

\[ \Delta S_\text{I} = \int \frac{(\mathcal{C}_p)_\text{I}}{T} dT \]

\[ \Delta S_\text{II} = \int \frac{(\mathcal{C}_p)_\text{II}}{T} dT \]

\[ \Delta S_\text{III} = \int \frac{(\mathcal{C}_p)_\text{III}}{T} dT \]

\[ \Delta S_\text{IV} = \int \frac{(\mathcal{C}_p)_\text{IV}}{T} dT \]

\[ \Delta S_\text{V} = \int \frac{(\mathcal{C}_p)_\text{V}}{T} dT \]

\[ \Delta S_\text{E} = \int \frac{(\mathcal{C}_p)_\text{E}}{T} dT \]
full calculation of $S^o_{298}$ for O$_2$ (g) (Example Problem 5.9, E&R pp103-104 [96-97]w)

<table>
<thead>
<tr>
<th>$\Delta S$</th>
<th>$J K^{-1} mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S(0 K)$</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta S_{I}(0 \rightarrow 23.66)$</td>
<td>8.182</td>
</tr>
<tr>
<td>$\Delta S_{II}(III \rightarrow II$ at 23.66K)</td>
<td>3.964</td>
</tr>
<tr>
<td>$\Delta S_{III} (23.66 \rightarrow 43.76)$</td>
<td>19.61</td>
</tr>
<tr>
<td>$\Delta S_{I}(II \rightarrow I$ at 43.76K)</td>
<td>16.98</td>
</tr>
<tr>
<td>$\Delta S_{I}(43.76 \rightarrow 54.39)$</td>
<td>10.13</td>
</tr>
<tr>
<td>$\Delta S_{I}(I \rightarrow g$ at 54.39K)</td>
<td>8.181</td>
</tr>
<tr>
<td>$\Delta S_{I}(54.39 \rightarrow 90.20)$</td>
<td>27.06</td>
</tr>
<tr>
<td>$\Delta S_{I}(90.20 \rightarrow 298.15)$</td>
<td>35.27</td>
</tr>
<tr>
<td>total $\Delta S$</td>
<td>204.9 $J K^{-1} mol^{-1}$</td>
</tr>
</tbody>
</table>

$\Delta S_{reaction}$ from absolute entropies

$n_A A + n_B B \rightarrow n_C C + n_D D$ at 298K

$\Delta S_{reaction} = n_C \left( \overline{S}^0_{298} \right)_C + n_D \left( \overline{S}^0_{298} \right)_D - n_A \left( \overline{S}^0_{298} \right)_A - n_B \left( \overline{S}^0_{298} \right)_B$

$\Delta S_{reaction}^{(298K)} = \sum_i v_i \left( \overline{S}^0_{298} \right)_i$

$\left( \overline{S}^0_{298} \right)_i$ are 3rd Law entropies (e.g. Appendix A)
Chemistry 163B Winter 2012
Handouts for Third Law and Entropy of Mixing
(ideal gas, distinguishable molecules)

qualitative factors affecting molecular entropy

• Higher T ⇒ \(\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_v}{T} > 0\)

• Higher P ⇒ usually \(\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0\)

• Phase S(g) vs S(l) vs S(s)
  (in a reaction the side with the greater number of moles of gas generally has higher S)

• Mixing or dissolving of components (l+l), (s+s), (l+s), (g+g) solutions ⇒
  • (g + l) or (g + s) solution ⇒

more qualitative factors affecting molecular entropy

• substances with higher mass have
  \(F_2(g) < Cl_2(g) < Br_2(g) < I_2(g)\)
  \(S^\circ_{298} 202.78 \quad 223.07 \quad 245.46 \quad 260.69 \quad \text{J K}^{-1}\text{mol}^{-1}\)
  (more closely spaced rotational and vibrational levels)

• more rigid substances have
  \(C(\text{gr}) < C(\text{dia})\)
  \(S^\circ_{298} 5.74 \quad 2.377 \quad \text{J K}^{-1}\text{mol}^{-1}\)

• more complex substances have
  \(HF(g) < H_2O(g) < D_2O(g)\)
  \(MW 20 \quad 18 \quad 20 \quad \text{amu}\)
  \(S^\circ_{298} 173.78 \quad 188.83 \quad 198.34 \quad \text{J K}^{-1}\text{mol}^{-1}\)
calculating entropy (see summary on review handout)

- Thermal properties of entropy and entropy calculations
  - \( \frac{dS}{T} \) = \( \frac{dQ}{T} \) \( \text{for reversible process} \)
  - \( \Delta S \geq \int_{T_i}^{T_f} \frac{dQ}{T} \) \( \text{for spontaneous [\textit{real}] process} \)
  - \( \Delta S_{\text{process}} = \Delta S_{\text{ reversible}} + \Delta S_{\text{irreversible}} \geq 0 \)
  - \( S \) is a state function; \( dS \) is an exact differential
  - Dependence of \( S \) on \( T \)
  - \( T \left( \frac{dS}{dT} \right)_P = \frac{C_v}{T} \)
  - \( P \left( \frac{dS}{dT} \right)_V = \frac{C_p}{T} \)
  - \( V \left( \frac{dS}{dT} \right)_P = \frac{C_v}{T} \)
  - Phase: \( \Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} \)
  - Calculation of entropy changes for changes in \( P, V, T, \) phase
  - Third Law and calculations using Third Law Entropies \( S(T) \)
  - \( \Delta S_{\text{process}}(T) = \int_{T_i}^{T_f} \frac{dQ}{T} \)
  - Entropy of mixing \( \Delta S = -k_B \sum_{i} n_i \ln X_i \) where \( X_i = \frac{n_i}{n_{\text{total}}} \)

HW#5 Prob 31

31.

a. Prove, in general (but \( T \to 0 \)), the relationship in equation 3.19 E&R

\[
\left( \frac{dU}{dV} \right)_{T} = T \left( \frac{dP}{dV} \right)_{T} - P
\]

b. Evaluate \( \left( \frac{dU}{dV} \right)_{T} \) for an ideal gas.

c. Evaluate \( \left( \frac{dU}{dV} \right)_{T} \) for a Van der Waals gas

\[
\left( P + \frac{n^2 a}{V^2} \right) \left( \frac{V - b}{V - b - n} \right) = nRT
\]

d. Interpret your (correct!) results for parts (b) and (c).

e. Prove, in general (but \( T \to 0 \)), the relationship in equation 3.44 E&R:

\[
\left( \frac{dH}{dV} \right)_{P} = P + T \left( \frac{dP}{dV} \right)_{T}
\]

Sample midterm 3a

analogous to 31a
the relationships

<table>
<thead>
<tr>
<th>definitions:</th>
<th>differentials of state functions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U \equiv$ internal energy</td>
<td>$dU = TdS - PdV$</td>
</tr>
<tr>
<td>$H \equiv U + PV$</td>
<td>$dH = TdS + VdP$</td>
</tr>
<tr>
<td>$A \equiv U - TS$</td>
<td>$dA = -SdT - PdV$</td>
</tr>
<tr>
<td>$G \equiv H - TS$</td>
<td>$dG = -SdT + VdP$</td>
</tr>
</tbody>
</table>

heat and temperature:

\[
\begin{align*}
\delta q_v &= n \bar{C}_v \, dT \\
\delta q_p &= n \bar{C}_p \, dT \\
dU &= \delta q + \delta w = \delta q - PdV \\
dS &= \frac{\delta q}{T} \\
dq &= Tds \\
\left( \frac{\partial S}{\partial T} \right)_v &= \frac{n \bar{C}_v}{T} \\
\left( \frac{\partial S}{\partial T} \right)_p &= \frac{n \bar{C}_p}{T} 
\end{align*}
\]

do some examples:

**HW#5 Prob 31a:**
derive E&R equation 3.19 ‘LATER is NOW’

\[
\left( \frac{\partial U}{\partial V} \right)_T = ???
\]

in terms of $P$, $V$, $T$ and their derivatives

technique applies to HW#6 Prob: 31e
do another example:

One mole of CO\textsubscript{2}(g) is expanded isothermally and reversibly from \( V_1 \) to \( V_2 \). Using the van der Waals equation of state

\[
\left( P + \frac{a}{V^2} \right)(V - b) = RT
\]

to describe CO\textsubscript{2}(g) calculate \( w \), \( \Delta U \), \( q \), and \( \Delta S \) in terms of \( V_1 \) and \( V_2 \) and the van der Waals constants \( a \) and \( b \).

Entropy of Mixing of Ideal Gasses

(EXTRA)

\( E&R \approx \text{Sec 6.6} \)
Entropy of mixing for ideal gas (distinguishable particles)

- isolated from surroundings
  \[ q_{\text{sys}} = q_{\text{surr}} = 0 \]
  \[ w = 0 \]

- \( \Delta S_{\text{surr}} = 0 \)

- \( \Delta S_{\text{universe}} > 0 \)

- \( \Delta S_{\text{sys}} > 0 = ??? \)

Reversible isothermal expansion to total volume

\[ \Delta S = n_R \ln \frac{V_{\text{final}}}{V_{\text{initial}}} \]

\[ \Delta S = n_a R \ln \frac{V_a + V_b}{V_a} \]

\[ \Delta S = n_b R \ln \frac{V_a + V_b}{V_b} \]
Handouts for Third Law and Entropy of Mixing
(ideal gas, distinguishable molecules)

**reversible recombining of volumes**

- \( n_a \) permeable to b
- not permeable to a

\[
\begin{align*}
T = \frac{n_a V_a + n_b V_b}{T} \\
T = \frac{n_b V_a + n_b V_b}{T}
\end{align*}
\]

- T const
- \( \Delta U = 0 \)
- \( P_{\text{ext}} = 0 \Rightarrow w = 0 \)
- \( q_{\text{rev}} = 0 \)
- \( \Delta S = 0 \)

**some arithmetic**

Note 'flip' leads to \(-\ln\)

\[
\Delta S_{\text{ideal}} = n_i R \ln \frac{V_i + V_2}{V_i}
\]

(only isothermal expansion steps contribute)

Partial pressure: \( P_i = \frac{n_i}{n_{\text{tot}}} P_{\text{tot}} \)

Mole fraction: \( X_i = \frac{n_i}{n_{\text{tot}}} \)

Ideal gas: at start \( PV = n_i RT \); at end \( PV = n_i \) RT

\[
\begin{align*}
\Delta S &= \frac{-n_i R \ln X_i - n_j R \ln X_j}{n_{\text{tot}}}
\end{align*}
\]

And per mole

\[
\Delta S = \sum_i X_i \ln X_i
\]

\[
\Delta S_{\text{mixing}} = -R \sum_i X_i \ln X_i
\]

\[
\Delta S_{\text{mixing}} = -n_{\text{tot}} R \sum_i X_i \ln X_i
\]
handouts for third law and entropy of mixing
(ideal gas, distinguishable molecules)

calculating entropy (see summary on review handout)

- Thermal properties of entropy and entropy calculations:
  - $\delta S = \frac{\delta q_{rev}}{T}$; \(\Delta S = \int \frac{\delta q_{rev}}{T} = 0\)
  - $\Delta S \geq \frac{1}{T} \left( \frac{\delta q}{T} - q_{rev} \right)$ \((-\text{for reversible process;} > \text{for spontaneous ["real"] process})$
  - $\Delta S_{\text{final}} - \Delta S_{\text{initial}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$
  - S is a state function; $\delta S$ is an exact differential
  - Dependence of $S$ on:
    - T: $\left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}$
    - p: $\left( \frac{\partial S}{\partial p} \right)_T = -\frac{\partial p}{\partial T}$
    - V: $\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V$
    - Phase: $\Delta S = \Delta S^{\text{equilibrium phase change}}$
  - Calculation of entropy changes for changes in P, V, T, phase
  - Third Law and calculations using Third Law Entropies: $S^0(T)$
  - $\Delta S^{\text{mix}}(T) = \sum_i n_i S^0_i(T)$
  - Entropy of mixing $\Delta S = -n_{\text{total}} R \sum_i X_i \ln X_i$, where $X_i = \frac{n_i}{n_{\text{total}}}$

What formulas I have to memorize for midterm and final?

[Handout on formulas for midterm and final]
Gibb’s Paradox: distinguishable vs identical (don’t fret)

\[ \Delta S_{\text{total}} = n_a R \ln \frac{V_a}{V_a} + n_b R \ln \frac{V_b}{V_b} \]

CORRECT

\[ \Delta S_{\text{total}} = 2n_a R \ln 2 \]

CORRECT TOO

Some references:

- www.mdpi.org/lin/entropy/Chua-Thermodynamics.ppt
where we have been

and

what’s next

observations: thermo \equiv heat

• Count Rumford, 1799
• observed water turning into steam when canon barrel was bored
• work \Leftrightarrow heat
observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines

guiding principles

- Conservation of heat and work (Joule, 1845)
  
  **1st LAW OF THERMODYNAMICS**

- Clausius, 1860 Entropy
  
  **2nd LAW OF THERMODYNAMICS**

- Boltzmann, late 19th century,
  molecular picture of entropy

the thermodynamic functions U, H, and S

*(1st and 2nd laws)*
“Applications”

How does knowledge about efficiencies of steam engines, mechanical systems, etc, relate to processes in chemical, biological, and geological systems?

ANSWERED BY:

J. W. Gibbs- arguably the first great American scientist who combined the concepts of heat and entropy and proposed “Gibbs Free Energy”, $G$, a thermodynamic state function that leads to a whole spectrum of applications.

End of Lecture
In 1872, long before women were admitted to Austrian universities, he met Henriette von Aigenflor, an aspiring teacher of mathematics and physics in Graz. She was refused permission to audit lectures unofficially. Boltzmann advised her to appeal, which she did, successfully.

In Vienna, Boltzmann not only taught physics but also lectured on philosophy. Boltzmann’s lectures on statistical philosophy were very popular and received considerable attention at that time. His first lecture was an enormous success. Even though the largest lecture hall had been chosen for it, the people stood all the way down the staircase. Because of the great successes of Boltzmann’s philosophical lectures, the Emperor invited him for a reception at the Palace.

On September 5, 1906, while on a summer vacation in Durno, near Trieste, Boltzmann hung himself during an attack of depression. He is buried in the Viennese Zentralfriedhof. His tombstone bears the inscription:

$S = k \cdot \log W$

To quote Planck, “The logarithmic connection between entropy and probability was first stated by L. Boltzmann in his kinetic theory of gases.” This famous formula for entropy $S$ is

$$S = k \log_{10} W$$

where $k = 1.3806505(24) \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann’s constant, and the logarithm is taken to the natural base $e$. $W$ is the number of occurrences of a macrostate, or, more precisely, the number of possible microstates corresponding to the macroscopic state of a system — number of