

# Entropy and other thermodynamic function, Third Law

Slides taken from Internet:  
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## MANIPULATING DIFFERENTIALS

$$\begin{array}{ccc}
 \text{1st Law} & + & \text{2nd Law} \\
 \downarrow & & \downarrow \\
 \boxed{dU = \delta w_{rev} + \delta q_{rev}}, & \longrightarrow & \boxed{dU = TdS - PdV} \\
 \uparrow & & \uparrow \\
 -PdV & & \delta q_{rev} = TdS
 \end{array}$$

Now, consider the total differential of  $U$  with respect to  $T$  and  $V$

$$C_V(T) \longrightarrow dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

We can equate these two expressions for  $dU$  and solve for  $dS$

## SOLUTION FOR $dS$

$$TdS - PdV = C_V(T)dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Which rearranges to:

$$dS = \frac{C_V(T)}{T} dT + \frac{1}{T} \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV$$

*= 0 for  
ideal gas*

Considering the total differential of  $S$  with respect to  $T$  and  $V$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

We have,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V(T)}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

## THE DIFFERENTIAL OF ENTHALPY

$$\begin{aligned}dH &= d(U + PV) & dU &= TdS - PdV \\&= dU + VdP + PdV \\&= TdS - PdV + VdP + PdV = TdS + VdP\end{aligned}$$

Now, consider the total differential of  $H$  with respect to  $T$  and  $P$

$$C_P(T) \longrightarrow dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

We can equate these two expressions for  $dH$  and solve for  $dS$

## SOLUTION FOR $dS$

$$TdS + VdP = C_P(T)dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Which rearranges to:

$$dS = \frac{C_P(T)}{T} dT + \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T - V \right] dP$$

*= 0 for  
ideal gas*

Considering the total differential of  $S$  with respect to  $T$  and  $P$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

We have,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P(T)}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

## ABSOLUTE ENTROPY VALUES

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P(T)}{T} \quad \begin{array}{l} \text{integrate with respect to } T \text{ at constant } P \text{ to} \\ \text{determine entropy change with temperature} \\ \text{change} \end{array}$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T) dT}{T}$$

Let  $T_1 = 0 \text{ K}$

$$S(T_2) = S(0) + \int_0^{T_2} \frac{C_P(T) dT}{T}$$

Thus, we can calculate the entropy of a substance at *any temperature*  $T_2$  if we know the entropy at 0 K and the constant pressure heat capacity

## WHAT ABOUT 0 K?



Walther Nernst 1864-1941  
Nobel Prize in Chemistry in 1920

Nernst suggested that the change in entropy for chemical reactions approached 0 as the absolute temperature approached 0

$$\Delta_r S \rightarrow 0 \text{ as } T \rightarrow 0$$



I think that the entropy of a pure substance approaches 0 at 0 K!

Max Planck, again

**The Third Law:** Every substance has a finite positive entropy, but at zero Kelvin the entropy may become 0, and it does so in the case of a perfectly crystalline substance.

## Standard Entropy



## THIRD-LAW ENTROPY VALUES

$$S(T) = \int_0^T \frac{C_P(T')dT'}{T'}$$

Valid in so far as the third law stipulates that  $S(0) = 0$

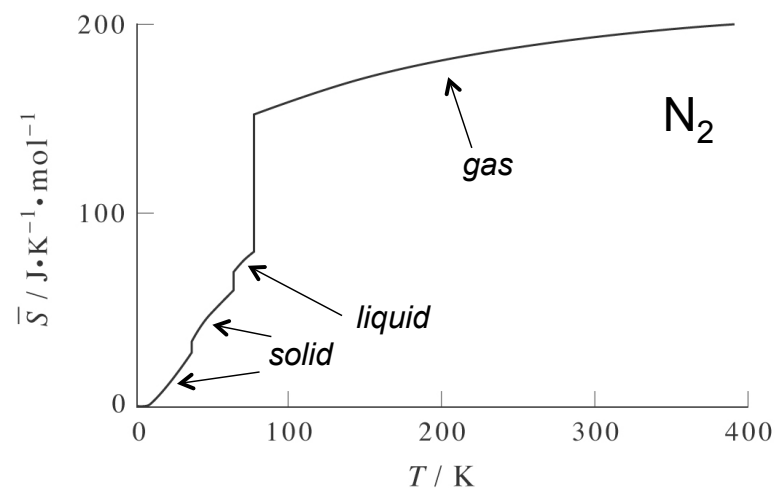
For this to be true, there must be no phase transition between 0 and  $T$ . For phase transitions (e.g., melting):

$$\Delta_{trs}S = \frac{q_{rev}}{T_{trs}} \quad \text{For a phase transition that takes place at fixed } P \quad \Rightarrow \quad \Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

$$S(T) = \int_0^{T_{fus}} \frac{C_P^s(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P^l(T)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^T \frac{C_P^g(T')dT'}{T'}$$

## CALORIMETRIC ENTROPY DETERMINATION

Process	$S, \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0.00 – 10.00 K	2.05
10.00 – 35.61 K	25.79
solid-solid phase transition	6.43
35.61 – 63.15 K	23.41
solid-liquid phase transition	11.20
63.15 – 77.36 K	11.46
liquid-gas phase transition	72.00
77.36 – 298.15 K	39.25
non-ideality	0.02
Total:	191.61



Values of entropies for gases given in the literature are *standard entropies*. These are by convention corrected for the non-ideality of real gases at 1 bar.

## 298 K STANDARD MOLAR ENTROPIES

*units of  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$*

### Solids

Carbon (diamond)	2.4	} <i>The stiffer lattice of diamond compared to graphite leads to lower entropy</i>
Carbon (graphite)	5.7	
Sodium	51.3	} <i>Insulators have substantially lower entropies than conductors as the latter have many states accessible to conduction electrons</i>
Potassium	64.7	
Silver	42.6	

## 298 K STANDARD MOLAR ENTROPIES

*units of  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$*

### Liquids vs Gases

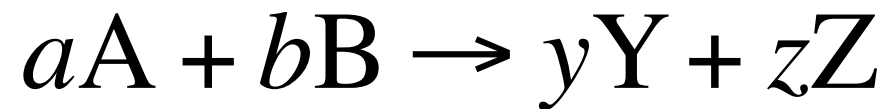
	<u>Liquid</u>	<u>Gas</u>
Water	70.0	188.8
Bromine	152.2	245.5

*The condensed nature of the liquid reduces entropy compared to the gas; the greater mass of  $\text{Br}_2$  compared to  $\text{H}_2\text{O}$  leads to greater entropy but in the gas phase this is somewhat balanced by an additional rotational degree of freedom for the non-linear water molecules.*

Entropy is additive

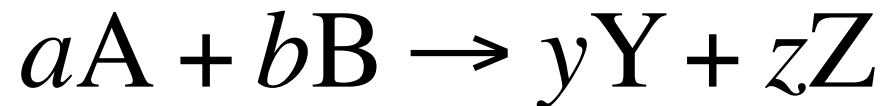
## ENTROPY IS ADDITIVE FOR REACTIONS

Just as was true for enthalpy, one may define the entropy of reaction to be

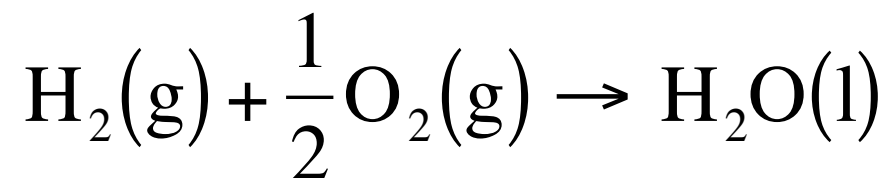


$$\Delta_r S^\circ = yS^\circ[Y] + zS^\circ[Z] - aS^\circ[A] - bS^\circ[B]$$

## HYDROGEN COMBUSTION EXAMPLE



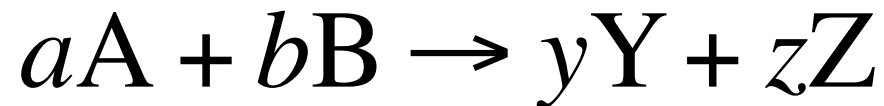
$$\Delta_r S^\circ = yS^\circ[Y] + zS^\circ[Z] - aS^\circ[A] - bS^\circ[B]$$



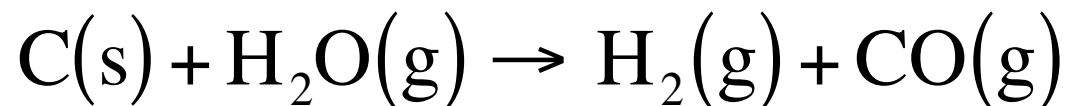
$$\Delta_r S^\circ = 70.0 - 130.7 - \frac{1}{2} \cdot 205.2 = -163.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

*very negative because the reaction converts 1.5 moles of “very disordered” gas into 1 mole of “less disordered” liquid*

## WATER SHIFT REACTION EXAMPLE



$$\Delta_r S^\circ = yS^\circ[Y] + zS^\circ[Z] - aS^\circ[A] - bS^\circ[B]$$



$$\Delta_r S^\circ = 130.7 + 197.7 - 5.7 - 188.8 = 133.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

*very positive because the reaction converts 1 mole of “very ordered” solid into 1 mole of “very disordered” gas*



## Review: L13-L14

1. Entropy variation with temperature may be determined as  $\left(\frac{\partial S}{\partial T}\right)_X = \frac{C_X(T)}{T}$  X = V, P

2. As integrating heat capacity determine enthalpy, integration of heat capacity divided by temperature can determine entropy

3. Third Law states that at non-zero temperatures, all substances have positive entropies, while at 0 K the entropy of a perfect crystal is equal to zero.

4. Entropy at a given temperature  $T$  can be computed as

$$S(T) = \int_0^{T_{fus}} \frac{C_P^S(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P^l(T)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^T \frac{C_P^g(T')dT'}{T'}$$

## Review: L13-L14

- 5. As for enthalpy (or any other state function), entropies of reaction are additive
- 6. Entropies of gases are much, much greater than those of their corresponding condensed phases



Next: Properties of pure substances & Steam table