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Feb 12

Self 6

(a) $q_{rev} = 10 \text{ kJ}$
 $T = 0^\circ\text{C} = 273 \text{ K}$

$n = 100 \text{ J/K} \cdot \text{mol} = 5.56 \text{ mol}$

$$\Delta S = \frac{q}{T} = \frac{10,000 \text{ J}}{273 \text{ K}}$$

$$= +36.6 \text{ J/K}$$

$$\Delta S_m = \frac{36.6 \text{ J/K}}{5.56 \text{ mol}}$$

$$= +6.6 \text{ J/mol-K}$$

(b) $T = 100^\circ\text{C} = 373 \text{ K}$

$$\Delta S = \frac{10,000}{373 \text{ K}} = +26.8 \text{ J/K}$$

$$\Delta S_m = 4.8 \text{ J/mol-K}$$

(c) $T = 100^\circ\text{C} = 373 \text{ K}$
 $q = -10 \text{ kJ}$
 $q = -10,000 \text{ J}$

$$\Delta S = -26.8 \text{ J/K}$$

$$\Delta S_m = -4.8 \text{ J/mol-K}$$

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Entropy Example - Slide 8

$$n = \frac{150}{44} = 3.41$$

Example: Calculate ΔS when 150 g of $\text{CO}_2(\text{g})$, initially at $P = 100 \text{ kPa}$ and $T = 25^\circ \text{C}$, is compressed to $P = 500 \text{ kPa}$ at $T = 25^\circ \text{C}$.

$M = 44 \text{ g/mol}$

$$V_1 = \frac{nRT}{P_1} = \frac{3.41 \times 8.31 \times 298}{100 \text{ kPa}} = 84.5 \text{ L} \quad V_2 = \frac{3.41 \times 8.31}{500} = 16.9 \text{ L}$$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = 3.41 \text{ mol} \left(8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \ln\left(\frac{16.9}{84.5}\right) = -145.6 \text{ J/K}$$

$$P_2 V_2 = P_1 V_1$$
$$\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{100}{500} = 0.20$$

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Example: Entropy on Heating
Slide #12

Example: Calculate ΔS when 80 g of $O_2(g)$, initially at $P = 100 \text{ kPa}$ and $V = 60 \text{ L}$, is heated at constant P until $V = 100 \text{ L}$.

$M = 32 \text{ g/mol}$
 $C_{P,m} = 29.4 \text{ J/mol-K}$

$$n = \frac{80}{32} = 2.5 \text{ mol}$$

$$T_1 = \frac{P_1 V_1}{nR} = \frac{100 (60)}{8.31 (2.5)} = 289 \text{ K}$$

$$T_2 = \frac{P_2 V_2}{nR} = 481 \text{ K}$$

$$\begin{aligned} \Delta S &= n C_{P,m} \ln\left(\frac{T_2}{T_1}\right) \\ &= 2.5 \text{ mol} (29.4 \text{ J/mol-K}) \ln\left(\frac{481 \text{ K}}{289 \text{ K}}\right) \\ &= 637 \text{ J/K} \end{aligned}$$

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Example: Entropy Change on Heating
Slide #15

Example: (a) Calculate $\Delta_{\text{fus}} S$ and $\Delta_{\text{vap}} S$ for benzene, C_6H_6 .

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{279K}$$

$$= \frac{9.87 \times 10^3 \text{ J/mol}}{279K} = 35.4 \text{ J/mol}\cdot\text{K}$$

$M = 78 \text{ g/mol}$
 $279K \Rightarrow T_m = 6^\circ\text{C}$
 $353K \Rightarrow T_b = 80^\circ\text{C}$
 $\Delta_{\text{fus}} H = 9.87 \text{ kJ/mol}$
 $\Delta_{\text{vap}} H = 30.8$

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{353K} = \frac{30.8 \times 10^3 \text{ J/mol}}{353K} = 87.3 \text{ J/mol}\cdot\text{K}$$

(b) Calculate ΔS for the crystallization of 250 g of benzene.

$$n = \frac{250g}{78 \text{ g/mol}} = 3.21 \text{ mol}$$

$$\Delta_{\text{cry}} H = -\Delta_{\text{fus}} H = -9.87 \text{ kJ/mol}$$

$$\Delta_{\text{cry}} S = \frac{-9.87 \times 10^3 \text{ J/mol}}{279K} = -35.4 \text{ J/mol}\cdot\text{K}$$

$$\Delta S = n \Delta_{\text{cry}} S = 3.21 \text{ mol} \times -35.4 \text{ J/mol}\cdot\text{K}$$

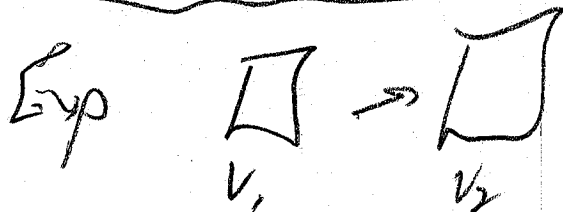
$$= -113.6 \text{ J/K}$$

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Comments on Rev. Adiab. v. Exp/Comp.

slides 9, 10

(1)



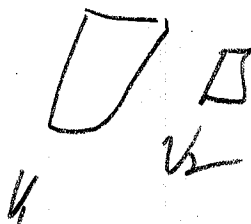
$$q = 0 \quad w < 0 \quad \Delta u = q + w < 0$$

$$\Delta u = n C_{v,m} \Delta T$$

$$\Delta T < 0$$

$$\Delta H = n C_{p,m} \Delta T$$

Comp. $v_2 < v_1$



$$q = 0$$

$$w > 0$$

$$w = \Delta u = n C_{v,m} \Delta T > 0$$

$$\Delta T > 0$$

$$\Delta H > 0$$

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Entropy Review Example - Not in your PP

48 grams of $\text{CH}_4(\text{g})$ [$M=16$] are initially at a volume of 60 L and pressure of 1.5 bar.

= 3 mol (2)

$$n = \frac{48 \text{ g}}{16 \text{ g/mol}}$$

The sample is reversibly changed to a final volume 20 L and pressure of 7.0 bar.

$$M = 16 \text{ g/mol}$$
$$C_{v,m} = 35 \text{ J/mol}\cdot\text{K}$$

Note: Assume this is a two step process:

- (a) isothermal compression to $V = 20 \text{ L}$
- (b) Heating at $V = 20 \text{ L}$ until the pressure reaches 7.0 bar

(a) Isotherm Compression: $\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$

$$V_1 = 60 \text{ L} \quad V_2 = 20 \text{ L}$$
$$\Delta S = 3 \text{ mol} \times 8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times \ln\left(\frac{20}{60}\right) = -27.4 \text{ J/K}$$

(b) Const Vol. Heating: $\Delta S_b = n C_{v,m} \ln\left(\frac{T_2}{T_1}\right)$

$$C_{v,m} = 35 \text{ J/mol}\cdot\text{K}$$

$$T_1 = \frac{P_1 V_1}{nR} = \frac{(1.5 \text{ bar})(60 \text{ L})}{3 \times 8.31 \text{ J/mol}\cdot\text{K}} = 361 \text{ K}$$

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(7.0 \text{ bar})(20 \text{ L})}{3 \text{ mol} / (8.31)} = 562 \text{ K}$$

$$\Delta S_b = 3 (35 \frac{\text{J}}{\text{mol}\cdot\text{K}}) \ln\left(\frac{562}{361}\right) = 67.6 \text{ J/K} \quad 46.5 \text{ J/K}$$

$$\Delta S_{\text{tot}} = -27.4 + 67.6 = 40.2 \text{ J/K}$$
$$\Delta S_{\text{tot}} = -27.4 + 46.5 = 19.1 \text{ J/K}$$

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Example: Freezing of Supercooled Water (Slide #22)

Calculate ΔS_{sys} , ΔS_{surr} and ΔS_{univ} for the freezing of one mole of supercooled water at -10°C .

$T = 213\text{K}$

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~~$\Delta_{\text{fus}}H = 6.01\text{ kJ/mol}$~~
 ~~$\Delta_{\text{fus}}S = 22.0\text{ J/mol-K}$~~

$\Delta S_{\text{sys}} = \Delta_{\text{fuz}}S = -22.0\text{ J/K}$

$q_{\text{sys}} = \Delta_{\text{fuz}}H = -6.01\text{ kJ}$

$q_{\text{surr}} = -\Delta_{\text{fuz}}H = \frac{(-6.01 \times 10^3\text{ J})}{213\text{ K}} = +22.85\text{ J/K}$

~~$\Delta_{\text{fuz}}H = -\Delta_{\text{fuz}}H$~~
 ~~$= -6.01\text{ kJ}$~~

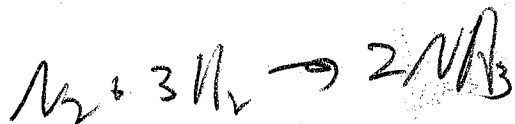
~~$\Delta_{\text{fuz}}S = -\Delta_{\text{fuz}}S$~~
 ~~$= -22.0\text{ J/K}$~~

$\Delta S_{\text{univ}} = -22.0 + 22.85 = +0.85\text{ J/K}$

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Example - 8.2

(4)



$$\Delta S^\circ = [2 S_m^\circ(\text{NH}_3)] - [1 S_m^\circ(\text{N}_2) + 3 S_m^\circ(\text{H}_2)]$$

$$= 2(192.5) - [1(191.6) + 3(130.7)]$$

$$= -198.7 \text{ J/K}$$

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Example: 2 H₂ + O₂ = 2 H₂O (Slide #28)

Cmpd.	$\Delta_f H^\circ$ [kJ/mol]	S_m° [J/mol-K]
H ₂ (g)		131
O ₂ (g)		205
H ₂ O(l)	-286	70

T = 25 °C = 298 K

Calculate ΔS_{sys} , ΔS_{surr} , ΔS_{univ} for the above reaction

$$\Delta S_{sys} = 2(70) - [2(131) + 1(205)] = -327 \text{ J/K}$$

$$q_{sys} = \Delta H^\circ = [2(-286)] - [2(0) + 1(0)] = -572 \text{ kJ}$$

$$q_{surr} = -q_{sys} = +572 \text{ kJ}$$

$$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{572 \times 10^3 \text{ J}}{298 \text{ K}} = +1919 \text{ J/K}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = -327 \text{ J/K} + (+1919 \text{ J/K}) = +1592 \text{ J/K}$$

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Example: $C_6H_{12}O_6 + 6 O_2 = 6 CO_2 + 6 H_2O$ (Slide #29)

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$$\Delta_r H^\circ = -2808 \text{ kJ}$$

$$T = 25^\circ \text{C} = 298$$

$$\Delta_r S^\circ = +243 \text{ J/K}$$

Calculate ΔS_{sys} , ΔS_{surr} , ΔS_{univ} for the above reaction

$$\Delta S_{\text{sys}} = +243 \text{ J/K}$$

$$\begin{aligned} \frac{S_{\text{surr}}}{q_{\text{surr}}} &= -\frac{q_{\text{sys}}}{T} = -\frac{\Delta_r H^\circ}{T} = -\frac{-2808 \text{ kJ}}{298 \text{ K}} \\ &= +2808 \text{ kJ} \end{aligned}$$

$$\Delta S_{\text{surr}} = \frac{+2808 \times 10^3 \text{ J}}{298 \text{ K}} = +9420 \text{ J/K}$$

$$\Delta S_{\text{univ}} = +243 + 9420 = 9663 \text{ J/K}$$

The Enthalpy of Vaporization of toluene is 37.1 kJ/mol.
The Entropy of Vaporization of toluene is 96.6 J/mol-K

$\Delta_{\text{cond}} H = -37.1 \text{ kJ/mol}$
 $\Delta_{\text{cond}} S = -96.6 \text{ J/mol-K}$

Calculate ΔS_{univ} when Two (2) moles of toluene gas are condensed to the liquid at 90 °C.

$\Delta H = 2 \Delta_{\text{cond}} H = 2(-37.1) = -74.2 \text{ kJ}$
 $\Delta S = 2 \Delta_{\text{cond}} S = 2(-96.6) = -193.2 \text{ J/K}$

$T = 90^\circ\text{C}$
 $= 363 \text{ K}$

$\Delta S_{\text{sys}} = -193.2 \text{ J/K}$

$q_{\text{sum}} = -q_{\text{sys}} = -(-74.2 \text{ kJ}) = +74.2 \text{ kJ}$
 $\Delta S_{\text{sum}} = \frac{q_{\text{sum}}}{T} = \frac{74.2 \times 10^3 \text{ J}}{363 \text{ K}}$
 $= +204.4 \text{ J/K}$
 $\Delta S_{\text{univ}} = -193.2 + 204.4$
 $= +11.2 \text{ J/K}$

Calculate ΔS_{univ} when Two (2) moles of toluene gas are condensed to the liquid at 111 °C.

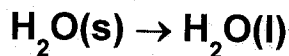
$T = 384 \text{ K}$

$\Delta S_{\text{sys}} = -193.2$
 $\Delta S_{\text{sum}} = \frac{74.2 \times 10^3 \text{ J}}{384 \text{ K}} = +193.2 \text{ J/K}$

$\Delta S_{\text{univ}} = 0$

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The Melting of Ice at various temperatures - Slide #



$$\Delta_{\text{fus}} H^\circ = 6.01 \text{ kJ/mol}$$

$$\Delta_{\text{fus}} S^\circ = 22.0 \text{ J/mol-K}$$

Calculate ΔG° for the melting
of one mole of water at:

(a) 0°C

(b) $+10^\circ \text{C}$

(c) -10°C

$$\Delta H = 1 \times 6.01 \text{ kJ/mol} = 6.01 \text{ kJ/mol}$$

$$\Delta S = 1(22.0) = 22.0 \text{ J/mol-K} \times \frac{1}{1000}$$

$$T = 0^\circ \text{C} = 273 \text{ K}$$

$$\Delta G = \Delta H - T\Delta S = 6.01 \times 10^3 \text{ J} - 273 \text{ K}(22.0 \text{ J/mol-K})$$
$$= 44 \text{ J/mol}$$

$$T = +10^\circ \text{C} = 283 \text{ K}$$

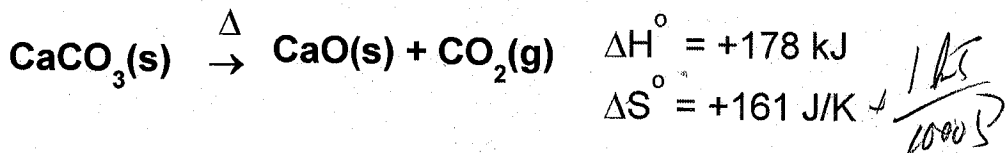
$$\Delta G = 6.01 \times 10^3 - 283(22.0) = +220 \text{ J/mol}$$

$$T = -10^\circ \text{C} = 263 \text{ K}$$

$$\Delta G = 6.01 \times 10^3 - 263(22.0)$$
$$= +220 \text{ J/mol}$$

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The decomposition of Calcium Carbonate - Slide #39



$T = 298 \text{ K}$ (a) Calculate ΔG° for this reaction at 25°C .

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = +178 \text{ kJ} - 298 \text{ K} (+0.161 \text{ kJ/K})$$
$$= +130 \text{ kJ}$$

(b) Calculate the temperature (in $^\circ \text{C}$), above which this reaction becomes spontaneous.

Rev:

$$\Delta G = \Delta H - T\Delta S = 0$$

$$T\Delta S = \Delta H$$

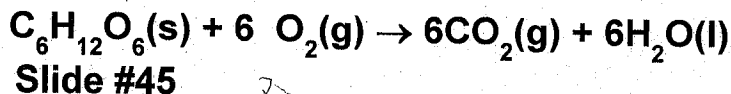
$$T = \frac{\Delta H}{\Delta S} = \frac{178 \text{ kJ}}{0.161 \text{ kJ/K}}$$

$$= 1106 \text{ K} - 273 = 833^\circ \text{C}$$

Range: $> 833^\circ \text{C}$

~~Notation: ΔH () ΔS () $\Delta G = 0$ at $T^\circ \text{C}$~~

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The enthalpy and entropy changes for this reaction are:

$$\Delta H^\circ = -2808 \text{ kJ} \text{ and } \Delta S^\circ = +243 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = +0.243 \text{ kJ/K}$$

(a) Calculate ΔG° for this reaction at 25°C from the above data.

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -2808 \text{ kJ} - (298 \text{ K})(0.243 \text{ kJ/K}) \\ &= -2880 \text{ kJ} \end{aligned}$$

(b) Calculate ΔG° for this reaction at 25°C from the Gibbs Energies of Formation.

$$\begin{aligned} \Delta G^\circ &= [6\Delta_f G^\circ(\text{CO}_2) + 6\Delta_f G^\circ(\text{H}_2\text{O})] \\ &\quad - [1\Delta_f G^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + 6(0)] \end{aligned}$$

Cmpd.	$\Delta_f G^\circ$ [kJ/mol]
$\text{C}_6\text{H}_{12}\text{O}_6$	-908.9
CO_2	-394.4
H_2O	-237.1

$$\begin{aligned} &= [6(-394.4) + 6(-237.1)] \\ &\quad - [1(-908.9) + 6(0)] \\ &= -2880.1 \approx -2880 \end{aligned}$$

Native \leftrightarrow Random Coil

$$\Delta H^\circ = +239 \text{ kJ/mol}$$

$$\Delta S^\circ = +770 \text{ J/mol-K} \times \frac{1}{1000}$$

(a) Predict the more stable form at 25 °C

(b) Predict the more stable form at 50 °C

(c) At what temperature does the denaturation become spontaneous?

$$\text{a)} T = 298 \text{ K} \quad \Delta G = +239 \text{ kJ} - (298)(0.77) = +69.5 \text{ kJ}$$

$$\text{b)} T = 323 \text{ K} \quad \Delta G = +239 - (323)(0.77) = -97 \text{ kJ}$$

$$\text{c)} \Delta G = 0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{+239 \text{ kJ}}{+0.77 \text{ kJ/K}} = 310 \text{ K} - 273$$

$$= +37^\circ \text{C}$$