

Chemical metallurgy tutorial

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Q1/liquid water at 100°c and 1 bar has an internal energy of 419.0 KJ.Kg⁻¹ and a specific volume of 1.044 cm³gm⁻¹

- A. What its enthalpy?
- B. The water is vaporized at 200°c and 800 KPa its enthalpy is 4838.6 KJ Kg⁻¹ and its sp.vol.is 260.79cm³g⁻¹calculate the change in internal energy and enthalpy for the process

Solution/

A) First we change the unit for vol.into m³and the unit of pressure into Pa (N/m²) and the gm into Kg

$$\begin{aligned}H_1 &= U + PV \\ &= (419 \text{ kJ/Kg}) + (10^5 \text{ N/m}^2 \cdot 1.044 \cdot 10^{-6} \text{ m}^3 / 10^{-6} \text{ Kg}) \\ H_1 &= 419.104 \text{ KJ/Kg}\end{aligned}$$

B) First we change KPa into Pa and change unit of vol. from cm³ into m³

$$\begin{aligned}\Delta H &= H_2 - H_1 \\ &= 4838.6 \text{ KJ/Kg} - 419.104 \text{ KJ/Kg} \\ \Delta H &= 4419.49 \text{ KJ/Kg}\end{aligned}$$

We can now calculate ΔU

$$\begin{aligned}\Delta H &= \Delta U + \Delta(PV) \\ \Delta H &= \Delta U + \Delta P \Delta V \\ &= \Delta U + (800 \cdot 10^3 \text{ Pa} - 10^5 \text{ Pa}) (260.79 \cdot 10^{-6} \text{ m}^3 / 10^{-3} \text{ Kg} - 1.044 \cdot 10^{-6} \text{ m}^3 / 10^{-3} \text{ Kg}) \\ \Delta U &= 4238.22 \text{ KJ/Kg}\end{aligned}$$

Q2/with a substance of 1 Kg

- A. How much change in elevation must be to change its potential energy by 1 KJ?
- B. Starting from rest, to what velocity must it accelerate so that the kinetic energy is 1 KJ?

Solution/

A) First we change KJ into J

$$\begin{aligned}\Delta E_p &= (m \cdot z_2 \cdot g) - (m \cdot z_1 \cdot g) \\ 10^3 \text{ J} &= m \cdot g (\Delta z)\end{aligned}$$

$$10^{-3} \text{N/m}^2 = 1 \text{kg} \cdot 9.8 \text{ m/s}^2 (\Delta z)$$

$$\Delta z = 9800 \text{m}$$

B) $u_1 = \text{zero}$ because starting from rest

$$\Delta E_k = 1/2 u_2^2 - 1/2 u_1^2$$

$$10^{-3} = 1/2 m (u_2^2 - u_1^2)$$

$$10^{-3} \text{J} = 1/2 (1 \text{Kg}) (u_2^2 - \text{zero})$$

$$u_2^2 = 500 \text{ m}^2/\text{s}^2$$

Q3/ the internal energy U^t of an amount of a gas is given by the equation:

$$U^t = 0.01 PV^2$$

Where P is in KPa, V^t in m^3 . the gas undergoes a mechanically reversible process from an initial state at 10.000 KPa and 280°K. during the process V^t is constant and equal to 0.3 m^3 and P increases by 50 percent. determine values for Q and ΔH in KJ for the process

Solution/

$$U_1 = 0.01(10^4 \text{pa}) \cdot 0.3 \text{m}^3$$

$$= 30 \text{KJ}$$

Pressure increases by 50% and that make the pressure in final state equal to 15000 KPa

$$U_2 = 0.01(15000) \text{KPa} \cdot 0.3 \text{m}^3$$

$$= 45 \text{KJ}$$

$$\Delta U = U_2 - U_1$$

$$= 15 \text{KJ}$$

$$\Delta U = Q - W$$

W = zero because no change in vol. occur

$$\Delta U = Q = 15 \text{KJ}$$

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

$$= 15 \text{KJ} + (15000 \text{KPa} - 10000 \text{KPa}) \cdot 0.3 \text{m}^3$$

Q4/one Kg of air is heated reversibly at constant pressure from an initial state of 300K° and 1 bar until its volume triples .calculate W, Q,ΔU and ΔH for the proc ess. Assume that air obey the relation PV/TR =83.14 bar cm³mole⁻¹K⁻¹ and that Cp =29 J mol⁻¹K⁻¹

Solution/

First we find V₁ and then V₂

$$P_1V_1/T_1 = 83.14$$

$$1 \text{ bar} \cdot V_1/300^\circ\text{K} = 83.14$$

$$V_1 = 25193 \text{ cm}^3$$

$$V_2 = 3V_1$$

$$V_2 = 75581 \text{ cm}^3$$

We change unit of vol. into m³

$$W = P\Delta V$$

$$= 1 \text{ bar} (0.075 - 0.025) \text{ m}^3$$

$$W = 5000 \text{ J}$$

$$P_2V_2/T_2 = 83.14$$

$$1 \text{ bar} (75581 \text{ cm}^3)/T_2 = 83.14$$

$$T_2 = 909^\circ \text{ K}$$

We can find ΔH

$$\Delta H = C_p \Delta T$$

$$= 29(909 - 300)$$

$$\Delta H = 17661 \text{ J} \cdot \text{mol}^{-1}$$

ΔH =Q at constant pressure

$$\Delta H = \Delta U + W$$

$$17661 \text{ J} \cdot \text{mol}^{-1} = \Delta U + 5000 \text{ J}$$

$$\Delta U = 12661 \text{ J}$$

Q5/the path followed by a gas during a particular mechanically reversible process is described by the equation:

$$P + aV^t = C$$

Where a and c are constant. In the initial state $P_1 = 60 \text{ bar}$ and $V_1^t = 0.002 \text{ m}^3$, in the final state $P_2 = 20 \text{ bar}$ and $V_2^t = 0.004 \text{ m}^3$ during the process heat in the amount of 5000 J is transferred to the gas .determine W and ΔU^t for the process. Suppose the gas followed a different path connecting the same initial and final states. Which of the quantities Q, W and, ΔU^t must be unchanged .why?

Solution/

$$W = \Delta(PV)$$

$$= P_1V_1 - P_2V_2$$

$$= (60 \text{ bar} \cdot 0.002 \text{ m}^3) - (20 \text{ bar} \cdot 0.004 \text{ m}^3)$$

$$= 0.04 \text{ bar} \cdot \text{m}^3$$

$$= 4000 \text{ J}$$

$$\Delta U = W - Q$$

$$= 5000 \text{ J} - 4000 \text{ J}$$

$$= 1000 \text{ J}$$

ΔU Will not changed during the process because it is state function while Q and W will changed because they are path functions

Q6/A particular power plant operates with heat – source reservoir at 300k and a heat sink reservoir at 25c.it has a thermal efficiency equal to 60% of Carnot engine thermal efficiency for the same temperature .

- What temperature is the thermal efficiency of the plant?
- To What temperature must the heat source reservoir be raised to increase the thermal efficiency of the plant to 40%?

Solution/

$$A) (\text{Efficiency})_{\text{Carnot}} = 1 - (T_c/T_H)$$

$$= 1 - (298^\circ\text{k}/300^\circ\text{k})$$

$$= 0.01$$

$$(\text{Efficiency})_{\text{process}} = 0.6(\text{efficiency})_{\text{Carnot}}$$

$$= 0.006$$

$$B) 0.4(0.006) = 0.0024$$

$$0.004 + 0.006 = 0.0084$$

$$0.0084 = 1 - (298^\circ \text{K} / T_H)$$

$$T_H = 301^\circ \text{K}$$

Q7/for an ideal gas show that:

- A. For a temp. increase from T_1 to T_2 , ΔS of the gas is greater when the change occurs at constant pressure than when it occurs at constant volume
- B. For pressure change from P_1 to P_2 , the sign of ΔS of an isothermal change is opposite that for a constant volume change

Solution/

A)

At constant volume

$$dw = \text{zero}$$

$$du = dQ - dw$$

$$= dQ - \text{zero}$$

$$du = dQ$$

$$dH = du + pdv + vdp$$

$$= du + \text{zero} + vdp$$

We found previously that $du = dQ$ and we know that $V = RT/P$

So:

$$dH = dQ_{\text{rev.}} + (RT/P) dp$$

$(C_p dT = dQ_{\text{rev.}} + (RT/P) dp)$ we divide by T

$$C_p dT/T = \Delta S_v + (R/P) dP$$

$$C_p \ln(T_2/T_1) = \Delta S_v + R \ln(p_2/p_1)$$

$$\Delta S_V = C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$$

At constant pressure

$$du = dQ - dW$$

$$dH = du + pdv + vdp$$

$$= du + pdv + \text{zero} \quad \text{at constant pressure } p dv = \text{zero}$$

$$= (dQ - dw) + pdv$$

$$= dQ - pdv + pdv$$

$$dH = dQ$$

$$dH = Q_{\text{rev.}} \quad \text{at constant pressure}$$

($C_p dT = Q_{\text{rev.}}$) We divide by T

$$C_p dT/T = Q_{\text{rev.}}/T$$

$$C_p \ln T_2/T_1 = \Delta S_p$$

$$\text{So } \Delta S_p > \Delta S_V$$

$$\text{B) } \Delta s = C_p \ln(T_2/T_1) - R \ln(p_2/p_1)$$

For isothermal $T_1 = T_2$

$$\Delta T = \text{zero}$$

$$\Delta s = C_p \ln 1 - R \ln(p_2/p_1)$$

$$= \text{zero} - R \ln(p_2/p_1)$$

$$\Delta s = -R \ln(p_2/p_1)$$

At constant volume

$$\Delta s = C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$$

We know that $T = PV/R$ so $T_1 = P_1 V_1/R$ and $T_2 = P_2 V_2/R$

$$T_2/T_1 = P_2/P_1$$

$$\Delta s = C_p \ln(p_2/p_1) - R \ln(p_2/p_1)$$

$$= \ln p_2/p_1 - (C_p - R)$$

$$= \ln(p_2/p_1) \cdot C_v$$

$$\Delta S = C_V \ln p_2/p_1$$

So ΔS at constant volume has opposite sign for that of ΔS at constant temperature

Q8/ one mole of an ideal gas, $C_p = (7/2)R$ and cylinder device from 1 bar and 40°C to 4 bar. The process is irreversible adiabatic compression from the same initial state to the same final pressure. What is the entropy change of the gas?

Solution/

$\Delta s = \text{zero}$ at reversible adiabatic process

$$\Delta s = C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$$

$$C_p \ln(T_2/T_1) = R \ln(p_2/p_1)$$

$$(7/2)R \cdot \ln(T_2/T_1) = R \cdot \ln(4/1) \quad R \text{ cancelled out and then we take the exp.}$$

$$(T_2/313 \text{ K})^{7/2} = 4/1$$

$$T_2 = 465.34 \text{ K} \quad \text{for reversible process}$$

$$du = dQ - dw$$

$$= \text{zero} - dw \quad dQ = \text{zero at adiabatic process}$$

$$\text{So } w = u = C_V \Delta T$$

$$= (5/2) R (465.34 - 313)$$

$$W_{\text{rev.}} = 3163 \text{ J}$$

$$W_{\text{irrever.}} = W_{\text{rev.}} (0.3)$$

$$= 4112.2 \text{ J}$$

We should find T_2 for irreversible process

$$W_{\text{irrev.}} = C_V \Delta T$$

$$4112.2 \text{ J} = C_V (T_2 - 313)$$

$$T_2 = 511^\circ\text{K}$$

$$\Delta S = (7/2) R \ln(511/313) - R \ln(4/1)$$

$$= 2.723 \text{ J/K}$$

Q9/ if heat in the amount of 5.275×10^5 KJ is added to 13.61 Kg mol of methane initially at 210°C in a steady flow process at approximately atmospheric pressure, what is its entropy change ?

Solution/

$$\Delta S = C_p \ln(T_2/T_1) - R \ln(p_2/p_1)$$

At atmospheric pressure $R \ln(p_2/p_1) \approx \text{zero}$

$$dH = dQ = nC_p \Delta T$$

$$5.275(10^5) = 13.61 \text{Kg} (7/2) R (T_2 - 483.15)$$

$$T_2 = 1815.22^\circ\text{K}$$

$$\Delta S = (7/2) R \ln(1815.22/483.18)$$

$$= 38.516 \text{ KJ}$$

Q10/ A device with no moving parts is claimed to provide a steady stream of chilled air at -20°C and 1 bar. The feed to the device is compressed air at 25°C and 4 bar. In addition to the stream of chilled air, a second stream of air flows at an equal mass rate from the device at 70°C and 1 bar. Are these claims in violation of the second law? Assume that air is an ideal gas for which $C_p = (7/2) R$

Solution/

$$\Delta S_1 = C_p \ln(T_2/T_1) - R \ln(p_2/p_1)$$

$$= (7/2) R \ln(343/298) - R \ln(1/4)$$

$$= 15.616 \text{ J}$$

$$\Delta S_2 = (7/2) R \ln(253/298) - R \ln(1/4)$$

$$= 6.76 \text{ J}$$

$$\Delta S_{\text{Total}} = 15.616 + 6.76$$

$$= 22.37 \text{ J}$$

So $\Delta S_{\text{total}} > \text{zero}$

$$\Delta S = C_p \ln(T_2/T_1) - R \ln(p_2/p_1)$$

$$= (7/2) R \ln(343/253) - R \ln(4/1)$$

$$\Delta S = -2.674 \text{ J}$$

The mathematical statement of the 2nd law is $\Delta S_{\text{total}} \geq \text{zero}$

So these claims are in violation with the 2nd law

Q11/A A rigid vessel of 0.05 m^3 volume contains an ideal gas, $C_v = (5/2) R$ at 500°K and 1 bar

- A. If heat in the amount of 12000 J is transferred to the gas, determine its entropy change
- B. If the vessel is fitted with a stirrer that is rotated by a shaft so that work in the amount of 12.000 J is done on the gas, what is the entropy change of the gas if the process is adiabatic? what is Δs total? What is the irreversible feature of the process?

Solution/

A) $\Delta U = Q - W$

$W = \text{zero}$ because the vessel is rigid

So $\Delta U = Q$

$$Q = C_v \Delta T$$

$$12000 = (5/2) R (T_2 - 500)$$

$$T_2 = 1072.34 \text{ K}$$

To find P_2 we use $P_1 V_1 / T_1 = P_2 V_2 / T_2$

$V_1 = V_2 = 0.05$ because vessel is rigid

$$1(0.05) / 500^\circ \text{K} = P_2 (0.05) / 1077.34^\circ \text{K}$$

$$p_2 = 2.15 \text{ bar}$$

$$\Delta s = C_p \ln(T_2 / T_1) - R \ln(p_2 / p_1)$$

$$\Delta s = (C_v + R) \ln(T_2 / T_1) - R \ln(p_2 / p_1)$$

$$= (5/2) R + R \ln(1077 / 500) - R \ln(2.5 / 1)$$

$$15.9 \text{ J}$$

B) The process is adiabatic so $Q = \text{zero}$

$$\Delta U = Q - W$$

$$\Delta U = -W$$

$$= -(12000) \text{ J}$$

Work is done on the system (gas) so the sign of W should be negative

$$W = 12000 \text{ J}$$

$$\Delta U = 12000 \text{ J}$$

$$\Delta U = C_v \Delta T$$

$$12000 = (5/2) R (T_2 - 500)$$

$$T_2 = 1077.3 \text{ K}$$

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

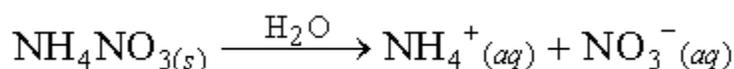
$$P = 2.15 \text{ bar}$$

$$\Delta S = (7/2) R \ln (T_2 / T_1) - R \ln (p_2 / p_1)$$

$$= 15.97 \text{ J}$$

$$\Delta S_{\text{Total}} = 31.94 \text{ J}$$

Q12/



Calculate ΔH° , ΔS° , and ΔG° for the above reaction to determine whether the reaction is spontaneous or not.

Compound	ΔH_f°	ΔS°
$\text{NH}_4\text{NO}_3(s)$	-365.56	151.08
$\text{NH}_4^+(aq)$	-132.51	113.4
$\text{NO}_3^-(aq)$	-205.0	146.4

Solution /

$$\Delta H^\circ = \sum nH_f^\circ \text{ products} - \sum mH_f^\circ \text{ reactants}$$

$$\Delta H^\circ = \left[\left(1 \text{ mol } \cancel{\text{NH}_4^+} \times \frac{-132.51 \text{ kJ}}{\text{mol}} \right) + \left(1 \text{ mol } \cancel{\text{NO}_3^-} \times \frac{-205.0 \text{ kJ}}{\text{mol}} \right) \right] - \left(1 \text{ mol } \cancel{\text{NH}_4\text{NO}_3} \times \frac{-365.56 \text{ kJ}}{\text{mol}} \right)$$

$$\Delta H^\circ = -337.51 + 365.56$$

$$\Delta H^\circ = 28.05 \text{ kJ}$$

$$\Delta S^\circ = \sum nS^\circ_{\text{products}} - \sum mS^\circ_{\text{reactants}}$$

$$\Delta S^\circ = \left[\left(1 \text{ mol } \cancel{\text{NH}_4^+} \times \frac{113.4 \text{ J}}{\text{mol} \cdot \text{K}} \right) + \left(1 \text{ mol } \cancel{\text{NO}_3^-} \times \frac{146.4 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right] - \left(1 \text{ mol } \cancel{\text{NH}_4\text{NO}_3} \times \frac{151.08 \text{ J}}{\text{mol} \cdot \text{K}} \right)$$

$$\Delta S^\circ = 259.8 - 151.08$$

$$\boxed{\Delta S^\circ = 108.7 \text{ J/K}}$$

Now, can plug in these values we've calculated into the free energy equation

$$T_K = 25^\circ\text{C} + 273.15 = 298.15 \text{ K}$$

$$\Delta S^\circ = 108.7 \cancel{\text{ J}}/\text{K} \times \frac{1 \text{ kJ}}{1000 \cancel{\text{ J}}} = 0.1087 \text{ kJ/K}$$

$$\Delta H^\circ = 28.05 \text{ kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Plug in } \Delta H^\circ, \Delta S^\circ, \text{ and } T$$

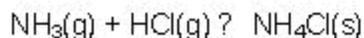
$$\Delta G^\circ = 28.05 \text{ kJ} - (298.15 \cancel{\text{ K}})(0.1087 \text{ kJ}/\cancel{\text{ K}})$$

$$\Delta G^\circ = 28.05 \text{ kJ} - 32.41 \text{ kJ}$$

$$\boxed{\Delta G^\circ = -4.4 \text{ kJ}}$$

Q13/

Calculate ΔG for the following reaction at 25°C . Will the reaction occur (be spontaneous)? How do you know?



Also given for this reaction:

$$\Delta H = -176.0 \text{ kJ} \quad \Delta S = -284.8 \text{ J}\cdot\text{K}^{-1}$$

Solution

We will calculate ΔG using the formula

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

but first we need to convert units for ΔS and temperature to Kelvin:

$$\Delta S = -284.8 \text{ J}\cdot\text{K}^{-1} = -0.2848 \text{ kJ}\cdot\text{K}^{-1}$$

$$\text{K} = 273 + ^\circ\text{C} = 273 + 25 = 298 \text{ K}$$

Now we can solve our equation:

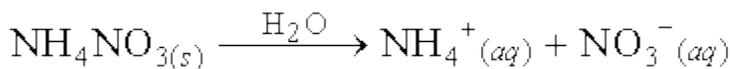
$$\Delta G = -176.0 - (298)(-0.2848)$$

$$\Delta G = -176.0 - (-84.9)$$

$$\Delta G = -91.1 \text{ kJ}$$

Sample free energy calculation (standard-state conditions):

Q14



Compound	ΔH_f°	ΔS°
$\text{NH}_4\text{NO}_3(s)$	-365.56	151.08
$\text{NH}_4^+(aq)$	-132.51	113.4
$\text{NO}_3^-(aq)$	-205.0	146.4

Calculate ΔH° , ΔS° , and ΔG° for the above reaction to determine whether the reaction is spontaneous or not.

First let's calculate ΔH_f° . Note that in the above reaction, one mole of NH_4NO_3 dissociates in water to give one mole each of NH_4^+ and NO_3^- :

Solution/

$$\Delta H^\circ = \sum nH_{f, \text{products}}^\circ - \sum mH_{f, \text{reactants}}^\circ$$

$$\Delta H^\circ = \left[\left(1 \text{ mol } \cancel{\text{NH}_4^+} \times \frac{-132.51 \text{ kJ}}{\text{mol}} \right) + \left(1 \text{ mol } \cancel{\text{NO}_3^-} \times \frac{-205.0 \text{ kJ}}{\text{mol}} \right) \right] - \left(1 \text{ mol } \cancel{\text{NH}_4\text{NO}_3} \times \frac{-365.56 \text{ kJ}}{\text{mol}} \right)$$

$$\Delta H^\circ = -337.51 + 365.56$$

$$\Delta H^\circ = 28.05 \text{ kJ}$$

Next, let's calculate ΔS° :

$$\Delta S^\circ = \sum nS_{\text{products}}^\circ - \sum mS_{\text{reactants}}^\circ$$

$$\Delta S^\circ = \left[\left(1 \text{ mol } \cancel{\text{NH}_4^+} \times \frac{113.4 \text{ J}}{\text{mol} - \text{K}} \right) + \left(1 \text{ mol } \cancel{\text{NO}_3^-} \times \frac{146.4 \text{ J}}{\text{mol} - \text{K}} \right) \right] - \left(1 \text{ mol } \cancel{\text{NH}_4\text{NO}_3} \times \frac{151.08 \text{ J}}{\text{mol} - \text{K}} \right)$$

$$\Delta S^\circ = 259.8 - 151.08$$

$$\Delta S^\circ = 108.7 \text{ J/K}$$

Now we can plug in these values we've calculated into the free energy equation.

• **NOTE:** The units of ΔH_f° is **kJ** and the units of ΔS° is **J/K**. Since ΔG° is generally reported in **kJ**, we can divide ΔS° by 1000 to convert it to units of **kJ/K**

- **NOTE:** The temperature in the free energy equation must be in Kelvin, so we must convert the given temperature in Celsius to Kelvin by adding 273.15.

$$T_K = 25^\circ\text{C} + 273.15 = 298.15 \text{ K}$$

$$\Delta S^\circ = 108.7 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 0.1087 \text{ kJ/K}$$

$$\Delta H^\circ = 28.05 \text{ kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Plug in } \Delta H^\circ, \Delta S^\circ, \text{ and } T$$

$$\Delta G^\circ = 28.05 \text{ kJ} - (298.15 \text{ K})(0.1087 \text{ kJ/K})$$

$$\Delta G^\circ = 28.05 \text{ kJ} - 32.41 \text{ kJ}$$

$$\Delta G^\circ = -4.4 \text{ kJ}$$

Temperature and Free Energy

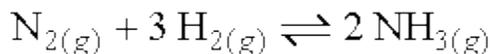
- If a reaction is favorable for enthalpy ($\Delta H^\circ < 0$), but unfavorable for entropy ($\Delta S^\circ < 0$), then the reaction becomes LESS SPONTANEOUS as temperature increases.
 - WHY? - The standard-state free energy equation states that:

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

If entropy is unfavorable, the ΔS° is negative. Subtracting a negative number is the same as adding the respective positive number. As the temperature increases, the $T \Delta S^\circ$ factor (which is ADDED to the enthalpy if the entropy is unfavorable) increases as well. Eventually, the $T \Delta S^\circ$ factor becomes larger than ΔH° and ΔG° becomes positive, i.e. the reaction is no longer spontaneous.

Sample Calculations (standard-state conditions):

Q15/



Compound	ΔH_f°	ΔS°
$\text{N}_{2(g)}$	0	191.61
$\text{H}_{2(g)}$	0	130.68
$\text{NH}_{3(g)}$	-46.11	192.45

1) Calculate ΔH° and ΔS° for the above reaction. Explain what each of the signs mean.

$$\Delta H^\circ = \sum nH_{f, \text{products}}^\circ - \sum mH_{f, \text{reactants}}^\circ$$

$$\Delta H^\circ = \left[\left(1 \text{ mol } \cancel{\text{N}_2} \times \frac{0 \text{ kJ}}{\text{mol}} \right) + \left(3 \text{ mol } \cancel{\text{H}_2} \times \frac{0 \text{ kJ}}{\text{mol}} \right) \right] - \left(2 \text{ mol } \cancel{\text{NH}_3} \times \frac{-46.11 \text{ kJ}}{\text{mol}} \right)$$

$$\Delta H^\circ = -92.22 \text{ kJ}$$

ΔH° is negative which is favorable.

$$\Delta S^\circ = \sum nS_{\text{products}}^\circ - \sum mS_{\text{reactants}}^\circ$$

$$\Delta S^\circ = \left(2 \text{ mol } \cancel{\text{NH}_3} \times \frac{192.45 \text{ J}}{\text{mol} - \text{K}} \right) - \left[\left(1 \text{ mol } \cancel{\text{N}_2} \times \frac{191.61 \text{ J}}{\text{mol} - \text{K}} \right) + \left(3 \text{ mol } \cancel{\text{H}_2} \times \frac{130.68 \text{ J}}{\text{mol} - \text{K}} \right) \right]$$

$$\Delta S^\circ = 384.9 - 583.65$$

$$\Delta S^\circ = -198.75 \text{ J/K}$$

S° is negative which is Δ unfavorable.

2) Predict whether the above reaction is spontaneous at 25°C.

$$T_K = 25^\circ\text{C} + 273.15 = 298.15\text{ K}$$

$$\Delta S^\circ = -198.75 \cancel{\text{ J}}/\text{K} \times \frac{1 \text{ kJ}}{1000 \cancel{\text{ J}}} = -0.19875 \text{ kJ}/\text{K}$$

$$\Delta H^\circ = -92.22 \text{ kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Plug in } \Delta H^\circ, \Delta S^\circ, \text{ and } T$$

$$\Delta G^\circ = -92.22 \text{ kJ} - (298.15 \cancel{\text{ K}})(-0.19875 \text{ kJ}/\cancel{\text{ K}})$$

$$\Delta G^\circ = -92.22 \text{ kJ} + 59.257 \text{ kJ}$$

$$\Delta G^\circ = -32.96 \text{ kJ}$$

ΔG° is negative, so the reaction is SPONTANEOUS.

3) Predict whether the above reaction is spontaneous at 500°C.

$$T_K = 500^\circ\text{C} + 273.15 = 773.15\text{ K}$$

$$\Delta S^\circ = -198.75 \cancel{\text{ J}}/\text{K} \times \frac{1 \text{ kJ}}{1000 \cancel{\text{ J}}} = -0.19875 \text{ kJ}/\text{K}$$

$$\Delta H^\circ = -92.22 \text{ kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Plug in } \Delta H^\circ, \Delta S^\circ, \text{ and } T$$

$$\Delta G^\circ = -92.22 \text{ kJ} - (773.15 \cancel{\text{ K}})(-0.19875 \text{ kJ}/\cancel{\text{ K}})$$

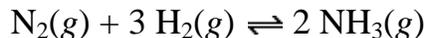
$$\Delta G^\circ = -92.22 \text{ kJ} + 153.66$$

$$\Delta G^\circ = 61.44 \text{ kJ}$$

ΔG° is positive, so the reaction is NOT SPONTANEOUS.

Q16/

Calculate ΔH° and ΔS° for the following reaction and decide in which direction each of these factors will drive the reaction.



Solution/

Using a standard-state enthalpy of formation and absolute entropy data table, we find the following information:

Compound	ΔH_f° (kJ/mol)	S° (J/mol-K)
$\text{N}_2(g)$	0	191.61
$\text{H}_2(g)$	0	130.68
$\text{NH}_3(g)$	-46.11	192.45

The reaction is exothermic ($\Delta H^\circ < 0$), which means that the enthalpy of reaction favors the products of the reaction:

$$\begin{aligned}\Delta H^\circ &= \Sigma H_f^\circ(\text{products}) - \Sigma H_f^\circ(\text{reactants}) \\ &= [2 \text{ mol NH}_3 \times 46.11 \text{ kJ/mol}] - [1 \text{ mol N}_2 \times 0 \text{ kJ/mol} + 3 \text{ mol H}_2 \times 0 \text{ kJ/mol}] \\ &= -92.22 \text{ kJ}\end{aligned}$$

The entropy of reaction is unfavorable, however, because there is a significant increase in the order of the system, when N_2 and H_2 combine to form NH_3 .

$$\begin{aligned}\Delta S^\circ &= \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants}) \\ &= [2 \text{ mol NH}_3 \times 192.45 \text{ J/mol-K}] - [1 \text{ mol N}_2 \times 191.61 \text{ J/mol-K} + 3 \text{ mol H}_2 \times 130.68 \text{ J/mol-K}] \\ &= -198.75 \text{ J/K}\end{aligned}$$

Q17/

Calculate ΔH° and ΔS° for the following reaction:



Use the results of this calculation to determine the value of ΔG° for this reaction at 25° C, and explain why NH_4NO_3 spontaneously dissolves in water at room temperature.

Solution/

Using a standard-state enthalpy of formation and absolute entropy data table, we find the following information:

Compound	ΔH_f° (kJ/mol)	S° (J/mol-K)
$\text{NH}_4\text{NO}_3(s)$	-365.56	151.08
$\text{NH}_4^+(aq)$	-132.51	113.4
$\text{NO}_3^-(aq)$	-205.0	146.4

This reaction is endothermic, and the enthalpy of reaction is therefore unfavorable:

$$\Delta H^\circ = \Sigma H_f^\circ(\text{products}) - \Sigma H_f^\circ(\text{reactants})$$

$$= [1 \text{ mol NH}_4 \times 132.51 \text{ kJ/mol} + 1 \text{ mol NO}_3^- \times -205.0 \text{ kJ/mol}] - [1 \text{ mol NH}_4\text{NO}_3 \times -365.56 \text{ kJ/mol}]$$

$$= 28.05 \text{ kJ}$$

The reaction leads to a significant increase in the disorder of the system, however, and is therefore favored by the entropy of reaction:

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$$

$$= [1 \text{ mol NH}_4 \times 113.4 \text{ J/mol-K} + 1 \text{ mol NO}_3^- \times 146.4 \text{ J/mol-K}] - [1 \text{ mol NH}_4\text{NO}_3 \times 151.08 \text{ J/mol-K}]$$

$$= 108.7 \text{ J/K}$$

To decide whether NH_4NO_3 should dissolve in water at 25°C we have to compare the ΔH° and $T\Delta S^\circ$ to see which is larger. Before we can do this, we have to convert the temperature from $^\circ\text{C}$ to kelvin:

$$T_{\text{K}} = 25^\circ\text{C} + 273.15 = 298.15\text{ K}$$

We also have to recognize that the units of ΔH° for this reaction are kilojoules and the units of ΔS° are joules per kelvin. At some point in this calculation, we therefore have to convert these quantities to a consistent set of units. Perhaps the easiest way of doing this is to convert ΔH° to joules. We then multiply the entropy term by the absolute temperature and subtract this quantity from the enthalpy term:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= 28,050\text{ J} - (298.15\text{ K} \times 108.7\text{ J/K}) \\ &= 28,050\text{ J} - 32,410\text{ J} \\ &= -4360\text{ J}\end{aligned}$$

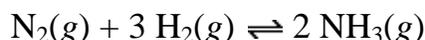
At 25°C , the standard-state free energy for this reaction is negative because the entropy term at this temperature is larger than the enthalpy term:

$$\Delta G^\circ = -4.4\text{ kJ}$$

The reaction is therefore spontaneous at room temperature.

Q18/

Use the values of ΔH° and ΔS° calculated in Practice Problem 5 to predict whether the following reaction is spontaneous at 25°C :



Solution/

According to Practice Problem 5, this reaction is favored by enthalpy but not by entropy:

$$\Delta H^\circ = -92.22\text{ kJ} \quad (\text{favorable})$$

$$\Delta S^\circ = -198.75\text{ J/K} \quad (\text{unfavorable})$$

Before we can compare these terms to see which is larger, we have to incorporate into our calculation the temperature at which the reaction is run:

$$T_K = 25^\circ \text{C} + 273.15 = 298.15 \text{ K}$$

We then multiply the entropy of reaction by the absolute temperature and subtract the $T \Delta S^\circ$ term from the ΔH° term:

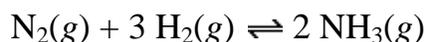
$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -92,220 \text{ J} - (298.15 \text{ K} \times -198.75 \text{ J/K}) \\ &= -92,220 \text{ J} + 59,260 \text{ J} \\ &= -32,960 \text{ J}\end{aligned}$$

$$\Delta G^\circ = -32.96 \text{ kJ}$$

According to this calculation, the reaction should be spontaneous at 25°C .

Q19/

Predict whether the following reaction is still spontaneous at 500°C :



Assume that the values of ΔH° and ΔS° used in Practice Problem 7 are still valid at this temperature.

Solution/

Before we can decide whether the reaction is still spontaneous we need to calculate the temperature of the kelvin scale:

$$T_K = 500^\circ \text{C} + 273 = 773 \text{ K}$$

We then multiply the entropy term by this temperature and subtract this quantity from the enthalpy term:

$$\begin{aligned}\Delta G^\circ_{773} &= \Delta H^\circ_{298} - T \Delta S^\circ_{298} \\ &= 92,220 \text{ J} - (773 \text{ K} \times -198.75 \text{ J/K}) \\ &= 92,220 \text{ J} - (-153,600 \text{ J}) \\ &= 61,380 \text{ J}\end{aligned}$$

$$\Delta G^\circ = 61.4 \text{ kJ}$$

Because the entropy term becomes larger as the temperature increases, the reaction changes from one which is favorable at low temperatures to one that is unfavorable at high temperatures.