

EXAM
DRILL

Thermodynamics

ANSWERS

1. Isothermal process.
2. Bomb calorimeter.
3. $\text{J K}^{-1}\text{g}^{-1}$ or $\text{cal K}^{-1}\text{g}^{-1}$
4. $\Delta S = -ve$

5. (d) : Since work is done against external pressure, hence process is irreversible. Then

$$w = -P\Delta V = -2.5(6 - 4) = -5.0 \text{ L atm}$$

$$= -5 \times 101.3 = -506.5 \text{ J} \quad (1 \text{ L atm} = 101.3 \text{ J})$$

We know $\Delta U = q + w$, but for isothermal process $\Delta U = 0$ then $q = -w$

$$\therefore q = 506.5 \text{ J}$$

$$\text{Also, } q = m \times c \times \Delta T$$

Where m is mass, c is specific heat and ΔT is change in temperature.

$$\Delta T = \frac{q}{m \times c} = \frac{506.5}{18 \times 4.184} = 6.725$$

$$\text{Final temperature} = T + \Delta T = 20 + 6.725 = 26.725^\circ\text{C}$$

6. (a) : For $A + 3B \rightleftharpoons 2C$,

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

$$= -90 - 400 \times (-200 \times 10^{-3}) = -10 \text{ kJ}$$

$$\therefore \text{For } \frac{1}{2}A + \frac{3}{2}B \rightleftharpoons C, \Delta G^\circ = -5 \text{ kJ}$$

7. (a) : $\Delta H = \Delta U + \Delta n_g RT$

$$\Delta H = \Delta U \text{ if } \Delta n_g = 0$$

For $\text{H}_{2(g)} + \text{I}_{2(g)} \longrightarrow 2\text{HI}_{(g)}; \Delta n_g = 0$

8. (c) : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 77200 - 400 \times 122$
 $= 28400 \text{ J}$

$$\text{Also } -\Delta G^\circ = 2.303 RT \log K_c$$

$$K_c = 1.958 \times 10^{-4}$$

9. (b) : For isothermal reversible expansion of an ideal gas

$$w = -2.303 nRT \log \left(\frac{V_2}{V_1} \right)$$

$$= -2.303 \times \frac{16}{32} \times 8.2 \times 10^{-2} \times 300 \times \log \left(\frac{25}{2.5} \right)$$

$$= -28.32 \text{ L atm}$$

Hence, work done by the system = 28.32 L atm.

10. (b) : $\Delta H = nC_p \Delta T$ [$n = 2, C_p = 5R/2$]

$$\Delta T = (125 - 225)^\circ\text{C} = -100^\circ\text{C} = -100 \text{ K}$$

$$\Delta H = 2 \times \frac{5R}{2} (-100) = -500R$$

11. (d) : At equilibrium, $\Delta G = 0, \Delta G^\circ \neq 0$. For a reaction to be spontaneous, the free energy should decrease.

12. (d) : Endothermic reactions are favoured at higher temperature and exothermic reactions are favoured at lower temperature.

For endothermic reaction, $\Delta H = +ve$

For exothermic reaction, $\Delta H = -ve$

13. (b)

14. (a) : There is decrease in entropy for an ordered state.

15. $V_1 = 300 \text{ cm}^3 = 300 \times 10^{-3} \text{ L} = 0.3 \text{ L}, V_2 = 2.5 \text{ L}$

$$T = 300 \text{ K}, P = 1.9 \text{ atm}$$

$$w = -P\Delta V = -1.9(2.5 - 0.3)$$

$$= -1.9 \times 2.2 = -4.18 \text{ L atm}$$

$$\text{As, } 1 \text{ L atm} = 101.33 \text{ J}$$

$$\therefore -4.18 \text{ L atm} = -4.18 \times 101.33 \text{ J} = -423.56 \text{ J}$$

OR

$$V_1 = 500 \text{ cm}^3 = 0.5 \text{ L}, P = 1.216 \times 10^5 \text{ Pa} = 1.2 \text{ atm}$$

$$w = 36.50 \text{ J} = 0.36 \text{ L-atm}$$

$$w = -P\Delta V$$

$$0.36 = -1.2 \times (V_2 - 0.5)$$

$$\frac{0.36}{1.2} = -(V_2 - 0.5)$$

$$0.3 = -V_2 + 0.5$$

$$\Rightarrow V_2 = 0.2 \text{ L} = 200 \text{ cm}^3$$

16. Maximum work is obtained from a system when :

- (i) Any change taking place in it is thermodynamically reversible.
- (ii) The change in the system takes place in an infinite number of steps.
- (iii) The driving force of the change is infinitesimally greater than the opposing force.
- (iv) The system is in mechanical equilibrium with its surroundings.

17.

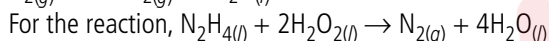
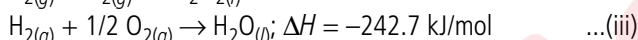
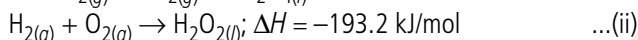
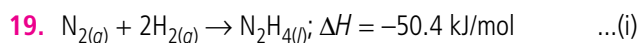
	Isothermal process	Adiabatic process
1.	The temperature of the system remains constant ($\Delta T = 0$).	The temperature of the system increases or decreases ($\Delta T \neq 0$).
2.	There is an exchange of heat between the system and its surroundings.	There is no exchange of heat between the system and its surroundings.
3.	The internal energy of the system remains constant ($\Delta E = 0$).	The internal energy of the system increases or decreases ($\Delta E \neq 0$).
4.	The system is not thermally isolated from its surroundings.	The system is thermally isolated from its surroundings.

$$18. w = -P_{\text{ext}} \Delta V = -P_{\text{ext}} (V_2 - V_1)$$

$$w = 44.9 \text{ L atm}, V_1 = 20 \text{ L}, V_2 = 8 \text{ L}$$

$$44.9 \text{ L atm} = -P_{\text{ext}} (8 \text{ L} - 20 \text{ L}) = P_{\text{ext}} \times 12 \text{ L}$$

$$P_{\text{ext}} = \frac{44.9 \text{ L atm}}{12 \text{ L}} = 3.74 \text{ atm}$$



by applying, $4 \times (iii) - (i) - 2 \times (ii)$

$$\Delta_r H = 4 \times (-242.7) - (-50.4) - 2 \times (-193.2) = -534 \text{ kJ/mol}$$

20. Entropy is a measure of randomness or disorder of the system.

(a) Gas at lower pressure has greater randomness than at high pressure at the same temperature. Hence, entropy decreases, *i.e.*, ΔS is $-ve$.

(b) Molecules at higher temperature have greater randomness than at lower temperature (at the same pressure). Thus, H_2O (at 330 K, 1 atm) will have higher entropy. (ΔS is $+ve$)

(c) Reactant is solid and all the products are gases. So, ΔS is $+ve$.

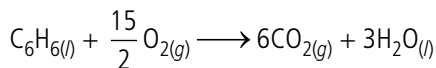
OR

Forward reaction will be endothermic. Thus, energy factor opposes the backward reaction. As backward reaction is spontaneous, randomness factor must favour, *i.e.*, ΔS will be positive for backward reaction. Hence ΔS will be negative for forward reaction. As forward reaction is non-spontaneous, ΔG is positive.

21. Molar heat of combustion at constant volume, *i.e.*,

$$\Delta U = \frac{-22.3}{0.532} \times 78 \text{ kJ mol}^{-1} = -3269.55 \text{ kJ mol}^{-1}$$

Equation of combustion is



$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2}$$

We know, $\Delta H = \Delta U + \Delta n_g RT$

$$= -3269.55 + \left(-\frac{3}{2}\right)(8.314 \times 10^{-3}) \times 353$$

$$\approx -3274 \text{ kJ mol}^{-1}$$

22. (i) (a) Specific heat capacity (c)

$$= \frac{\text{Heat absorbed by the substance}}{\text{Mass of the substance} \times \text{Rise in temperature}}$$

$$c = \frac{221.4 \text{ J}}{30 \text{ g} (18^\circ\text{C} - 15^\circ\text{C})} = \frac{221.4}{30 \times 3} \text{ J g}^{-1}\text{C}^{-1} = 2.46 \text{ J g}^{-1}\text{C}^{-1}$$

(b) Molar heat capacity, $c_m = \text{Specific heat} \times \text{Molar mass}$

Therefore, c_m (ethanol) = $2.46 \times 46 = 113.2 \text{ J mol}^{-1}\text{C}^{-1}$

(ii) It is a spontaneous process. Though, the enthalpy change is zero but ΔS is $+ve$. Hence, in equation, $\Delta G = \Delta H - T\Delta S$, the term $T\Delta S$ will be negative, then ΔG becomes $-ve$.

OR

Consider ' n ' moles of an ideal gas enclosed in a cylinder at temperature T . When the volume of the gas increases by an infinitesimal amount dV in a single step, the small quantity of work done is given by,

$$dw = -P_{\text{ext}} dV \quad \dots(i)$$

Because the expansion is reversible, the pressure of the gas is greater by a very small amount dP than P_{ext} .

$$\text{Hence, } P - P_{\text{ext}} = dP \text{ or } P_{\text{ext}} = P - dP \quad \dots(ii)$$

Combining eq (i) and (ii) we get

$$dw = -(P - dP)dV = -PdV + dP \cdot dV$$

Neglecting the product $dP \cdot dV$ which is very small, we get,

$$dw = -PdV \quad \dots(iii)$$

$$\int_1^2 dw = - \int_{V_1}^{V_2} PdV$$

$$w_{\text{max}} = - \int_{V_1}^{V_2} PdV \quad \dots(iv)$$

Ideal gas equation for n moles is $PV = nRT$

$$w_{\text{max}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

Since expansion is isothermal, T is constant

$$w_{\text{max}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\begin{aligned}
 &= -nRT (\ln V_2 - \ln V_1) \\
 &= -nRT \ln \left(\frac{V_2}{V_1} \right) = -2.303 nRT \log \left(\frac{V_2}{V_1} \right)
 \end{aligned}$$

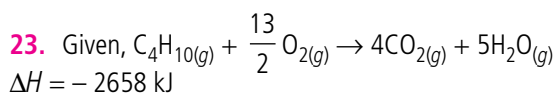
According to Boyle's law; $P_1 V_1 = P_2 V_2$

$$\text{or } \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\text{So } w_{\max} = -2.303 nRT \log \left(\frac{P_1}{P_2} \right)$$

Since number of moles, $n = 2$

$$\begin{aligned}
 w_{\max} &= -2.303 \times 2RT \log \left(\frac{P_1}{P_2} \right) \\
 &= -4.606RT \log \left(\frac{P_1}{P_2} \right)
 \end{aligned}$$



Molecular weight of $C_4H_{10} = 58 \text{ g/mol}$

58 g of butane on combustion produces 2658 kJ heat

$$\begin{aligned}
 \therefore 11.2 \text{ kg of butane will produce } &\frac{2658}{58} \times 11.2 \times 10^3 \text{ kJ} \\
 &= 513268.97 \text{ kJ heat}
 \end{aligned}$$

The family needs 20,000 kJ of energy per day

$$\therefore \text{Number of days} = \frac{513268.97 \text{ kJ}}{20000} = 25.66 \text{ days}$$

OR

1 mole (or 78 g) of benzene requires energy for vapourisation = 30.8 kJ

$$\begin{aligned}
 \therefore 100 \text{ g benzene will require energy} &= \frac{30.8}{78} \times 100 \\
 &= 39.49 \text{ kJ}
 \end{aligned}$$

200 W electric heater gives energy 200 J per second

$$(\because 1 \text{ h} = 1 \text{ J sec}^{-1})$$

$$\begin{aligned}
 \therefore \text{Time required for getting } 39.49 \text{ kJ of energy} \\
 &= \frac{39.49 \times 1000}{200} = 197.45 \text{ sec}
 \end{aligned}$$

24. $T_{\text{system}} = 130^\circ\text{C} = 130 + 273 \text{ K} = 403 \text{ K}$,

$$T_{\text{surr}} = 32^\circ\text{C} = 32 + 273 \text{ K} = 305 \text{ K}$$

$$q_{\text{system}} = -340 \text{ J}, q_{\text{surr}} = +340 \text{ J}$$

$$(i) \Delta S_{\text{system}} = \frac{q_{\text{system}}}{T_{\text{system}}} = \frac{-340 \text{ J}}{403 \text{ K}} = -0.84 \text{ J K}^{-1}$$

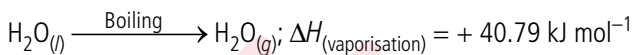
$$(ii) \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{+340 \text{ J}}{305 \text{ K}} = +1.11 \text{ J K}^{-1}$$

$$(iii) \Delta S_{\text{total}} \text{ or } \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} \\ = -0.84 \text{ J K}^{-1} + 1.11 \text{ J K}^{-1} = 0.27 \text{ J K}^{-1}$$

- 25.** (i) (a) Irreversible (b) Irreversible
 (c) Irreversible (d) Reversible

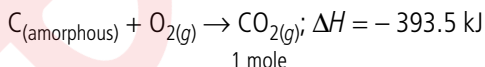
(ii) In an ideal gas, there are no intermolecular forces of attraction. Hence, no energy is required to overcome these forces. Moreover, when a gas expands against vacuum, work done is zero as $P_{\text{ex}} = 0$. Hence, internal energy of the system does not change *i.e.*, there is no absorption or evolution of heat.

26. (a) **Enthalpy or heat of vaporisation** : It is the enthalpy change in converting 1 mole of the substance from liquid state to gaseous state (or vapour state) at its boiling point.

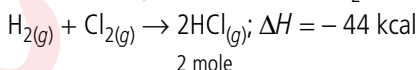


Enthalpy of vaporisation of a liquid gives an idea about the strength of intermolecular forces operating between the molecules of the liquid.

(b) **Enthalpy or heat of formation** : It is the amount of heat evolved or absorbed when 1 mole of the substance is directly obtained from its constituent elements, in their most stable states.



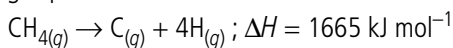
Thus, enthalpy of formation of CO_2 is -393.5 kJ .



Thus, enthalpy of formation of HCl is not -44 kcal but it is

$$-\frac{44}{2} = -22 \text{ kcal.}$$

(c) **Enthalpy of atomisation** : It is the enthalpy change in breaking 1 mole of bonds completely to obtain atoms in the gas phase.



27. (a) Since, the given process is in equilibrium, $\Delta G = 0$

Putting this value in the relationship,

$$\Delta G = \Delta H - T\Delta S, \text{ then,}$$

$$0 = \Delta H - T\Delta S \text{ or } T\Delta S = \Delta H \text{ or } \Delta S = \frac{\Delta H}{T}$$

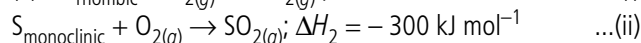
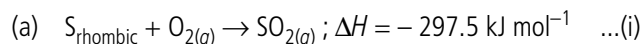
$$\Delta H = 6.0 \text{ kJ mol}^{-1} = 6000 \text{ J mol}^{-1} \text{ and } T = 0^\circ\text{C} = 273 \text{ K}$$

$$\therefore \Delta S = \frac{6000 \text{ J mol}^{-1}}{273 \text{ K}} = 21.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

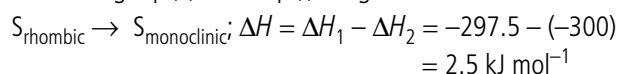
(b) Heat capacity of the system is defined as the quantity of heat required to raise the temperature of the system by one degree. this is denoted by C_v (at constant volume) and C_p (at constant pressure). So, heat capacity = $\frac{dq}{dT}$.

(c) The heat of neutralisation of a strong acid and a strong base is 57 kJ. When the acid is weak, it ionises and for complete ionisation it absorbs heat from the system. Thus, the net heat evolved during the complete neutralisation will be less than 57 kJ. The heat required for dissociation of one mole of weak electrolyte is referred as heat of ionisation.

OR



Subtracting eq. (ii) from eq. (i) we get



$$(b) 5.6 \text{ dm}^3 \text{ of a gas at STP} = \frac{5.6}{22.4} = 0.25 \text{ mol}$$

For 10° rise in temperature, 0.25 moles of the gas at constant volume requires heat = 52.25 J

\therefore For 1° rise in temperature, 1 mole of the gas at constant volume requires heat = $\frac{52.25}{10 \times 0.25} = 20.9 \text{ J}$

$$\therefore C_V = 20.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_P = C_V + R = 20.9 + 8.314 = 29.214 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\gamma = \frac{C_P}{C_V} = \frac{29.214}{20.9} = 1.4$$

\therefore The atomicity of gas is diatomic.

$$\begin{aligned} 28. (a) \Delta S &= 2.303nR \log_{10} \left(\frac{T_2}{T_1} \right) \\ &= 2.303 \times \frac{1000}{18} \times 18 \times \log_{10} \left(\frac{373}{273} \right) \\ &= 311 \text{ cal K}^{-1} \end{aligned}$$

$$\begin{aligned} (b) \Delta S_{\text{reservoir}} &= \frac{\Delta q}{T} \\ \Delta q &= mc\Delta T = 1000 \times 1 \times 100 = 10^5 \text{ cal} \\ \Delta S &= \frac{-10^5}{373} = -268.1 \text{ cal K}^{-1} \end{aligned}$$

$$(c) \Delta S_{\text{universe}} = \Delta S_{\text{water}} + \Delta S_{\text{reservoir}} = 312 - 268.1 = 43.9 \text{ cal K}^{-1}$$

(d) $\Delta S > 0$, the process will be spontaneous.

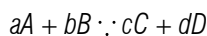
OR

(a) (i) **Second law of thermodynamics** : It states that the total entropy of the system and its surrounding (universe) increases in a spontaneous process.

$$\Delta S_{\text{universe}} = \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

(ii) **First law of thermodynamics** : According to first law of thermodynamics, energy can neither be created nor be destroyed although it may be changed from one form to another.

(b) Consider the following reversible reaction,



$$\text{The reaction quotient } Q \text{ is } Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ or } Q_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

The free energy change ΔG for the reaction is

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

At equilibrium, $\Delta G = 0$ and $Q = K$, the equation becomes

$$0 = \Delta G^\circ + RT \ln K$$

$$\text{Hence, } \Delta G^\circ = -RT \ln K = -2.303 RT \log K$$

29. As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\begin{aligned} \Delta H_f^\circ &= \Delta H_f^\circ(\text{product}) - \Delta H_f^\circ(\text{reactant}) \\ \therefore \Delta H^\circ &= [6\Delta H_f^\circ(\text{CO}_2) + 6\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + 6\Delta H_f^\circ(\text{O}_2)] \\ &= [6 \times (-393.5) + 6 \times (-285.8)] - [(-1274.5) + 6 \times 0] \\ &= -2361.0 - 1714.8 + 1274.5 = -2801.3 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= S^\circ(\text{product}) - S^\circ(\text{reactant}) \\ \Delta S^\circ &= [6S^\circ(\text{CO}_2) + 6S^\circ(\text{H}_2\text{O})] - [S^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + 6S^\circ(\text{O}_2)] \\ &= [6 \times (213.6) + 6 \times (69.9)] - [(212.1) + 6 \times (205.0)] \\ &= [1281.6 + 419.4] - [212.1 + 1230] = 258.9 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

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

$$\Delta H^\circ = -2801.3 \text{ kJ} = 2801300 \text{ J mol}^{-1}, \Delta S^\circ = 258.9 \text{ JK}^{-1} \text{ mol}^{-1}, T = 298 \text{ K}$$

$$\therefore \Delta G^\circ = -2801300 - 298 \times (258.9) = -2878.4 \text{ kJ mol}^{-1}$$

OR

(a) For a non-spontaneous reaction $\Delta G = +ve$

$$\text{As } \Delta G = \Delta H - T\Delta S$$

$$\therefore \Delta H - T\Delta S \text{ should be } +ve \text{ or } \Delta H > T\Delta S$$

which is possible if $T < \frac{\Delta H}{\Delta S}$

$$\text{Given, } \Delta H = 30 \times 10^3 \text{ J mol}^{-1}; \Delta S = 70 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore T < \frac{30 \times 10^3}{70} \Rightarrow T < 428.57 \text{ K}$$

$$\begin{aligned} (b) \text{CH}_2 = \text{CH}_2 + 3\text{O}_2 &\rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \\ \Delta H &= [\text{B.E. (C=C)} + 4 \text{ B.E. (C-H)} + 3 \text{ B.E. (O=O)}] \\ &\quad - [2 \times 2 \text{ B.E. (C=O)} + 2 \times 2 \text{ B.E. (O-H)}] \\ &= [619 + 4 \times 414 + 3 \times 499] - [4 \times 724 + 4 \times 460] \\ &= [619 + 1656 + 1497] - [2896 + 1840] \\ &= 3772 - 4736 = -964 \text{ kJ mol}^{-1} \end{aligned}$$

$$30. (i) \text{ We know, } \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{m.p.}}$$

$$= \frac{6 \times 1000}{273} = 21.98 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$(ii) \Delta S = 2.303 nR \log \left(\frac{V_2}{V_1} \right)$$

$$= 2.303 \times 2 \times 8.314 \log \left(\frac{100}{10} \right) = 38.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

(iii) $T = 25^\circ\text{C} = 273 + 25 = 298 \text{ K}$, $\Delta H^\circ = -238.6 \text{ kJ}$
 $\Delta S^\circ = +36.7 \text{ J K}^{-1}$;

$$\Delta S_{\text{surr}} = \frac{-\Delta H^\circ}{T} = -\left(\frac{-238.6 \text{ kJ}}{298 \text{ K}}\right)$$
$$= 0.8006 \text{ kJ K}^{-1} = 800.6 \text{ J K}^{-1}$$

$$\Delta S_{\text{sys}} = \Delta S^\circ = +36.7$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$= +36.7 + 800.6 = +837.3 \text{ J K}^{-1}$$

Since $\Delta S > 0$, the reaction is spontaneous.

(iv) $\Delta_f H^\circ = -238.9 \text{ kJ / mol} = -238900 \text{ J/mol}$

$$\Delta S_{\text{surr}} = \frac{-\Delta H^\circ}{T} = -\left(\frac{-238900}{298}\right) = 801.67 \text{ J K}^{-1}$$

(v) $\Delta G^\circ = 2879 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -210 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 0.210 \text{ kJ K}^{-1} \text{ mol}^{-1}$; $T = 298 \text{ K}$

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

$$2879 = \Delta H^\circ - (298 \times -0.210)$$

$$2879 = \Delta H^\circ + 62.58$$

$$\Delta H^\circ = 2879 - 62.58 = 2816.42 \text{ kJ}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T} = -\frac{2816.42}{298} = -9.45 \text{ kJ K}^{-1}$$

© MXTG

