

## Detailed Solutions

### Gibbs Free Energy — DPP-4 (Numerical)

**Q1. Standard enthalpy & entropy for oxidation of  $\text{NH}_3$  at 298 K are  $-382.64 \text{ kJ mol}^{-1}$  and  $-145.6 \text{ J mol}^{-1} \text{ K}^{-1}$ . Find  $\Delta G^\circ$  at 298 K.**

- (1) **Incorrect** Compute  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -382.64 - 298(-0.1456) \approx -339.3 \text{ kJ}$ .
- (2) **Correct**  $-339.3 \text{ kJ}$  matches the calculation.
- (3) **Incorrect** Too large in magnitude.
- (4) **Incorrect** Way off.

**Final Answer:** (2)  $-339.3 \text{ kJ mol}^{-1}$

**Q2. At  $27^\circ\text{C}$  (300 K),  $\Delta G = -26 \text{ kcal}$ ,  $\Delta S = -60 \text{ cal K}^{-1}$ . Find  $\Delta H$ .**

- (1) **Correct**  $\Delta H = \Delta G + T\Delta S = -26 + 300(-0.06) = -44 \text{ kcal}$ .
- (2) **Incorrect** Uses wrong sign.
- (3) **Incorrect** Wrong sign and value.
- (4) **Incorrect** Arithmetic error.

**Final Answer:** (1)  $-44 \text{ kcal}$

**Q3. At  $25^\circ\text{C}$  (298 K),  $\Delta H = -11.7 \times 10^3 \text{ J mol}^{-1}$ ,  $\Delta S = -105 \text{ J mol}^{-1} \text{ K}^{-1}$ . Nature of reaction?**

- (1) **Incorrect**  $\Delta G = -11.7 - 298(-0.105) \approx +19.6 \text{ kJ} > 0$ .
- (2) **Correct**  $\Delta G > 0$  hence non-spontaneous.
- (3) **Incorrect** Would require  $\Delta G = 0$ .
- (4) **Incorrect** We *can* say from given data.

**Final Answer:** (2) Non-spontaneous

**Q4.  $\Delta H = -2.5 \times 10^3 \text{ cal}$ ,  $\Delta S = 7.4 \text{ cal K}^{-1}$  at 298 K. Predict nature.**

- (1) **Correct**  $\Delta G = -2500 - 298 \cdot 7.4 \approx -4705 \text{ cal} < 0$ .
- (2) **Incorrect** Reversible means  $\Delta G = 0$ .
- (3) **Incorrect** “Irreversible” isn’t the spontaneity label; sign says spontaneous.
- (4) **Incorrect** Not supported.

**Final Answer:** (1) Spontaneous

**Q5. At 400 K which is spontaneous *and* endothermic?**

- (1) **Incorrect**  $\Delta H < 0$  (exo).
- (2) **Incorrect**  $\Delta H < 0$  (exo) and  $\Delta S < 0$ .
- (3) **Correct** Endothermic  $\Delta H > 0$  and  $\Delta S > 0 \Rightarrow \Delta G = \Delta H - T\Delta S < 0$  at high  $T$ .
- (4) **Incorrect**  $\Delta H > 0$  but  $\Delta S < 0 \Rightarrow$  never spontaneous.

Final Answer: (3)

Q6.  $\text{Ag}_2\text{O}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$  is at equilibrium when  $\Delta G^\circ = 0$ . Given  $\Delta H = 30.56 \text{ kJ mol}^{-1}$ ,  $\Delta S = 0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$ . Find  $T$ .

- (1) **Correct**  $T = \Delta H / \Delta S = 30.56 / 0.066 \approx 463 \text{ K} \approx 462.1 \text{ K}$ .
- (2) **Incorrect**
- (3) **Incorrect**
- (4) **Incorrect**

Final Answer: (1)  $\approx 462.1 \text{ K}$

Q7. Same reaction with  $\Delta H = 30.56 \text{ kJ mol}^{-1}$ ,  $\Delta S = 66 \text{ J K}^{-1} \text{ mol}^{-1}$ .  $T$  for  $\Delta G^\circ = 0$ ?

- (1) **Incorrect**
- (2) **Incorrect**
- (3) **Correct**  $T = 30.56 / 0.066 \approx 463 \text{ K}$ .
- (4) **Incorrect**

Final Answer: (3) 463 K

Q8.  $\frac{1}{2}\text{A}_2 + \frac{1}{2}\text{B}_2 \rightarrow \text{AB}_2$ ,  $\Delta H = -20 \text{ kJ}$ ;  $S^\circ(\text{A}_2, \text{B}_2, \text{AB}_2) = (60, 40, 50) \text{ J K}^{-1} \text{ mol}^{-1}$ . Temperature for equilibrium?

- (1) **Incorrect**
- (2) **Incorrect**
- (3) **Incorrect**
- (4) **Incorrect**

Final Answer: Note:  $\Delta S = 50 - (0.5 \cdot 60 + 0.5 \cdot 40) = 0$ , so  $\Delta G^\circ = \Delta H^\circ = -20 \text{ kJ}$  (independent of  $T$ ). No finite  $T$  makes  $\Delta G^\circ = 0$ . The question data are inconsistent with the options.

Q9. 1 mol water at  $100^\circ\text{C}$ , 1 atm  $\rightarrow$  steam at same  $T, P$ .  $\Delta G$ ?

- (1) **Incorrect** Latent heat value, not  $\Delta G$ .
- (2) **Incorrect**
- (3) **Incorrect**
- (4) **Correct** Phase equilibrium at  $100^\circ\text{C} \Rightarrow \Delta G = 0$ .

Final Answer: (4) 0

Q10.  $\text{Br}_2(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{BrCl}(\text{g})$ ;  $\Delta H = 30 \text{ kJ}$ ,  $\Delta S = 105 \text{ J K}^{-1}$ .  $T$  for equilibrium?

- (1) **Correct**  $T = \Delta H / \Delta S = 30 / 0.105 \approx 285.7 \text{ K}$ .
- (2) **Incorrect**
- (3) **Incorrect**
- (4) **Incorrect**

Final Answer: (1) 285.7 K

Q11. Vaporization of water at 1 atm:  $\Delta H = 40.63 \text{ kJ mol}^{-1}$ ,  $\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ .  $T$  for  $\Delta G = 0$ ?

- (1) **Incorrect**
- (2) **Correct**  $T = 40.63/0.1088 \approx 373.4 \text{ K}$ .
- (3) **Incorrect**
- (4) **Incorrect**

Final Answer: (2) 373.4 K

Q12.  $\frac{1}{2}\text{X}_2 + \frac{3}{2}\text{Y}_2 \rightleftharpoons \text{XY}_3$ ,  $S^\circ(\text{X}_2, \text{Y}_2, \text{XY}_3) = (60, 40, 50) \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta H = -30 \text{ kJ}$ .  $T$  for equilibrium?

- (1) **Incorrect**
- (2) **Incorrect**
- (3) **Correct**  $\Delta S = 50 - (0.5 \cdot 60 + 1.5 \cdot 40) = -40 \text{ J K}^{-1}$ ,  $T = \frac{\Delta H}{\Delta S} = (-30)/(-0.04) = 750 \text{ K}$ .
- (4) **Incorrect**

Final Answer: (3) 750 K

Q13.  $\Delta H = 35.5 \text{ kJ}$ ,  $\Delta S = 83.6 \text{ J K}^{-1}$ . When spontaneous?

- (1) **Correct** Threshold  $T > \Delta H/\Delta S = 35.5/0.0836 \approx 425 \text{ K}$ .
- (2) **Incorrect**
- (3) **Incorrect**
- (4) **Incorrect**

Final Answer: (1)  $T > 425 \text{ K}$

Q14.  $\text{C}(\text{graphite}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ ;  $\Delta H = 170 \text{ kJ}$ ,  $\Delta S = 170 \text{ J K}^{-1}$ . Spontaneous at:

- (1) **Incorrect**
- (2) **Incorrect**
- (3) **Incorrect** Needs  $T > 1000 \text{ K}$ .
- (4) **Correct**  $T > 1000 \text{ K}$ , so 1110 K works.

Final Answer: (4) 1110 K

Q15.  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ ;  $\Delta H^\circ = +179.1 \text{ kJ}$ ,  $\Delta S^\circ = 160.2 \text{ J K}^{-1}$  at 298 K. Above which  $T$  is it spontaneous (assume const.  $\Delta H, \Delta S$ )?

- (1) **Incorrect**
- (2) **Incorrect**
- (3) **Incorrect**
- (4) **Correct**  $T > \Delta H/\Delta S = 179.1/0.1602 \approx 1118 \text{ K}$ .

Final Answer: (4) 1118 K

Q16.  $X_2O_4(l) \rightarrow 2XO_2(g)$ ;  $\Delta U = 2.1 \text{ kcal}$ ,  $\Delta S = 20 \text{ cal K}^{-1}$  at 300 K. Find  $\Delta G$ .

(1) **Incorrect**

(2) **Correct**  $\Delta n_g = 2$ ,  $\Delta H = \Delta U + \Delta n_g RT \approx 2.1 + 2(0.001987 \cdot 300) \approx 3.29 \text{ kcal}$ ;  $\Delta G = \Delta H - T\Delta S \approx 3.29 - 300(0.02) \approx -2.7 \text{ kcal}$ .

(3) **Incorrect**

(4) **Incorrect**

Final Answer: (2)  $\approx -2.7 \text{ kcal}$

Q17.  $2A(g) + B(g) \rightarrow 2C(g)$  at 298 K:  $\Delta U^\circ = -10 \text{ kJ}$ ,  $\Delta S^\circ = -45 \text{ J K}^{-1} \text{ mol}^{-1}$ . Find  $\Delta G^\circ$ .

(1) **Correct**  $\Delta n_g = 2 - (2 + 1) = -1$ ,  $\Delta H^\circ = \Delta U^\circ + \Delta n_g RT \approx -10 - 2.48 = -12.48 \text{ kJ}$ ;  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \approx -12.48 - 298(-0.045) \approx +0.93 \text{ kJ} \approx +930 \text{ J}$ .

(2) **Incorrect**

(3) **Incorrect**

(4) **Incorrect**

Final Answer: (1)  $\approx +930 \text{ J mol}^{-1}$

Q18.  $\Delta S_{\text{total}} = -40 \text{ kJ K}^{-1} \text{ mol}^{-1}$ ,  $\Delta H_{\text{sys}} = 2000 \text{ kJ mol}^{-1}$ ,  $T = 400 \text{ K}$ . Find  $\Delta S_{\text{system}}$ .

(1) **Correct**  $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T = -2000/400 = -5 \text{ kJ K}^{-1}$ ; so  $\Delta S_{\text{sys}} = \Delta S_{\text{total}} - \Delta S_{\text{surr}} = -40 - (-5) = -35$ .

(2) **Incorrect**

(3) **Incorrect**

(4) **Incorrect**

Final Answer: (1)  $-35 \text{ kJ K}^{-1} \text{ mol}^{-1}$

Q19.  $\Delta H = -x \text{ cal mol}^{-1}$  at 298 K and reaction is spontaneous. About  $\Delta S$  at 298 K:

(1) **Incorrect** Would make  $\Delta S < -x/298$ , giving  $\Delta G > 0$ .

(2) **Correct** Can be negative but must satisfy  $\Delta S > -x/298$  (i.e., numerically smaller than  $x/298$ ).

(3) **Incorrect** It *can* be negative if small in magnitude.

(4) **Incorrect** It can also be positive.

Final Answer: (2)