- please answer all **5 questions** in the spaces provided
- you have **two hours** to write this test
- a calculator and the equation sheets provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

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1. 25.0 L of ideal gas initially at 4.00 bar and 300 K expands isothermally against an external pressure of 1.00 bar to a final volume of 100.0 L.

   a) Show $w = -7500$ J.

   $$w = -\int P_{ext} \, dV \;\overset{const.}{=}\; -P_{ext}\int_{V_i}^{V_f} dV = -P_{ext}(V_f - V_i)$$

   $$W = -(1.00\ bar)(100.0 - 25.0)\ L$$
   $$= -75.0\ L\ bar$$
   $$= -(75.0\ L\ bar)(10^{-3} m^3 L^{-1})(10^5 Pa\ bar^{-1})$$
   $$\boxed{W = -7500\ J}$$

   b) Show $\Delta S = 46.2$ J K^{-1}.

   ideal gas: $dS = \dfrac{C_V}{T} dT + \dfrac{nR}{V} dV$

   const. T: $dS = \dfrac{nR}{V} dV$

   $$\Delta S = \int \frac{nR}{V} dV = nR \ln\left(\frac{V_f}{V_i}\right)$$
   $$= (4.009\ mol)(8.314\ JK^{-1}mol^{-1})\ln\left(\frac{100.0L}{25.0L}\right) = \boxed{46.2\ J\ K^{-1}}$$

   $$\left(\begin{array}{l} n = \dfrac{P_i V_i}{RT} \\[2mm] = \dfrac{(4.00\ bar)(25.0 L)}{(0.08314\ \frac{L\,bar}{K\,mol})(300\ K)} \\[2mm] n = 4.009\ mol \end{array} \right)$$

   c) Calculate q, ΔU and ΔH.

   isothermal ideal gas:
   $$\boxed{\begin{array}{l}\Delta U = 0 \\ \Delta H = 0\end{array}}$$

   $$\Delta U = q + w = 0$$
   $$\boxed{q = -w = +7500J}$$

   d) Use the values of q and ΔS to prove the expansion is spontaneous.

   $$\int \frac{dq}{T} \overset{(isothermal)}{=} \frac{1}{T}\int dq = \frac{q}{T} = \frac{7500\ J}{300\ K} = 25\frac{J}{K} \neq \Delta S \left(= \int \frac{dq_{rev}}{T}\right)$$

   $$\therefore q \neq q_{rev}$$

   $$\underline{\underline{OR}}\quad notice \quad q < T\Delta S$$
   $$(7500\ J < 13860J)_1$$

   $$\left(\begin{array}{l} \underline{\underline{OR}}\ (\Delta S + \Delta S_{sur})_{isolated} \\[2mm] = \left(46.2 + \frac{-7500}{300}\right)\frac{J}{K} \\[2mm] = +21.2\frac{J}{K} > 0 \end{array} \right)$$

2. a) For a reversible Carnot engine: $\dfrac{q_C}{T_C} + \dfrac{q_H}{T_H} = 0$. How did this result help lead to the discovery of entropy?

$\dfrac{q_c}{T_c} + \dfrac{q_H}{T_H}$ is for one engine cycle: $\displaystyle\oint \dfrac{dq_{rev}}{T} = 0$

suggesting that S defined by $dS = \dfrac{dq_{rev}}{T}$ is

a state function : $\displaystyle\oint \dfrac{dq_{rev}}{T} = \oint dS = S_i - S_i = 0$

b) The Lingan Station on Cape Breton generates one quarter of Nova Scotia's electricity. 4000 tons of coal are burned per day, providing 1.2×10^{14} J of heat (q_H) at 570 K (T_H) to run steam turbines producing 5×10^{13} J ($-w$) of electrical work per day. Seawater at 290 K (T_C) is used for cooling.

i) Calculate the efficiency ε of the turbines.

$\varepsilon = \dfrac{-w}{q_H} = \dfrac{\text{work done on surroundings}}{\text{heat absorbed at } T_H}$

$= \dfrac{5 \times 10^{13}\,J}{1.2 \times 10^{14}\,J} = \boxed{0.42}$ (42 % efficient)

ii) Are the turbines operating reversibly? Justify your answer.

if reversible $\varepsilon_{rev} = 1 - \dfrac{T_c}{T_H} = 1 - \dfrac{290K}{570K} = 0.491$

turbines less efficient than reversible turbines

$\Rightarrow$ not reversible

iii) How much heat is absorbed by the seawater per day?

engine cycle $\Delta U = \displaystyle\oint dU = U_i - U_i = q + w = 0$

$q_H + q_c + w = 0$ \qquad $q_c = -q_H - w$

$q_c = -1.2 \times 10^{14}\,J - (-5 \times 10^{13}\,J) = -7 \times 10^{13}\,J$

$-q_c = \boxed{7 \times 10^{13}\,J}$ per day absorb by seawater

iv) Water boils at 1 bar and 373 K. Why is high-pressure steam (50 bar at 570 K) used to run the turbines?

$\varepsilon_{rev} = 1 - \dfrac{T_c}{T_H}$ \qquad increasing T_H from 373 K to 570K improves efficiency

3. Calcium carbonate ($CaCO_3$) is found in nature in two different crystalline forms: aragonite (found in the Aragon region of Spain) and calcite. Calorimetric data at 25 °C and 1 bar:

$$\Delta H_{fm}°(\text{aragonite}) = -1207.13 \text{ kJ mol}^{-1} \qquad S_m°(\text{aragonite}) = 88.7 \text{ J K}^{-1} \text{ mol}^{-1}$$
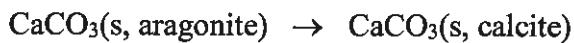$$\Delta H_{fm}°(\text{calcite}) = -1206.92 \text{ kJ mol}^{-1} \qquad S_m°(\text{calcite}) = 92.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

a) The values of $S_m°(\text{aragonite})$ and $S_m°(\text{calcite})$ are absolute entropies, not entropies of formation. How are absolute entropies measured?

$$S_m°(T) = S_m°(T=0) + \int_0^T \frac{dq_{rev}}{T}$$
$$= 0 + \int_0^T \frac{C_{pm}}{T} dT$$

measure the heat capacities of calcite and aragonite, integrate $\frac{C_{pm}}{T}$ as a function of T

b) Calculate $\Delta H_R°$, $\Delta S_R°$ and $\Delta G_R°$ at 25 °C for the reaction

$$CaCO_3(\text{s, aragonite}) \rightarrow CaCO_3(\text{s, calcite})$$

$$\Delta H_R° = \Delta H_{fm}°(\text{calc.}) - \Delta H_{fm}°(\text{arag.}) = -1206.92 - (-1207.13) \frac{kJ}{mol}$$
$$\Delta H_R° = 0.21 \text{ kJ mol}^{-1} = \boxed{210 \text{ J mol}}$$
$$\Delta S_R° = S_m°(\text{calc.}) - S_m°(\text{arag.}) = (92.9 - 88.7) \frac{J}{K mol} = \boxed{4.2 \frac{J}{K mol}}$$
$$\Delta G_R° = \Delta H_R° - \Delta(TS)_R = \Delta H_R° - T\Delta S_R° = [210 - (298.15)(4.2)] \frac{J}{mol}$$
$$= \boxed{-1040 \text{ J mol}^{-1}}$$

c) Which form of calcium carbonate is stable at 25 °C and 1 bar? Justify your answer.

calcite
$$\Delta G_R° < 0 \quad (\text{fixed } T, P)$$

d) To decide which form of calcium carbonate is more stable, why not just wait to see if aragonite spontaneously converts to calcite or calcite spontaneously converts to aragonite?

Could take billions of years for aragonite to convert to the more stable calcite (activation energies for solid state reactions are large, leading to very slow reaction rates)

e) This question illustrates that calorimetric data can be used to predict whether or not a reaction is spontaneous *without carrying out the reaction*. Why is the result important?

Some reactions might appear to be nonspontaneous because they are never observed, but are very slow. Also, some reactions are difficult to perform (may have side reactions, for example). 3

$$\Delta G_R^\circ = -2\Delta G_{fm}^\circ(HgO, s)$$

4. This question refers to the reaction $2HgO(s) = 2Hg(l) + O_2(g)$ with equilibrium constant $K = p_{O2}$.

Experiments give $\ln K = 26.05 - (21850\ K)\dfrac{1}{T}$ for $\ln K$ as a function of $1/T$.

a) Show $\Delta H_R^\circ = 181.7\ kJ\ mol^{-1}$, independent of the temperature.

$$\Delta H_R^\circ = -R\frac{d\ln K}{d\frac{1}{T}} = -R\frac{d}{d\frac{1}{T}}\left[26.05 - (21850K)\frac{1}{T}\right]$$

$$= -R(-21850K) = -(8.314\ J\ K^{-1}mol^{-1})(-21850K)$$

$$= -181700\ J\ mol^{-1}$$

b) Calculate K at 25 °C. Use the value of K to calculate $\Delta G_{fm}^\circ(HgO, s)$ at 25 °C.

$$\ln K_{25c} = 26.05 - \frac{21850\ K}{298.15K} = -47.24$$

$$\boxed{K_{25c} = 3.062 \times 10^{-21}} = e^{-\Delta G_R^\circ/RT}$$

$$\ln K_{25c} = -\Delta G_R^\circ/RT \qquad \Delta G_R^\circ = -RT\ln K$$

$$\Delta G_R^\circ = -(8.314\ J\ K^{-1}mol^{-1})(298.15)(-47.24) = \boxed{117100\ J\ mol^{-1}}$$

$$\Delta G_{fm}^\circ(HgO, s) = \tfrac{1}{2}\Delta G_R^\circ = \boxed{58540\ J\ mol^{-1}}$$

c) Show $HgO(s)$ is stable in air ($p_{O2} = 0.20$ bar) at 25 °C.

$$Q = p_{O2} = 0.20\ bar \ggg K_{25c}$$

d) Calculate the decomposition temperature of $HgO(s)$ heated in air.* ← in air

$$Q = K \text{ at equilibrium at } Q = p_{O2} = 0.20\ bar$$

$$\ln K = \ln 0.20 = 26.05 - \frac{21850\ K}{T_{decomp}}$$

$$\frac{21850K}{T_{decomp}} = 26.05$$

$$\boxed{T_{decomp} = 839\ K \quad (566\ °C)}$$

*This vivid chemical reaction (frequently performed by medieval alchemists for their research sponsors) converts bright red mercuric oxide to oxygen and shiny droplets of quicksilver (liquid mercury).

5.   **a)** At 400 °C the equilibrium constant for the reaction $N_2(g) + 3H_2(g) = 2NH_3(g)$ is 0.00016.

A tank contains N_2, H_2 and NH_3 at 400 °C and respective pressures 4.00 bar, 2.00 bar, 0.050 bar. Show the gas mixture is not at equilibrium and give the direction of the spontaneous reaction.

$$Q = \frac{P_{NH_3}^2}{P_{N_2}\, P_{H_2}^3} = \frac{0.050^2}{4.00\,(2.00)^3} = 0.000078 < K$$

not at equilibrium (where $Q = K$)

$\boxed{Q < K}$ reaction to form $\boxed{\text{more } NH_3}$ is spontaneous

b) Changing variables converts the van der Waals equation from $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$

to $p_r = \dfrac{8}{3}\dfrac{T_r}{V_r - \dfrac{1}{3}} - \dfrac{3}{V_r^2}$ (eqn. 1).

i) Why is eqn. 1 a "universal' equation of state?

• holds for all gases

• no "human-defined" units (such as bar, K, L, mole)

• no "human-defined" physical constants (such as R)

ii) Use eqn. 1 to calculate the pressure in a tank containing CO_2 at 350 K and a molar volume of 0.120 L mol^{-1}. For CO_2: $p_c = 73.8$ bar, $V_{mc} = 0.0941$ L mol^{-1}, $T_c = 304$ K.

$$T_r = \frac{T}{T_c} = \frac{350\ K}{304\ K} = 1.151 \qquad V_r = \frac{V_m}{V_{mc}} = \frac{0.120\ L\,mol^{-1}}{0.0941\ L\,mol^{-1}} = 1.275$$

$$P_r = \frac{8}{3}\frac{1.151}{1.275 - \frac{1}{3}} - \frac{3}{1.275^2} = 1.414 = \frac{P}{P_c}$$

$$P = 1.414\, P_c = 1.414\,(73.8\ bar)$$

$$\boxed{P = 104\ bar}$$

iii) Why can eqn. 1 be unreliable if $T_r < 1$?

liquid might form

(van der Waals equations are for gases)