Chemistry 231 **Test 2** (23 November 2020) **Name:** ______________________

- please answer all **4 questions** in the spaces provided
- this is a **50-minute 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

$p_{ext} = p$

1. **a)** 75.0 L of helium (assumed to be an ideal gas) at 300 K and 2.00 bar is compressed isothermally and reversibly to a final pressure of 6.00 bar. Calculate q, w, ΔU and ΔS. *Hint*: $n = p_iV_i/RT$ = constant

$\boxed{\Delta U = 0}$ (isothermal ideal gas) $\left(\frac{V_f}{V_i} = \frac{P_i}{P_f}\right)$

moles of gas $\quad n = \frac{P_iV_i}{RT} = \frac{(2.00\text{ bar})(75.0\text{ L})}{(0.08314\text{ L bar K}^{-1}\text{mol}^{-1})(300\text{ K})} = 6.014\text{ mol}$

$$w = -\int P_{ext}\,dV = -\int p\,dV = -nRT\int \frac{1}{V}\,dV = -nRT\ln\left(\frac{V_f}{V_i}\right)$$

$$w = -(6.014\text{ mol})(8.314\text{ J K}^{-1}\text{mol}^{-1})(300\text{ K})\ln(2.00\text{ bar}/6.00\text{ bar})$$

$\boxed{w = 16{,}480\text{ J}}$ $\quad \boxed{q = -16{,}480\text{ J}}$ $(= \Delta U - w = q_{rev})$

$$\Delta S = \int \frac{1}{T}\,dq_{rev} = \frac{1}{T}\int dq_{rev} = \frac{-16480\text{ J}}{300\text{ K}} \boxed{\Delta S = -54.9\,\frac{\text{J}}{\text{K}}}$$

b) 75.0 L of helium (assumed to be an ideal gas) at 300 K and 2.00 bar is isothermally compressed to 6.00 bar using a constant 6.00 bar external pressure.

i) Calculate q, w, ΔU and ΔS.

from a:

$\Delta U = 0$	$\Delta S = -54.9\,\frac{\text{J}}{\text{K}}$

(U, S are state functions, so ΔU, ΔS are path-independent)

$$w = -\int P_{ext}\,dV = -P_{ext}\int dV = -P_{ext}\Delta V = -P_f(V_f - V_i)$$

$$w = -P_f\left(\frac{nRT}{P_f} - \frac{nRT}{P_i}\right) = -nRT\left(1 - \frac{P_f}{P_i}\right) \quad \boxed{q = -w = -30{,}000\text{ J}}$$

$$w = -(6.014\text{ mol})(8.314\text{ J K}^{-1}\text{mol}^{-1})(300\text{ K})\left(1 - \frac{6.00}{2.00}\right) = 30{,}000\text{ J}$$

ii) Use the values of q and ΔS (*not your equation sheets*!) to prove this compression is irreversible.

$$\int \frac{1}{T}\,dq = \frac{1}{T}\int dq = \frac{q}{T} = \frac{-30{,}000\text{ J}}{300\text{ K}} = -100.0\,\frac{\text{J}}{\text{K}} \neq \Delta S$$

$\therefore$ irreversible

(also: $\Delta S_{sys} + \Delta S_{surr}$
$= -54.9\,\frac{\text{J}}{\text{K}} + \frac{30000\text{ J}}{300\text{ K}} = +45.1\,\frac{\text{J}}{\text{K}} > 0$)

for one engine cycle

Q2. **a)** The analysis of reversible Carnot engines shows $\overbrace{\frac{q_C}{T_C} + \frac{q_H}{T_H}} = 0$. How did this result lead to the discovery of the entropy?

suggests $\oint_i^i \frac{dq_{rev}}{T} = 0$

$= S_i - S_i$

$\frac{dq_{rev}}{T}$ must be the differential of a state function

b) A heat engine operating with $T_C = 300$ K and $T_H = 500$ K absorbs 100 kJ heat at 500 K and does 20 kJ work on the surroundings. Is the engine operating reversibly? Justify your answer.

reversible-engine efficiency $\varepsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{300\,K}{500\,K} = 0.400$

actual engine efficiency $= \frac{-w}{q_H} = \frac{20\text{ kJ}}{100\text{ kJ}} = 0.200 < \varepsilon$

$\boxed{\text{not reversible} \quad \varepsilon < 1 - \frac{T_C}{T_H}}$

c) What is a heat pump? Why are these devices useful?

* a heat engine running in reverse
* work is done on the pump to remove heat from the T_C reservoir and add heat to the T_H reservoir
* used for space heating, refrigeration, air conditioning

d) The internal energy is conserved in physical and chemical processes: $\Delta U_{system} + \Delta U_{surroundings} = 0$. Is the entropy conserved in these processes? Explain briefly.

entropy is not conserved

spontaneous processes increase the entropy

$(\Delta S_{sys} + \Delta S_{surr})_{\text{spont. process}} > 0$

e) Burning hydrogen using pure oxygen produces a flame that is much hotter (*by about 1,000 K*!) than the flame produced by burning hydrogen in air. Why?

using pure oxygen, the exothermic combustion reaction heats up the $H_2O(g)$ product

using air, the combustion reaction heats up the $H_2O(g)$ product and inert N_2 (higher heat capacity)

→ lower temperature reached

Q3. **a)** Derive the thermodynamic equation of state: $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_T - p$

Hint: Start with $dU = TdS - pdV$. $\div dV_T$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p\underbrace{\cancel{\left(\frac{\partial V}{\partial V}\right)_T}}_{=1} = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

from $dA = -SdT - pdV$ get $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

b) For an ideal gas, prove $(\partial U/\partial V)_T = 0$.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial}{\partial T}\frac{nRT}{V}\right)_V - p = T\frac{nR}{V}\underbrace{\cancel{\left(\frac{\partial T}{\partial T}\right)_V}}_{1} - p = p - p = 0$$

c) For an ideal gas, prove $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$

Hint: $C_V = (\partial U/\partial T)_V$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\underbrace{\cancel{\left(\frac{\partial U}{\partial V}\right)_T}}_{0}\right]_V = 0$$

d) For an ideal gas undergoing a reversible process, rearranging the First Law ($dU = C_V dT = dq_{rev} - pdV$) gives

$$\frac{dq_{rev}}{T} = \frac{C_V}{T}dT + \frac{p}{T}dp \qquad \text{(A)}$$

Use equation (A) and the test for an exact differential to prove dq_{rev}/T is the differential of a state function. Name the state function.

$$\left(\frac{\partial \frac{C_V}{T}}{\partial p}\right)_T = \frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

$$\boxed{\therefore \frac{dq_{rev}}{T} \text{ is exact} = dS \quad S \text{ is the entropy}}$$

constant at constant V

$$\left(\frac{\partial \frac{p}{T}}{\partial T}\right)_V = \left(\frac{\partial \frac{nRT/V}{T}}{\partial T}\right)_V = \left(\frac{\partial \frac{nR}{V}}{\partial T}\right) = 0$$

Q4. This question refers to the isomerization of 1,2-dichloroethylene (DCE) at 25 °C.

$$\underset{10.0\ \text{mol} - x}{\textit{trans}\text{-DCE}(g)} = \underset{x}{\textit{cis}\text{-DCE}(g)}$$

Data at 25 °C: $\Delta H_{fm}°(\textit{trans}\text{-DCE}, g) = 6.15\ \text{kJ mol}^{-1}$ $\quad$ $\Delta G_m°(\textit{trans}\text{-DCE}, g) = 28.57\ \text{kJ mol}^{-1}$

$\Delta H_{fm}°(\textit{cis}\text{-DCE}, g) = 3.77\ \text{kJ mol}^{-1}$ $\quad$ $\Delta G_m°(\textit{cis}\text{-DCE}, g) = 26.31\ \text{kJ mol}^{-1}$

a) 10.0 moles of *trans*-DCE are loaded into a 250.0 L tank at 25 °C. Calculate the number of moles of *trans*-DCE and the number of moles of *cis*-DCE at equilibrium.

$$\Delta G° = \Delta G_{fm}°(cis) - \Delta G_{fm}°(trans) = 26.31 - 28.57 = -2.26\ kJ$$

$$K = \frac{P_{cis}}{P_{tran}} = e^{-\Delta G°/RT} = e^{-(-2260J)/(8.314 J K^{-1} mol^{-1})298.15K}$$

$$K = e^{0.9117} = 2.489 = \frac{\frac{n_{cis}RT}{V}}{\frac{n_{trans}RT}{V}} = \frac{n_{cis}}{n_{trans}}$$

$$K = \frac{x}{10.0\ mol - x} = 2.489 \qquad x = 7.13\ mol$$

$$n_{trans} = (10.00 - 7.13)\ mol = \boxed{n_{trans}\ 2.87\ mol}$$

$$\boxed{n_{cis} = 7.13\ mol}$$

b) The Gibbs energy of formation of *cis*-DCE is lower than that of *trans*-DCE, indicating *trans*-DCE is unstable relative to *cis*-DCE. Why doesn't the unstable *trans*-DCE convert completely to *cis*-DCE?

back reaction of the pure cis isomer to produce the trans isomer produces a lower Gibbs energy due to ΔG_{mix}

c) For a higher yield of the *cis*-DCE product, should the temperature be increased? Justify your answer.

$$\Delta H° = \Delta H_{fm}°(cis) - \Delta H_{fm}°(trans)$$
$$= (3.77 - 6.15)\ kJ$$
$$= -2.38\ kJ\ (\text{exothermic})$$

$$\frac{d\ln K}{dT} = \frac{\Delta H°}{RT^2} < 0$$

$\boxed{\text{lower } T}$ to get more cis isomer

d) For a higher yield of *cis*-DCE, should the pressure in the tank be increased? Justify your answer.

$\boxed{\text{pressure has no effect}}$ on the yield of the cis isomer

$$(\Delta n_{gas} = 0)$$