- 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. 2.00 moles of helium (assumed to be an ideal gas) expands isothermally from 15.0 L to 75.0 L at 300 K. For this process $w = -6000$ J.

a) Explain why $q = 6000$ J.   (Isothermal ideal gas $\Rightarrow$ $\boxed{\Delta U = 0}$)

$$\Delta U = 0 = q + w \qquad q = -w = 6000 \text{ J}$$

b) Calculate ΔG.   (isothermal $\Rightarrow$ $dT = 0$)

$$dG = -S\,dT + V\,dp = V\,dp = \frac{nRT}{P}\,dp$$

$$\Delta G = \int_{G_i}^{G_p} dG = \int_{P_i}^{P_f} \frac{nRT}{P}\,dp = nRT\int_{P_i}^{P_f} \frac{dp}{P} = nRT\,\ln\!\left(\frac{P_f}{P_i}\right)$$

$$\Delta G = nRT\,\ln\!\left(\frac{nRT/V_f}{nRT/V_i}\right) = (2.00\text{ mol})\left(8.314\,\frac{J}{K\,mol}\right)(300K)\,\ln\!\left(\frac{15.0L}{75.0L}\right) = \boxed{-8028\ J}$$

c) Show that ΔS is **26.8** J K^{-1}.

$$dS = \frac{C_v}{T}\,dT + \frac{nR}{V}\,dV \qquad \Delta S = \int_{S_i}^{S_f} dS = \int_{V_i}^{V_f} \frac{nR}{V}\,dV = nR\int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S = nR\,\ln\!\left(\frac{V_f}{V_i}\right) = (2.00\text{ mol})\left(8.314\,\frac{J}{K\,mol}\right)\,\ln\!\left(\frac{75.0L}{15.0L}\right) = \boxed{26.76\,\frac{J}{K}}$$

or, for b, use $\Delta G = \Delta H^{0\;(isothermal\;ideal\;gas)} - T\Delta S \Rightarrow \Delta G = -T\Delta S$

d) The expansion of the helium causes its entropy to increase: $\Delta S > 0$. Does this prove the expansion of the gas is irreversible? Explain.

$\boxed{No!}$ $\Delta S > 0$ proves a process is irreversible only for isolated systems, and the $\boxed{\text{gas is not isolated}}$ ($q = 6000J$, $w = -6000J$)

(For example, $\Delta S = nR\,\ln(V_f/V_i)$ is >0 for reversible isothermal expansions)

e) Is the expansion of the gas irreversible? Justify your answer.

$\boxed{Yes!}$ for a reversible expansion from 15.0 to 75.0 L

$$W_{rev} = -nRT\,\ln(V_f/V_i) = -(2.00)(8.314)300\ln\!\left(\frac{75.0}{15.0}\right)$$

$$\boxed{W_{rev} = -8028\ J \neq w}\;(-6000J)$$

or, $\Delta S + \Delta S_{surr}$
$= \left(26.8 + \frac{-6000}{300}\right)\frac{J}{K}$
$= 6.8\frac{J}{K}$ for the universe (isolated)

or, $q \neq q_{rev}$ because, $\Delta S = 26.8\,\frac{J}{K}$ $\neq \frac{q}{T} = \frac{6000J}{300K} = 20\,\frac{J}{K}$

(a reversible engine) $q_H = 1000\,J$

Q2. a) What is the maximum amount of work that can be performed by a steam engine that absorbs 1000 J of heat from a hot reservoir at 100 °C if the temperature of the cold reservoir is 20 °C?

$$T_H = (273 + 100)K = 373\,K \qquad T_C = (273 + 20)K = 293\,K$$

max. engine efficiency (for a reversible engine)

$$\varepsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{293\,K}{373\,K} = 0.214 = \frac{-W}{q_H}$$

max. work done on the surroundings

$$-W = q_H \varepsilon = (1000\,J)(0.214) = \boxed{214\,J}$$

b) If the boiler temperature is raised by using supercritical steam, what is the maximum amount of work that can be performed by a steam engine that absorbs 1000 J of at 280 °C? Assume the cold reservoir remains at 20 °C.

$$T_H = (273 + 280)K = 553\,K \qquad T_C = (273 + 20)K = 293\,K$$

max. engine efficiency (for a reversible engine)

$$= 1 - \frac{T_C}{T_H} = 1 - \frac{293\,K}{553\,K} = 0.470$$

max. work done on the surroundings

$$-W = q_H \varepsilon = (1000\,J)\,0.470 = \boxed{470\,J}$$

c) The efficiency of real engines is significantly lower than the value $\varepsilon = 1 - (T_C/T_H)$ derived using the Second Law. Why?

Real engines are not reversible, so $\varepsilon_{real} < 1 - \frac{T_C}{T_H}$. (Real engines also have mechanical inefficiencies, such as friction.)

d) A heat pump operating between 0 °C and 20 °C absorbs 1000 J of heat from the cold reservoir.

$$T_H = (273 + 20)K = 293\,K \qquad T_C = (273 + 0)K = 273\,K$$

i) What is the maximum amount of heat that can be delivered to the hot reservoir at 20 °C?

$$q_C = 1000\,J$$
$$q_H = ?$$

for a reversible heat pump

$$\frac{q_C}{T_C} + \frac{q_H}{T_H} = 0$$

$$-q_H = \frac{T_H}{T_C} q_C = \frac{293\,K}{273\,K}(1000\,J) = \boxed{1073\,J} \checkmark$$

ii) What is the minimum amount work that must be supplied to the heat pump in order to absorb 1000 J of heat from the cold reservoir?

$$\varepsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{273\,K}{293\,K} = 0.068 = \frac{-W}{q_H}$$

$$-W = \varepsilon\, q_H = 0.068(-1073\,J) \qquad \boxed{W = 73\,J}$$

73 J work provides 1000 J heat!

2

equilibrium constant $K = P_{CO_2}$

3. This question refers to the chemical reaction $CaCO_3(s) = CaO(s) + CO_2(g)$

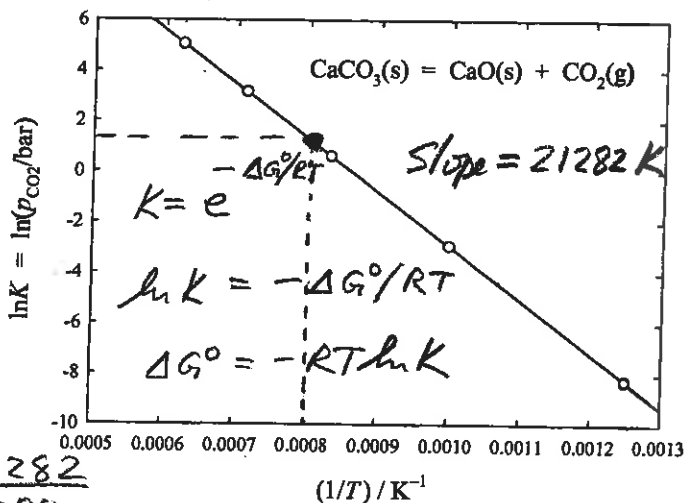a) How many different phases are present at equilibrium?   (see PSet #8, Q1)
                                                                        Q3

three   calcium carbonate (s)
           calcium oxide (s)
           carbon dioxide (g)

b) The logarithm of the equilibrium constant for the reaction is given by the equation

$$\ln K = 18.328 - \frac{21282}{T}$$

The graph shows $\ln K$ plotted against $1/T$.

$CaCO_3(s) = CaO(s) + CO_2(g)$

$K = e^{-\Delta G^\circ/RT}$

Slope = 21282 K

$\ln K = -\Delta G^\circ/RT$

$\Delta G^\circ = -RT\ln K$

(1/T) / K^{-1}

i) Calculate ΔG_R° at 1000 K.

at 1000 K : $\ln K = 18.328 - \dfrac{21282}{1000}$

$\ln K = -2.954$

$\Delta G^\circ = -RT\ln K = -(8.314\ J\ K^{-1}mol^{-1})(1000K)(-2.954) = \boxed{24560\ J}$

ii) Calculate ΔH_R° at 1000 K.

van't Hoff
equation $\dfrac{d\ln K}{d\frac{1}{T}} = \dfrac{-\Delta H_R^\circ}{R} = \dfrac{d}{d\frac{1}{T}}\left(18.328 - 21282\frac{1}{T}\right) = -21282\ K$

$\Delta H_R^\circ = -R(-21282\ K) = -(8.314\ J\ K^{-1}mol^{-1})(21282K)$

$\boxed{\Delta H_R^\circ = 177000\ J\ mol^{-1}}$

iii) Calculate ΔS_R° at 1000 K.   (isothermal)

$\left[\ \Delta G = \Delta(U + pV - TS) = \Delta(H - TS) = \Delta H - \Delta(TS) = \Delta H - T\Delta S\ \right]$

$\Delta G_R^\circ = \Delta H_R^\circ - T\Delta S_R^\circ$ $\Delta S_R^\circ = \dfrac{\Delta H_R^\circ - \Delta G_R^\circ}{T}$

$\Delta S_R^\circ = \dfrac{177000 - 24560}{1000}\ \dfrac{J}{K} = \boxed{152.4\ \dfrac{J}{K}}$ $\left(\begin{array}{l}\text{expect } \Delta S_R^\circ > 0 \\ \Delta n_{gas} = +1\ mol\end{array}\right)$

c) A tank contains $CaCO_3(s)$, $CaO(s)$ and CO_2 gas at a pressure of 5.00 bar at 1250 K. Is the system at equilibrium? If not, is the forward reaction spontaneous or is the back reaction spontaneous? Justify your answer. $\dfrac{1}{T} = \dfrac{1}{1250\ K} = 0.0008\ K^{-1}$

$\ln K = 18.328 - \dfrac{21282}{1000} = 1.3024$ $K = e^{1.302} = 3.68 = P_{CO_2}\ equil.$

$\boxed{P_{CO_2} = 5.00\ bar > P_{CO_2}(equil.)}$ $\underline{too\ much\ CO_2}$
                                                      $\boxed{back\ reaction\ is\ spont.}$

4. a) Starting with the equation $dG = -SdT + Vdp$, show:

i) $(\partial G/\partial T)_p = -S$

$$dG = -SdT + Vdp$$

Note: "Prove" does not mean "copy from equations sheets"!

at fixed pressure $(dp = 0)$: $dG_p = -SdT_p$

$$\frac{dG_p}{dT_p} = \boxed{-S} = \left(\frac{\partial G}{\partial T}\right)_p$$

i) $(\partial G/\partial p)_T = nRT/p$ for an ideal gas.

$$dG = -SdT + Vdp$$

at fixed temperature $(dT = 0)$: $dG_T = Vdp_T$

$$\frac{dG_T}{dp_T} = \boxed{V} = \left(\frac{\partial G}{\partial P}\right)_T = \frac{nRT}{P} \quad \text{for an ideal gas} \quad (PV = nRT)$$

ii) $-(\partial S/\partial p)_T = (\partial V/\partial T)_p$

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right]_P$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

b) Write the van't Hoff equation and briefly explain why it is useful.

$$\frac{d\ln K}{d\left(\frac{1}{T}\right)} = \frac{\Delta H^0}{R}$$

use enthalpy data to predict how equilibrium constants change with T

or, without calorimetry, use equilibrium constants measured at different temperatures to calculate ΔH

c) A 50.0 L tank contains methane at 200.0 K and 110.0 bar. Use the diagram below to calculate the number of moles of methane in the tank. *Data for methane:* $p_c = 46.0$ bar, $T_c = 190.6$ K

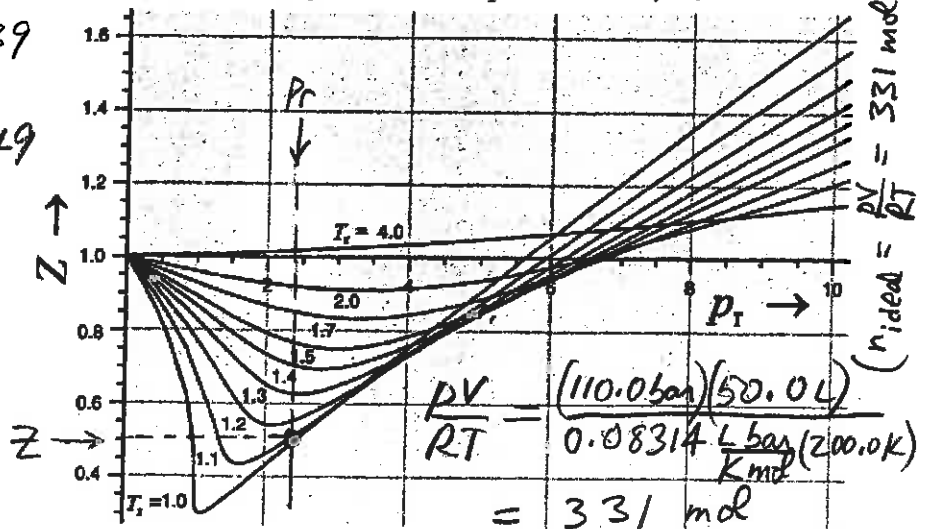$$P_r = \frac{P}{P_c} = \frac{110.0\,bar}{46.0\,bar} = 2.39$$

$$T_r = \frac{T}{T_c} = \frac{200.0\,K}{190.6\,K} = 1.049$$

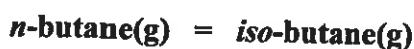read from graph $Z = 0.50$

$$\boxed{Z = \frac{PV}{nRT} = 0.50}$$

$$n = \frac{PV}{RT}\frac{1}{Z} = \frac{330\,mol}{0.50}$$

$$\boxed{n = 661\,mol}$$

$\sim$ twice as many moles compared to an ideal gas at 110.0 bar

$$\frac{PV}{RT} = \frac{(110.0\,bar)(50.0\,L)}{0.08314\frac{L\,bar}{K\,mol}(200.0\,K)} = 331\,mol$$

$\left(n_{ideal} = \frac{PV}{RT} = 331\,mol\right)$

5. This question refers to the isomerization reaction of *n*-butane and *iso*-butane at 1000 K:

$$\text{n-butane(g)} \; = \; \text{iso-butane(g)} \qquad \left(\begin{array}{c} \text{see Test 2 (2015)} \\ \text{Q 5} \end{array} \right)$$

Data at 1000 K: $\quad \Delta G_{fm}°(\text{n-butane, g}) = 270.0 \text{ kJ mol}^{-1} \qquad \Delta G_{fm}°(\text{iso-butane, g}) = 276.6 \text{ kJ mol}^{-1}$

a) Show that the equilibrium constant of the reaction at 1000 K is $K = 0.452$.

$$\Delta G_R° = \Delta G_{fm}°(\text{iso-b, g}) - \Delta G_{fm}°(\text{n-b, g}) = 276600 - 270000 = 6600 \frac{J}{mol}$$

$$\boxed{K = \exp(-\Delta G_R°/RT) = \exp[-6600/(8.314)(1000)] = 0.452}$$

b) 1.00 mole of *iso*-butane is placed in a tank. How many moles of *n*-butane and *iso*-butane are in the tank at equilibrium at 1000 K?

x moles of iso-butane react to reach equilibrium

$$\begin{array}{ccc} \text{n-butane} & = & \text{isobutane} \\ x \text{ mol} & & 1.00 - x \end{array}$$

at equilibrium : $K = \dfrac{P_{iso-b}}{P_{n-b}} = \dfrac{n_{isob}RT/V}{n_{n-b}RT/V} = \dfrac{1.00 - x}{x} = 0.452$

$1.00 = 0.452x + x$

$x = 1.00/1.452 = 0.688$ $\qquad \boxed{n_{n-b} = 0.688 \qquad n_{isob} = 0.312}$

c) 1.00 mole of *n*-butane is placed in a tank. How many moles of *n*-butane and *iso*-butane are in the tank at equilibrium at 1000 K?

y moles of n-butane react to reach equilibrium

$$\begin{array}{ccc} \text{n-butane} & = & \text{isobutane} \\ 1.00 - y & & y \end{array}$$

$K = \dfrac{y}{1.00 - y} = 0.452$

$y = 0.452 - 0.452y$
$y = 0.452/1.452 = 0.311$

$\boxed{n_{iso-b} = 0.312 \qquad n_{n-b} = 0.688}$

d) $\Delta G_{fm}°(\text{n-butane, g}) < \Delta G_{fm}°(\text{iso-butane, g})$, indicating that *n*-butane is more stable than *iso*-butane. But *n*-butane partially isomerizes to form *iso*-butane (as shown in part c)! Explain.

$\boxed{\text{MIXING !}}$

$\Delta G_{fm}°$ values refer to pure n-butane and iso-butane at 1 bar

Reaction of pure n-butane or pure iso-octane and mixing reduces the Gibbs energy.

e) This question shows that pure *n*-butane partially isomerizes to form *iso*-butane and that pure *iso*-butane partially isomerizes to form *n*-butane. These are spontaneous reactions. But pure *n*-butane and pure *iso*-butane can be purchased from chemical companies! Why is this possible?

The $\boxed{\text{rates}}$ of the isomerization reactions are $\boxed{\text{slow}}$, especially at low temperatures. (Thermodynamics (and ΔG_R) says nothing about the rates of chemical reactions.)

Q1
Q2
Q3
Q4
Q5