

*Your lowest assignment mark will not be used to calculate your average assignment mark. So if you've handed in all the assignments (#1,2,3,4,5,6,7), and are happy with the results, a zero mark for assignment #8 will not affect your course mark.

Q1. Calcium oxide is produced on a large scale by the decomposition of the mineral calcite (CaCO_3).



a) The equilibrium constant for this reaction is $K = p_{\text{CO}_2}$. What about the $\text{CaCO}_3(\text{s})$ and $\text{CaO}(\text{s})$? Are these compounds ignored in the equilibrium? Explain briefly.

[3] b) Calculate K at 25 °C.

c) Calculate the decomposition temperature of calcite at 1.00 bar pressure. *Hint:* Calculate the temperature at which the equilibrium CO_2 pressure is 1.00 bar using $\text{dln}K/\text{d}(1/T) = -\Delta H^\circ/R$.

Data at 25 °C:	$\Delta G_{\text{fm}}^\circ(\text{CaCO}_3, \text{s}) = -1128.8 \text{ kJ mol}^{-1}$	$\Delta H_{\text{m}}^\circ(\text{CaCO}_3, \text{s}) = -1206.9 \text{ kJ mol}^{-1}$
	$\Delta G_{\text{fm}}^\circ(\text{CaO}, \text{s}) = -604.0 \text{ kJ mol}^{-1}$	$\Delta H_{\text{fm}}^\circ(\text{CaO}, \text{s}) = -635.1 \text{ kJ mol}^{-1}$
	$\Delta G_{\text{fm}}^\circ(\text{CO}_2, \text{g}) = -394.4 \text{ kJ mol}^{-1}$	$\Delta H_{\text{fm}}^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ mol}^{-1}$

Q2. The $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ reaction is the basis of an industry valued at about 700 billion dollars annually. Name the product that is manufactured and its main uses.

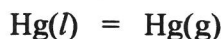
[2]

Q3. A proposal is made to reduce atmospheric carbon dioxide levels by using CaO to absorb CO_2 . Is this proposal feasible? Explain briefly.

[1]

Q4. Standard Gibbs energies of formation are widely used to calculate equilibrium constants for chemical reactions. This question shows $\Delta G_{\text{f}}^\circ$ data can also be used to predict **phase equilibria**.

a) Use the data given below to calculate the vapor pressure of liquid mercury at 25 °C.



[4] b) Also use the data to calculate the boiling point of liquid mercury at 1.00 bar.

c) The measured boiling point of liquid mercury (357 °C) is slightly different from the value calculated in part b. Why?

Data at 25 °C:	$\Delta G_{\text{fm}}^\circ(\text{Hg}, \text{g}) = 31.82 \text{ kJ mol}^{-1}$	$\Delta H_{\text{m}}^\circ(\text{Hg}, \text{g}) = 61.32 \text{ kJ mol}^{-1}$
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Q5. This question refers to the **reduced van der Waals equation**:

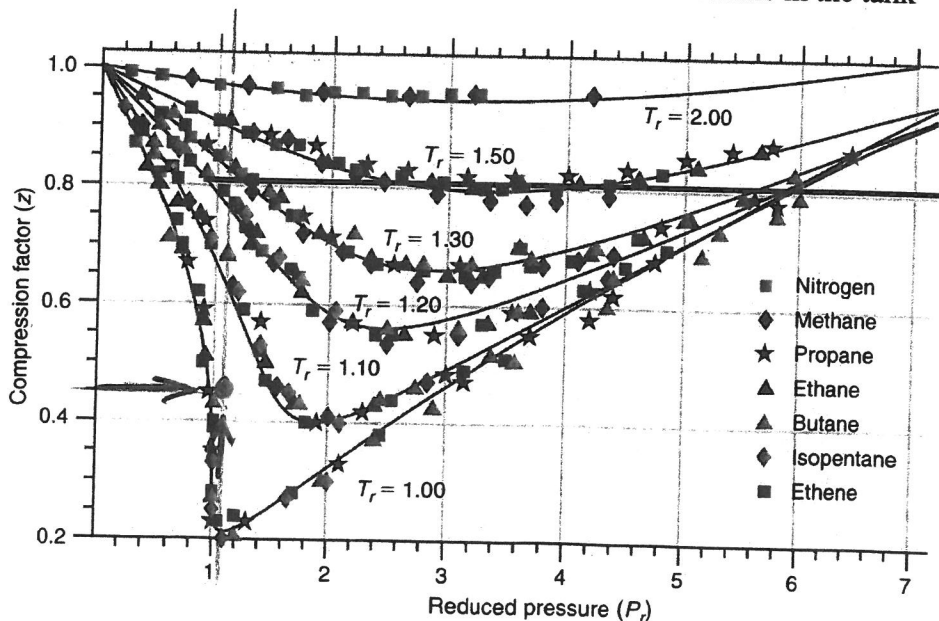
$$p_r = \frac{8}{3} \frac{T_r}{V_r - \frac{1}{3}} - \frac{3}{V_r^2}$$

- This is a “universal” equation of state. Why?
 - Use the equation to calculate the reduced compression factor Z_r at the critical point.
- [6]
- Use the equation to show the reduced isothermal compressibility $-V_r^{-1}(\partial V_r/\partial p_r)_{T_r}$ is infinite at the critical point.
 - What does “reduced” mean in this context?
 - Show the reduced isothermal compressibility $\kappa_r = -V_r^{-1}(\partial V_r/\partial p_r)_{T_r}$ is infinite at the critical point! *Suggestion:* $(\partial V_r/\partial p_r)_{T_r}$ is difficult to evaluate. Instead, evaluate $(\partial p_r/\partial V_r)_{T_r}$ and use the inverse rule.

Q6. Some models of paint-ball guns use capsules of compressed carbon dioxide to fire projectiles with muzzle velocities of about 100 meters per second. After firing a few shots, the carbon dioxide pressure might be expected to drop, causing lower velocities and poor accuracy. Yet consistent muzzle velocities are maintained until the capsules are almost empty. Explain.

Q7. A 50.0 L tank contains butane ($T_c = 425$ K, $p_c = 38.0$ bar) at 450 K and 42.0 bar.

- [3]
- Calculate the number of moles of butane in the tank using the ideal gas law. Why is this calculation likely to be inaccurate?
 - Use the corresponding-states graph given below to calculate:
 - the compression factor Z
 - an accurate value for the number of moles of butane in the tank





a) equilibrium constant $K = P_{\text{CO}_2}$ only P_{CO_2} ?

are $\text{CaCO}_3(s)$ and $\text{CaO}(s)$ being ignored?

No! $K = e^{-\Delta G^\circ/RT} = e^{-[\Delta G_{\text{fm}}^\circ(\text{CaO}) + \Delta G_{\text{fm}}^\circ(\text{CO}_2) - \Delta G_{\text{fm}}^\circ(\text{CaCO}_3)]/RT}$

but $\text{CaCO}_3(s)$ and $\text{CaO}(s)$ have such small molar volumes that $G(\text{CaCO}_3, s)$ and $G(\text{CaO}, s)$ are virtually independent of the pressure and therefore equal to the standard values $G^\circ(\text{CaCO}_3, s)$ and $G^\circ(\text{CaO}, s)$

b) $\Delta G^\circ = \Delta G_{\text{fm}}^\circ(\text{CaO}, s) + \Delta G_{\text{fm}}^\circ(\text{CO}_2, g) - \Delta G_{\text{fm}}^\circ(\text{CaCO}_3, s)$
 $= [-604.0 - 394.4 - (-1128.8)] \text{ kJ mol}^{-1}$

$\Delta G^\circ = 130.4 \text{ kJ mol}^{-1}$

$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{130400 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K})}\right]$

$K = e^{-52.60} = 1.424 \times 10^{-23} \text{ bar}$

c) $\Delta H^\circ = \Delta H_{\text{fm}}^\circ(\text{CaO}, s) + \Delta H_{\text{fm}}^\circ(\text{CO}_2, g) - \Delta H_{\text{fm}}^\circ(\text{CaCO}_3, s)$
 $= -635.1 - 393.5 - (-1206.9)$
 $\Delta H^\circ = 178.3 \text{ kJ (endothermic)}$

(Q1 c) cont.)

van't Hoff equation $\frac{d \ln K}{d \frac{1}{T}} = - \frac{\Delta H^\circ}{R}$

gives $d \ln K = - \frac{\Delta H^\circ}{R} d \frac{1}{T}$

integrate from T_1 to T_2 $\int_{\ln K(T_1)}^{\ln K(T_2)} d \ln K = - \frac{\Delta H^\circ}{R} \int_{\frac{1}{T_1}}^{\frac{1}{T_2}} d \frac{1}{T}$ (assuming ΔH° is constant)

$$\ln K_2 - \ln K_1 = - \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

at $T_1 = 298.15 \text{ K}$, $K_1 = 1.424 \times 10^{-23} = P_{\text{CO}_2}$ at T_1

at $T_2 = ?$, $K_2 = 1.00 \text{ bar} = P_{\text{CO}_2}$ at T_2

$$\ln(1) - \ln(1.424 \times 10^{-23}) = - \frac{178300 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_2} - \frac{1}{298.15 \text{ K}} \right)$$

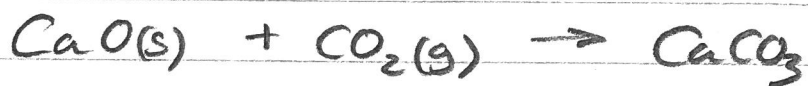
solve for $T_2 = 1110 \text{ K}$

this is the decomposition temp. of $\text{CaCO}_3(\text{s})$ at 1.00 bar

(Q2) CaO along with clay minerals (aluminosilicates) and gypsum is used to make cement

mixing cement with water and "aggregate" (sand or gravel) makes concrete — essential construction material for foundations, roads, pipes, floors, ...

Q3 Calcium oxide is very efficient at absorbing carbon dioxide gas:



$$K = \frac{1}{P_{\text{CO}_2}} = 7.02 \times 10^{22} \text{ bar}^{-1} \text{ at } 25^\circ\text{C}$$

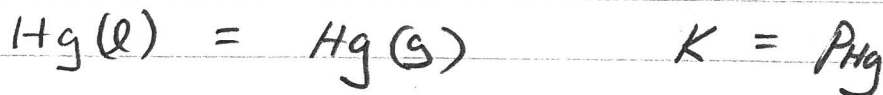
(from Q1)

but removing atmospheric CO_2 using CaO is not feasible!

an equal amount of atmospheric CO_2 is released when CaO is manufactured ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$)!

also, large amounts of fossil fuels (oil, coal or natural gas) must be burned to heat CaCO_3 to its decomposition temperature, releasing more atmospheric CO_2 !

Q4 a) liquid-vapor equilibrium for mercury:



$$\Delta G^\circ = \Delta G_{\text{fm}}^\circ(\text{Hg, g}) - \Delta G_{\text{fm}}^\circ(\text{Hg, l})$$

$$\Delta G^\circ = 31820 \text{ J mol}^{-1} - 0$$

(an element, pure and in its most stable state)
 $\therefore \Delta G_f^\circ = 0$

$$K = e^{-\Delta G^\circ/RT} = e^{-31820/(8.314)(298.15)}$$

$$= e^{-12.84} = \boxed{2.661 \times 10^{-6} \text{ bar}} \quad (\text{at } 25^\circ\text{C})$$

(QA cont.)

b) at $T_1 = 298.15 \text{ K}$, $K_1 = 2.661 \times 10^{-6} \text{ bar}$

at $T_2 = ?$, $K_2 = 1.00 \text{ bar}$

(from Q1:) $[\Delta H^\circ = \Delta H_{\text{fm}}^\circ(\text{Hg}, \text{g}) - \Delta H_{\text{fm}}^\circ(\text{Hg}, \text{l}) = 61320 \text{ J mol}^{-1}]$

$$\ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln(1.00) - \ln(2.661 \times 10^{-6}) = -\frac{61320 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{T_2} - \frac{1}{298.15 \text{ K}} \right)$$

solve for $T_2 = 620 \text{ K}$ (346 °C)

c) the actual (measured) boiling point of mercury at 1.00 bar is 357 °C, slightly different from the value calculated in part b)

why? the calculation assumed ΔH° is constant from 25 °C to 346 °C, when in fact ΔH° decreases slightly with increasing T

Q5

a) the reduced van der Waals equation

$$P_r = \frac{8}{3} \frac{T_r}{V_r^{-1/3}} - \frac{3}{V_r^2} \quad \left(\begin{array}{l} \text{in the limit } V_r \rightarrow \infty \\ (P \rightarrow 0), \text{ the ideal gas} \\ \text{equation is } P_r = \frac{8 T_r}{3 V_r} \end{array} \right)$$

is a "universal" equation of state because

P_r, T_r, V_r are "natural" quantities (no arbitrarily defined "human" units such as bar, K, L) and there are no arbitrarily defined constants (such as $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \Rightarrow$ human-defined)

b) at the critical point ($T = T_c, P = P_c, V_m = V_{mc}$) the reduced temperature, pressure, and molar volume are:

$$T_r = \frac{T}{T_c} = \frac{T_c}{T_c} = 1 \quad P_r = \frac{P}{P_c} = \frac{P_c}{P_c} = 1 \quad V_r = \frac{V_m}{V_{mc}} = \frac{V_{mc}}{V_{mc}} = 1$$

and the reduced compression factor is

$$Z_r = \frac{P_{\text{actual}}}{P_{\text{ideal}}} = \frac{P_{\text{actual}}}{\frac{8 T_r}{3 V_r}} = \frac{(1)}{\frac{8 (1)}{3 (1)}} = \boxed{\frac{3}{8}}$$

$$c) \quad P_r = \frac{8}{3} \frac{T_r}{V_r^{-1/3}} - \frac{3}{V_r^2}$$

$$\left(\frac{\partial P_r}{\partial V_r} \right)_{T_r} = \frac{8}{3} T_r \frac{\partial (V_r^{-1/3})^{-1}}{\partial V_r} - 3 \frac{\partial V_r^{-2}}{\partial V_r}$$

$$= \frac{8}{3} T_r \frac{(-1)}{(V_r^{-1/3})^2} - 3 \frac{(-2)}{V_r^3} = -\frac{8}{3} \frac{1}{(\frac{2}{3})^2} + \frac{6}{1} = 0$$

(Q5 cont.)

d) reduced means divided by the corresponding value at the critical point

(Q6) the capsules contain compressed CO_2 vapor and liquid at the boiling point

after each shot, some $\text{CO}_2(\text{l})$ evaporates to maintain a steady pressure of $\text{CO}_2(\text{g})$ in the capsule

(Q7) a) $n = \frac{PV}{RT} = \frac{(42.0 \text{ bar})(50.0 \text{ L})}{(0.08314 \frac{\text{L bar}}{\text{K mol}})(450 \text{ K})} = \boxed{56.1 \text{ mol}}$

b) reduced pressure $P_r = \frac{P}{P_c} = \frac{42.0 \text{ bar}}{38.0 \text{ bar}} = 1.105$

reduced temperature $T_r = \frac{T}{T_c} = \frac{450 \text{ K}}{425 \text{ K}} = 1.059$

i) read $Z \approx 0.45$ on the Z vs P_r graph

ii) $Z = \frac{PV}{nRT}$ $n = \frac{1}{Z} \frac{PV}{RT} = \frac{1}{0.45} (56.1 \text{ mol})$

$n = \boxed{125 \text{ mol}}$