NAME and ID NUMBER:

There should be 11 pages to this exam, counting this cover sheet. Please check this exam NOW!

There are 6 pages of formulae/data, and a periodic table (with molar masses) at the back of this exam. It is advisable to check the information provided on these pages before you begin working. Books, notes, etc. are not permitted, however calculators are. Write all of your answers in the blue books provided. Partial credit will be given but only if your answers can be deciphered. Therefore, make sure that your writing is neat and that your logic is clear, organized, and easy to follow. Unreadable answers will be given no credit. Not all questions are equally difficult, and spending too much time on any one question is generally a bad idea. Good luck.

GRADING

1. (20 points)

2. (25 points)

3. (30 points)

4. (25 points)

TOTAL: 100 points
1. (20 points)

   a. (5 points)
   Both Raoult’s law and Henry’s law express the vapor pressure of a component (say component 1) above a solution as a linear function of the mole fraction \( x_1 \) of that component in the solution. This general relation is \( P_1 = cx_1 \), where \( c \) is a constant appropriate for each law. Explain how Raoult’s law and Henry’s law differ, and describe the range of validity of each law. To what situation or approximation does each law pertain?

   b. (5 points)
   Consider liquid toluene mixed with a small amount of liquid benzene (both shown below). Would you expect the vapor pressure of benzene to be given more accurately by Raoult’s law or by Henry’s law? Explain your answer.

   c. (5 points)
   Next, consider liquid chloroform (trichloromethane) mixed with a small amount of liquid acetone (both shown below). Would you expect the vapor pressure of acetone to be given more accurately by Raoult’s law or by Henry’s law? Explain your answer.

   d. (5 points)
   For the two cases you considered in parts b and c, would you expect the difference
   \[ P_1(\text{Raoult’s law}) - P_1(\text{Henry’s law}) \]
   to be positive, negative, or zero? Explain your answer.

2. (25 points)
   It is often more cost effective to operate plug-flow reactors in conditions other than steady-state conditions. Consider the first-order, irreversible reaction \( A \rightarrow B \) in a plug-flow reactor that is not operating in a steady state. The mass-balance condition for the concentration \([A](x, t)\) of A at location \( x \) in the reactor at time \( t \) is
   \[
   \frac{\partial [A]}{\partial t} + u \frac{\partial [A]}{\partial x} = -k[A]
   \]
a. (5 points)
The most general solution to this mass-balance equation is

\[ [A](x, t) = e^{-kt} f(x - ut) \]

where \( f(y) \) is any smooth, differentiable function. Verify this solution by substituting it into the mass-balance equation and show that it does, indeed, satisfy the equation.

b. (5 points)
Suppose that the reactant A is fed into the plug-flow reactor in well-separated pulses. The shape of each pulse when it enters the reactor at \( t = 0 \) is a Gaussian shape centered about the point \( x = 0 \), i.e.,

\[ [A](x, 0) = C_0 e^{-x^2/2\sigma^2} \]

where \( \sigma \) characterizes the width of the pulse, and \( C_0 \) is a constant having units of concentration. Based on the result of part a, find a choice for \( f(x - ut) \) that is consistent with this initial concentration pulse profile, write down the complete solution \([A](x, t)\) for on such pulse based on your choice of \( f \), and show that your solution \([A](x, t)\) both satisfies the mass-balance equation and gives the correct initial profile shape at \( t = 0 \).

c. (5 points)
If we define the fractional conversion as

\[ [A](L, \tau) = (1 - X)[A](0, 0) \]

show that \( X \) has the expected form for a first-order reaction in a plug-flow reactor.

d. (10 points)
Now suppose that A satisfies a second-order reaction \( 2A \xrightarrow{k} B \) rather than a first-order reaction. The mass-balance equation now reads

\[ \frac{\partial [A]}{\partial t} + u \frac{\partial [A]}{\partial x} = -2k[A]^2 \]

Verify by direct substitution into this equation that the most general solution is

\[ [A](x, t) = \frac{1}{2kt + f(x - ut)} \]

where \( f(y) \) is any smooth, differentiable function of \( y \), and find a choice for \( f \) that gives the same initial pulse profile as in part b.

3. (30 points)
In the treatment of a patient with a particular and possibly fatal viral infection, two possible drugs are available that inhibit an enzyme E belonging to the enzyme. The enzyme is targeted for its critical role in the viral replication cycle. The two drugs are denoted \( I_1 \) and \( I_2 \), and they work in different ways. The inhibitor (drug) \( I_1 \) binds slowly and irreversibly to E but has a side effect in the form of a rapid yet reversible binding to an enzyme \( E' \) that is necessary for a patient’s continued survival. The overall reaction mechanism (mechanism 1) is

\[ E + I_1 \xrightarrow{k_1} EI \]

\[ E' + I_1 \xrightarrow{k'_1/k'_2} E'I_1 \]
In this mechanism, $k_1 \ll k'_1$. The inhibitor (drug) $I_2$ binds rapidly and reversibly to the enzyme $E$ but has a side effect of binding slowly and irreversibly to the enzyme $E'$. The reaction mechanism (mechanism 2) is

$$E + I_2 \xrightarrow{k_2} EI_2$$

$$E' + I_2 \xrightarrow{k'_2} E'I_2$$

In this mechanism, $k_2 \gg k'_2$. You must decide which drug to prescribe for your patient.

a. (15 points)
   For each inhibition mechanism, write down the complete set of rate equations for all of the species in the reactions.

b. (5 points)
   Let $[E]_0$ and $[E']_0$ be the initial concentrations of $E$ and $E'$. For mechanism 1, how are the concentrations $[E](t), [E'](t), [EI_1](t)$, and $[E'I_1](t)$ related to these initial concentrations? What are the corresponding relations for mechanism 2?

c. (10 points)
   For each of the two sets of rate equations in part a, make the steady state approximation that $d[I]/dt \approx 0$. Using this approximation and, if necessary, the conditions in part b, decide which is the drug you should prescribe. Remember, the patient’s life is in your hands, so there is no credit for prescribing the wrong drug. There is also no credit for guessing. Your choice must be supported by a clear, logical derivation and argument.

   **Hint:** After you make the steady state approximation, have a look at the rate $d[E]/dt$ at which the enzyme $E$, which is needed by the virus, is consumed, and on this basis, decide which drug will be the more effective of the two.

4. (25 points)
   A simple model of the solid-gas equilibrium treats the gas phase as a monatomic ideal gas of $N_g$ particles of mass $m$, all assumed to be identical, and it treats the solid as a collection of $N_s$ classical anharmonic oscillators, each of which is described by a potential energy of the form

$$U(x) = \frac{1}{2}m\omega^2x^2 + kx^4$$

where $\omega$ is the frequency of the oscillator, and $k$ is a constant such that $\beta kx^4 \ll 1$. The two phases are also assumed to be in thermal equilibrium with a common temperature $T$. Using this model, derive an expression for the vapor pressure $P$ above the solid in terms $T$, $\omega$, $m$, $k$, and basic physical constants such as $\hbar$ and $k_B$. You may assume that the volume of the solid phase is negligible compared to the volume of the gas phase. Based on the stated assumptions, make any approximations you deem reasonable, but each assumption must be properly justified.
POSSIBLY USEFUL INFORMATION

\[ N_A = N_0 = 6.022 \times 10^{23} \text{ mol}^{-1} \]

\[ R = 8.31441 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.082057 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \]

\[ k_B = 1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} = 1.36262 \times 10^{-25} \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \]

\[ h = 6.62609 \times 10^{-34} \text{ J} \cdot \text{s}, \quad \hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-34} \text{ J} \cdot \text{s} \]

\[ 1 \text{ N} = 1 \text{ kg} \cdot \text{m} \cdot \text{s}^{-2} \]

Some conversion factors and unit definitions

\[ 1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} \]
\[ 1 \text{ L} = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3 \]
\[ 1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \]
\[ 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mm Hg} \text{ at } 0^\circ\text{C} = 760 \text{ torr} \]
\[ 1 \text{ Pa} = 1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} \]
\[ 1 \text{ L} \cdot \text{atm} = 101.325 \text{ J} \]

Formulas

\[ S(N, V, E) = k_B \ln \Omega(N, V, E), \quad \Delta S_{AB} = \int_A^B \frac{dQ_{\text{rev}}}{T} = k_B \ln \left( \frac{\Omega_B}{\Omega_A} \right) \]

\[ E = Q + W, \quad \beta = \frac{1}{k_B T} \]

\[ P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \]

At a critical point: \[ \frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0 \]

\[ F_i = m_i a_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} \]
\[E(x) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(r_1, ..., r_N)\]

\[\Omega(N, V, E) = C_N \int_{E(x)=E} dx, \quad Q(N, V, T) = C_N \int dx \ e^{-\beta E(x)}, \quad \Delta(N, P, T) = \int_0^\infty dV \ e^{-\beta PV} Q(N, V, T)\]

\[E = -\frac{\partial}{\partial \beta} \ln Q(N, V, T), \quad P = k_B T \left(\frac{\partial \ln Q(N, V, T)}{\partial V}\right),\]

\[S = k_B \ln Q(N, V, T) + \frac{E}{T}\]

\[H = -\frac{\partial}{\partial \beta} \ln \Delta(N, P, T), \quad (V) = -k_B T \left(\frac{\partial \ln \Delta(N, P, T)}{\partial P}\right),\]

\[S = k_B \ln \Delta(N, P, T) + \frac{H}{T}\]

\[A(N, V, T) = F(N, V, T) = -k_B T \ln Q(N, V, T), \quad G(N, P, T) = N \mu(P, T) = -k_B T \ln \Delta(N, P, T), \quad \bar{G}(P, T) = \mu(P, T)\]

\[P = -k_B T \left(\frac{\partial \ln Q(N, V, T)}{\partial V}\right) = -\left(\frac{\partial A}{\partial V}\right)_{N,T}, \quad S = -\left(\frac{\partial G}{\partial T}\right)_{N,P} = k_B \ln \Delta + \frac{H}{T}, \quad (V) = -k_B T \left(\frac{\partial \ln \Delta(N, P, T)}{\partial P}\right),\]

\[N! \approx N^N e^{-N}, \quad (N - 1)! \approx N^{N/2} e^{-N/2}\]

\[\sigma_{AB} = \frac{1}{2} \left[\frac{\sigma_A + \sigma_B}{2} + \sqrt{\sigma_A \sigma_B}\right], \quad \gamma = \rho \sigma \langle v_{AA}\rangle, \quad \lambda = \frac{1}{\sqrt{2} \rho \sigma}\]

\[D = \frac{\langle |v_{AA}| \rangle}{4 \rho \sigma}, \quad \Delta r^2(t) = 6Dt\]

\[P(r, t) = \frac{\pi r^2}{2(\pi Dt)^{3/2}} e^{-r^2/4Dt}, \quad \frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial z^2}, \quad \frac{\partial \rho}{\partial t} + \frac{\partial J}{\partial z} = 0\]

\[D = \frac{1}{3} \int_0^\infty \langle v \cdot v(t)\rangle dt\]

If \(x \in [a, b]\), \(\int_a^b f(x)dx = 1\), \(P(X) = \int_a^X f(x)dx \in [0, 1]\)

\[P(X) = R, \quad \text{where } R \text{ is uniform on } [0, 1]\]

\[r_i(t + \Delta t) = r_i(t) + \Delta t v_i(t) + \frac{\Delta t^2}{2m_i} F_i(r(t))\]

\[v_i(t + \Delta t) = v_i(t) + \frac{\Delta t}{2m_i} [F_i(r(t)) + F_i(r(t + \Delta t))}\]
\[ P(v_x)dv_x = \left( \frac{\beta m}{2\pi} \right)^{1/2} e^{-\beta m v_x^2/2} dv_x, \quad P(v)dv = \left( \frac{\beta m}{2\pi} \right)^{3/2} e^{-\beta m|v|^2/2} dv \quad P(v)dv = 4\pi \left( \frac{\beta m}{2\pi} \right)^{3/2} v^2 e^{-\beta mv^2/2} dv \]

\[ x_1d\mu_1 + x_2d\mu_2 = 0, \]

\[ \mu_j^{(soln)} = \mu_j^{(vap)} = \mu_j^o + RT \ln \left( \frac{P_j}{P_j^o} \right) = \mu_j^* + RT \ln \left( \frac{P_j}{P_j^o} \right) = \mu_j^* + RT \ln a_j \]

\[ P_j = x_j P_j^o, \quad P_j = k_{H,j} x_j, \quad P_j(x_j) = x_j P_j^o e^{b(1-x_j)^2+c(1-x_j)^3} \]

\[ \text{Molarity}(M) = \frac{\text{moles of solute}}{\text{liters of solvent}}, \quad \text{molality}(m) = \frac{\text{moles of solute}}{\text{kilograms of solvent}} \]

\[ x_1 = \frac{1}{1 + M_1 m/1000}, \quad x_k = \frac{M_k m_k/1000}{1 + M_1 m/1000} \]

\[ \mu(P,T) = \bar{G}(P,T) = \left( \frac{\partial G}{\partial n} \right)_{P,T} = \frac{G(n,P,T)}{n} \]

\[ \Delta T_{\text{fus}} = K_1 m, \quad \Delta T_{\text{vap}} = K_1 m \]

\[ K = e^{\Delta_r G^*/RT} = \left( \frac{P_C/P^o}{P_A/P^o} \right)^{c} \left( \frac{P_B/P^o}{P_A/P^o} \right)^{d} \]

\[ K = \left( \frac{[C]/c_{\text{ref}}}{[D]/c_{\text{ref}}} \right)^{c} \left( \frac{[A]/c_{\text{ref}}}{[B]/c_{\text{ref}}} \right)^{d} \]

\[ K = \frac{a_C a_B}{a_A a_B}, \quad a = \frac{\gamma c}{c^o}, \quad a = \frac{\gamma P}{P^o} \]

\[ \Delta_r G = RT \ln \left( \frac{q}{k} \right) \]

\[ k = Ae^{-E_A/RT}, \quad k = \sigma_{AB} \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} N_A^2 e^{-(E_A/RT)}, \quad k = \frac{k_B T}{h} e^{-\Delta G^*/RT} \]

\[ r_j = \pm \frac{1}{\nu_j} \frac{d[j]}{dt}, \quad r = \pm k \prod_j |[j]|^{\nu_j} \]

First order : \( r = -k[A] \), Second order : \( r = -k[A]^2 \)

\[ \frac{1}{r} = \frac{K_M}{k_2[E]_0} \frac{1}{|S|} + \frac{1}{k_2[E]_0} \]

\[ V \frac{d[j]}{dt} = v([j]_0 - [j]) + V \nu_j |[j]|^{\nu_j}, \quad [j]_0 - [j] = -\tau r_j \]
\[ X = \frac{k\tau}{1 + k\tau} \]

\[ [A]_n = \frac{[A]_0}{(1 + k\tau)^n} \]

\[ \frac{dE}{dt} = \frac{dQ}{dt} + \sum_{j=1}^n F_j^{(in)}(C_{P,j})(T_0 - T) - \Delta r H(T) F_A^{(in)} X \]

\[ T = T_0 - \frac{F_A^{(in)} X \Delta r H(T)}{\sum_j F_j^{(in)} C_{P,j}} \]

\[ \frac{\partial[j]}{\partial t} + u \frac{\partial[j]}{\partial x} = \nu_j r_j \]

\[ \frac{d[j]}{dx} = \frac{\nu_j r_j}{u} \]

\[ X = 1 - e^{-k\tau} \]
Mathematics

**Vectors:**

\[ \mathbf{a} = (a_x, a_y, a_z) \]

\[ |\mathbf{a}| = \sqrt{a_x^2 + a_y^2 + a_z^2} \]

\[ \mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z \]

\[ \mathbf{a} + \mathbf{b} = (a_x + b_x, a_y + b_y, a_z + b_z) \]

\[ |\mathbf{a} + \mathbf{b}| = \sqrt{|\mathbf{a}|^2 + |\mathbf{b}|^2 + 2 \mathbf{a} \cdot \mathbf{b}} \]

\[ \theta = \cos^{-1} \left( \frac{\mathbf{a} \cdot \mathbf{b}}{|\mathbf{a}| |\mathbf{b}|} \right) \]

**Identities**

\[ \ln x + \ln y = \ln(xy), \quad \ln x - \ln y = \ln \left( \frac{x}{y} \right) \]

\[ e^{x+y} = e^x e^y, \quad \frac{1}{e^x} = e^{-x} \]

**Integrals and series:**

\[ f(x) = \sum_{k=0}^{\infty} \frac{1}{k!} f^{(k)}(x_0)(x - x_0)^k, \quad \text{(Taylor series expansion about } x = x_0), \quad e^{ax} \approx 1 + ax \]

\[ \int \frac{dx}{x} = \ln x + C, \quad \int \frac{dx}{x^2} = -\frac{1}{x} + C, \quad \int x^n dx = \frac{x^{n+1}}{n+1} + C, \quad \int e^{-ax} dx = -\frac{1}{a} e^{-ax} = C \]

\[ \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a \sqrt{\pi}}, \quad \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = \frac{3}{4a^2 \sqrt{\pi}} \]

\[ \int_{0}^{\infty} x^n e^{-x} dx = n! \]

**Fundamental Theorem of Calculus:**

\[ \int_{a}^{b} f(x) dx = F(b) - F(a) \]

\[ \frac{dF}{dx} = f(x) \]
Spherical Coordinates:

\[
x = r \sin \theta \cos \phi \\
y = r \sin \theta \sin \phi \\
z = r \cos \theta \\
x^2 + y^2 + z^2 = r^2
\]

Differential Equations:

If \( \frac{dy}{dt} = -ay \), \( y(t) = y(0)e^{-at} \)

If \( \frac{dy}{dt} = c - ay \), \( y(t) = y(0)e^{-at} + \frac{c}{a} (1 - e^{-at}) \)
FIG. 1. Periodic table.

* Lanthanide series

** Actinide series