

- Calculate the equilibrium constant at 25°C and write the equilibrium expression ($K_{eq} = Q_{\alpha}$, where Q_{α} is written out) for the following (unbalanced) chemical reactions, using the thermodynamic data in Appendix 4
 - $H_{2(g)} + F_{2(g)} \rightleftharpoons HF_{(g)}$
 - $H_{2(g)} + O_{2(g)} \rightleftharpoons H_2O_{(l)}$
- Based on the (realistic) assumption that ΔH and ΔS are weak functions of temperature, estimate the "autoionization constant" of water at 10.0°C. The "autoionization constant" of water is K_{eq} for the following chemical reaction: $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$
- Calculate the pH of freshly distilled water (nothing but $H_2O_{(l)}$ and fragments of the same) at 10.0°C.
- Write the equilibrium expression ($Q_{\alpha} = \text{blah}$) for each of the following balanced chemical reactions. Convert activities into measurable quantities, but don't calculate a numerical value for K_{eq} :
 - $Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+_{(aq)} + CO_3^{2-}_{(aq)}$
 - $NH_3_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$
Hint: This reaction occurs in aqueous solution [(aq)], so water is the solvent!
 - $CHCl_3_{(l)} \rightleftharpoons CHCl_3_{(g)}$
 - $Cu[H_2O]_6^{2+}_{(aq)} + 4NH_3_{(aq)} \rightleftharpoons Cu(NH_3)_4^{2+}_{(aq)} + 6 H_2O_{(l)}$
Hint: The (aq) state labels tell you this is occurring in aqueous solution, that is, in a solution of water!
- Phosgene gas, $COCl_2$, dissociates according to the following reaction:

$$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$$

If a mixture of these three gases is compressed at constant temperature,

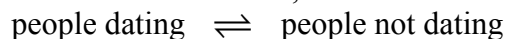
 - Will the number of CO molecules in the mixture increase, decrease, or remain nearly the same?
 - Will the equilibrium constant for the reaction increase, decrease, or remain about the same?
 - Will the partial pressure of $COCl_2$ in the mixture increase, decrease, or remain the same?

Explain the reasoning that led you to each of your answers.
- Consider the following reaction: $C_{(s)} + CO_{2(g)} \rightleftharpoons 2 CO_{(g)}$
If the reaction were at initially at equilibrium, what would be the effect of:
 - adding more $CO_{2(g)}$ at constant pressure
 - adding $C_{(s)}$ at constant pressure
 - increasing the total system pressure by compressing the system at constant temperature
 - increasing the total system pressure by adding an inert gas at constant temperature and volume
 - adding an inert gas at constant temperature and pressure
 - adding a catalyst
 - removing $CO_{(g)}$ at constant pressure
 - removing $CO_{(g)}$ at constant volume

Clearly explain your reasoning for each answer.

7. This last question comes from Emily Kuross, a former Chem 123 student, and it does a really nice job of demonstrating the dynamic nature of equilibrium. It's worth working through, it will help you understand!

Up on the mountain of the gods, Cupid is being taught chemistry by Branius Hurtum, the god of science. Right now, Cupid is learning about equilibrium, and Branius realizes that the best way to teach this is from a perspective that the god of love will appreciate and understand. So, for a long period of time he has Cupid observe the relationships of students at Carleton College. At the point when he starts observing the 1800 students on campus, 400 are involved in some sort of amorous relationship; but, by the end of each week, 10% of the people in a relationship have broken it up, while 25% of those not in a relationship have begun a new one. Cupid writes an equation for the "reaction," which looks like this:



- How many weeks does it take for the school to reach "dating equilibrium"?
- At equilibrium, what is the rate of the forward reaction (in people per week)? What is the rate of the reverse reaction? (Round up to whole people, or in case of break-ups, whole couples!)
- What is the equilibrium constant, K_{eq} , if the activity of people is equal to their dimensionless concentration based on their type (dating vs. single)?
- Cupid notices a nice, single girl who is very sad, for she believes that now that Carleton has reached dating equilibrium, she'll never find someone. What should Cupid tell her? Can he quell her fears, or are they well-grounded?

Solutions:

- Before we can do anything, we have to balance these reactions. The way we choose to balance them will actually affect (have an effect on) the K_{eq} we get, because it will have a corresponding effect on the Q_{α} expression we write!

- Let me first answer this question assuming I write the balanced reaction so that it leads to the production of 2 moles of product.

In that case the balanced reaction would be $\text{H}_{2(\text{g})} + \text{F}_{2(\text{g})} \rightarrow 2\text{HF}_{(\text{g})}$. Then

$$\Delta G_{\text{rxn}}^{\circ} = \left(\sum \chi_i \Delta G_f^{\circ}[i] \right) = (+2) \Delta G_f^{\circ}[\text{HF}_{(\text{g})}] + (-1) \Delta G_f^{\circ}[\text{H}_{2(\text{g})}] + (-1) \Delta G_f^{\circ}[\text{F}_{2(\text{g})}] = +2 \left(-273 \frac{\text{kJ}}{\text{mol}} \right) - 0 - 0 = -546 \frac{\text{kJ}}{\text{mol}}$$

and (remembering that we must use absolute temperatures when doing anything involving R, and that $25^{\circ}\text{C} = 298 \text{ K}$), we get

$$K_{\text{eq}} = e^{\left(\frac{-\Delta G_{\text{rxn}}^{\circ}}{RT} \right)} = e^{\left(\frac{\left[\frac{-546 \frac{\text{kJ}}{\text{mol}}}{1000 \frac{\text{kJ}}{\text{mol}}} \right]}{\left[\frac{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}{1000 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \right] [298 \text{ K}]} \right)} = e^{(220.377)} = 5.11 \times 10^{95} \text{ [dimensionless]}$$

(Note that we use a heretofore rarely invoked rule for sig figs here, that being that the digits in the exponent count as significant figures in working across a logarithm or an exponential: so the three sig figs in 220.377 carry over into K_{eq} as the 9 and the 5 in the exponent, plus the 5 in the 5.11 . Note also how honkin' big this number is...close to blowing the stack of most calculators!)

We can now write the equilibrium expression, keeping in mind that the value above applies to activities, and the activity of a gas can be reasonably approximated as the numerical value of the partial pressure of that gas, measured in atmospheres:

$$K_{\text{eq}} = \frac{(\alpha_{\text{HF}_{(\text{g})}})^2}{\alpha_{\text{H}_{2(\text{g})}} \alpha_{\text{F}_{2(\text{g})}}} = \frac{\left(\frac{P_{\text{HF}}}{\text{atm}} \right)^2}{\left(\frac{P_{\text{H}_2}}{\text{atm}} \right) \left(\frac{P_{\text{F}_2}}{\text{atm}} \right)} = \frac{P_{\text{HF}}^2 \left(\frac{1}{\text{atm}} \right)^2}{P_{\text{H}_2} P_{\text{F}_2} \left(\frac{1}{\text{atm}} \right)^2} = \frac{P_{\text{HF}}^2}{P_{\text{H}_2} P_{\text{F}_2}} = 5.11 \times 10^{95} = K_{\text{P}}$$

Notice that things would have been different along the way, but would have led to the same result, had I started out by balancing the reaction differently, say $\frac{1}{2}\text{H}_{2(\text{g})} + \frac{1}{2}\text{F}_{2(\text{g})} \rightarrow \text{HF}_{(\text{g})}$. Then the process above would look like this:

$$\Delta G_{\text{rxn}}^{\circ} = \left(\sum \chi_i \Delta G_f^{\circ}[i] \right) = (+1) \Delta G_f^{\circ}[\text{HF}_{(\text{g})}] + (-\frac{1}{2}) \Delta G_f^{\circ}[\text{H}_{2(\text{g})}] + (-\frac{1}{2}) \Delta G_f^{\circ}[\text{F}_{2(\text{g})}] = +1 \left(-273 \frac{\text{kJ}}{\text{mol}} \right) + 0 + 0 = -273 \frac{\text{kJ}}{\text{mol}}$$

and

$$K_{\text{eq}} = e^{\left(\frac{-\Delta G_{\text{rxn}}^{\circ}}{RT} \right)} = e^{\left(\frac{\left[\frac{-273 \frac{\text{kJ}}{\text{mol}}}{1000 \frac{\text{kJ}}{\text{mol}}} \right]}{\left[\frac{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}{1000 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \right] [298 \text{ K}]} \right)} = e^{(110.188)} = 7.15 \times 10^{47} \text{ [dimensionless]}$$

$$K_{\text{eq}} = \frac{\alpha_{\text{HF}_{(\text{g})}}}{(\alpha_{\text{H}_{2(\text{g})}})^{\frac{1}{2}} (\alpha_{\text{F}_{2(\text{g})}})^{\frac{1}{2}}} = \frac{\left(\frac{P_{\text{HF}}}{\text{atm}} \right)}{\sqrt{\frac{P_{\text{H}_2}}{\text{atm}}} \sqrt{\frac{P_{\text{F}_2}}{\text{atm}}}} = \frac{P_{\text{HF}} \left(\frac{1}{\text{atm}} \right)}{\sqrt{P_{\text{H}_2} P_{\text{F}_2}} \left(\frac{1}{\sqrt{\text{atm}} \sqrt{\text{atm}}} \right)} = \frac{P_{\text{HF}} \left(\frac{1}{\text{atm}} \right)}{\sqrt{P_{\text{H}_2} P_{\text{F}_2}} \left(\frac{1}{\text{atm}} \right)} = \frac{P_{\text{HF}}}{\sqrt{P_{\text{H}_2} P_{\text{F}_2}}} = 7.15 \times 10^{47} = K_{\text{P}}$$

This isn't really any different from the result we got above, because if we square both sides of this equation, we get

$$\left(\frac{P_{\text{HF}}}{\sqrt{P_{\text{H}_2}} \sqrt{P_{\text{F}_2}}} = 7.15 \times 10^{47} \right)^2 \Rightarrow \frac{(P_{\text{HF}})^2}{(\sqrt{P_{\text{H}_2}})^2 (\sqrt{P_{\text{F}_2}})^2} = (7.15 \times 10^{47})^2 \Rightarrow \frac{P_{\text{HF}}^2}{P_{\text{H}_2} P_{\text{F}_2}} = 5.11 \times 10^{95}$$

- b. I'm only going to balance this reaction one way; $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\ell)$. If you balanced it "the other way," you should be able to obtain my result by taking the square root of both sides of your final $K_{\text{eq}} = Q_{\alpha}$ expression.

$$\Delta G_{\text{rxn}}^{\circ} = \left(\sum \chi_i \Delta G_f^{\circ}[i] \right) = (+2) \Delta G_f^{\circ}[2\text{H}_2\text{O}(\ell)] + (-2) \Delta G_f^{\circ}[\text{H}_2(\text{g})] + (-1) \Delta G_f^{\circ}[\text{O}_2(\text{g})] = +2 \left(-237 \frac{\text{kJ}}{\text{mol}} \right) - 2(0) - 1(0) = -474 \frac{\text{kJ}}{\text{mol}}$$

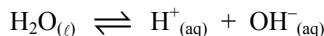
$$K_{\text{eq}} = e^{\left(\frac{-\Delta G_{\text{rxn}}^{\circ}}{RT} \right)} = e^{\left(\frac{\left[\frac{-474 \text{ kJ}}{\text{mol}} \right]}{\left[8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right] \left[298 \text{ K} \right] \left[\frac{1 \text{ kJ}}{1000 \text{ J}} \right]} \right)} = e^{(191.316)} = 1.22 \times 10^{83} \text{ [dimensionless]}$$

Because H_2O is a pure liquid, it has an activity of one as long as there is at least one drop of liquid water present. Then

$$K_{\text{eq}} = \frac{(\alpha_{\text{H}_2\text{O}(\ell)})^2}{(\alpha_{\text{H}_2(\text{g})})^2 \alpha_{\text{O}_2(\text{g})}} = \frac{(1)^2}{\left(\frac{P_{\text{H}_2}}{\text{atm}} \right)^2 \left(\frac{P_{\text{F}_2}}{\text{atm}} \right)} = \frac{1}{P_{\text{H}_2}^2 P_{\text{F}_2} \left(\frac{1}{\text{atm}} \right)^3} = \frac{(\text{atm})^3}{P_{\text{H}_2}^2 P_{\text{F}_2}} = 1.22 \times 10^{83}$$

$$\text{Note: the pressure equilibrium constant, } K_p = P_{\text{H}_2}^{-2} P_{\text{F}_2}^{-1} = 1.22 \times 10^{83} (\text{atm})^{-3}$$

2. In order to do this, we need to determine $\Delta G_{\text{rxn}}^{\circ}$ at a temperature other than the standard 25°C . We have a means of doing this, because while ΔG° generally has a strong temperature dependence, ΔH and ΔS generally do not. So we can use ΔH° and ΔS° as good approximations of ΔH and ΔS over a range of temperatures. (The $^{\circ}$ symbol on S and H indicates that the value is for 25°C and 1 atm, but the same symbol on G is used to indicate that we are talking about the value of G for standard activities, that is, for one atm partial pressure of each gas, 1 M concentration of each solute, and the presence of any amount of [nearly] pure solid or liquid. The temperature of G° is generally assumed to be 25°C unless otherwise stated, but technically, the $^{\circ}$ doesn't indicate it.)



$$\Delta H_{\text{rxn}}^{\circ} = \left(\sum \chi_i \Delta H_f^{\circ}[i] \right) = (+1) \Delta G_f^{\circ}[\text{H}^+(\text{aq})] + (+1) \Delta G_f^{\circ}[\text{OH}^-(\text{aq})] + (-1) \Delta G_f^{\circ}[\text{H}_2\text{O}(\ell)] = 0 + \left(-230 \frac{\text{kJ}}{\text{mol}} \right) - \left(-286 \frac{\text{kJ}}{\text{mol}} \right) = +56 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_{\text{rxn}}^{\circ} = \left(\sum \chi_i S^{\circ}[i] \right) = (+1) \Delta S^{\circ}[\text{H}^+(\text{aq})] + (+1) S^{\circ}[\text{OH}^-(\text{aq})] + (-1) S^{\circ}[\text{H}_2\text{O}(\ell)] = +0 + \left(-11 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) - \left(+70 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) = -81 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Because $\Delta G^{\circ} = \Delta H - T \Delta S$ for any transformation carried out at constant temperature (that is, where the reaction takes place at a constant temperature, in our case, 10.0°C water dissociates and the temperature remains 10.0°C), we can approximate

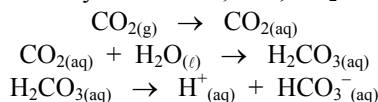
$$\Delta G_{\text{rxn}}^{\circ}[283.15 \text{ K}] \approx \Delta H^{\circ} - T \Delta S^{\circ} = +56 \frac{\text{kJ}}{\text{mol}} - (283.15 \text{ K}) \left(-81 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \left(\frac{\text{kJ}}{1000 \text{ J}} \right) = +56 \frac{\text{kJ}}{\text{mol}} + 22.935 \frac{\text{kJ}}{\text{mol}} = +78.935 \frac{\text{kJ}}{\text{mol}} \text{ and so}$$

$$K_{\text{eq}} = e^{\left(\frac{-\Delta G_{\text{rxn}}^{\circ}}{RT} \right)} = e^{\left(\frac{\left[\frac{-78.935 \text{ kJ}}{\text{mol}} \right]}{\left[8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right] \left[283.15 \text{ K} \right] \left[\frac{1 \text{ kJ}}{1000 \text{ J}} \right]} \right)} = e^{(-33.53)} = 2.74 \times 10^{-15} \text{ [dimensionless]}$$

$$\text{In terms of } Q_{\alpha}, \text{ this means that } Q_{\alpha} = \frac{\alpha_{\text{H}^+(\text{aq})} \alpha_{\text{OH}^-(\text{aq})}}{\alpha_{\text{H}_2\text{O}(\ell)}} = \frac{\left(\frac{[\text{H}^+]}{\text{M}} \right) \left(\frac{[\text{OH}^-]}{\text{M}} \right)}{1} = \frac{[\text{H}^+][\text{OH}^-]}{\text{M}^2} = 2.75 \times 10^{-15} \text{ at equilibrium.}$$

Zumdahl (and many others) prefer to write this as $[\text{H}^+][\text{OH}^-] = 2.75 \times 10^{-15} \text{ M}^2 = K_c$ (A concentration-based equilibrium constant.) The measured value is $2.92 \times 10^{-15} \text{ M}^2$ at 10.0°C , so this is actually pretty darn close.

3. $\text{pH} = -\log_{10}[\text{H}^+]$, and we determined up above that $[\text{H}^+][\text{OH}^-] = 2.75 \times 10^{-15} \text{ M}^2$. Since we have distilled water, it contains only H_2O and things that come from H_2O , and so all the H^+ and OH^- ions in it must come from H_2O . Since H_2O breaks up to form one H^+ ion and one OH^- ion, the concentration of these two ions must be the same. So $[\text{H}^+] = [\text{OH}^-]$ and $[\text{H}^+][\text{OH}^-] = 2.75 \times 10^{-15} \text{ M}^2 = [\text{H}^+][\text{H}^+] = [\text{H}^+]^2 \Rightarrow [\text{H}^+] = 5.244 \times 10^{-8} \text{ M} \Rightarrow \text{pH} = -\log_{10} [\text{H}^+] = 7.28$
Note that the pH of freshly distilled water is only 7.0 at 25°C ; also, CO_2 dissolves readily from the air into water and undergoes the following sequence of reactions:



which leads to an increase in $[\text{H}^+]$ and thus a decrease in pH. Distilled water that has been exposed to air for even a few hours typically has a pH down around 5.6. So does clean rain water, for the same reason (this does not qualify as "acid rain!")

4. This is a straightforward application of the definitions of Q_α and activities. The reactions are already balanced.

$$a. \quad Q_\alpha = \frac{(\alpha_{\text{Ag}^+(\text{aq})})^2 \alpha_{\text{CO}_3^{2-}(\text{aq})}}{\alpha_{\text{Ag}_2\text{CO}_3(\text{s})}} = \frac{\left(\frac{[\text{Ag}^+]}{M}\right)^2 \frac{[\text{CO}_3^{2-}]}{M}}{1} = \frac{[\text{Ag}^+]^2 [\text{CO}_3^{2-}]}{M^3} \quad (\text{The pure solid Ag}_2\text{CO}_3(\text{s}) \text{ has an activity of one.})$$

$$b. \quad Q_\alpha = \frac{\alpha_{\text{NH}_4^+(\text{aq})} \alpha_{\text{OH}^-(\text{aq})}}{\alpha_{\text{NH}_3(\text{aq})} \alpha_{\text{H}_2\text{O}(\ell)}} = \frac{\alpha_{\text{NH}_4^+(\text{aq})} \alpha_{\text{OH}^-(\text{aq})}}{\alpha_{\text{NH}_3(\text{aq})}} \frac{\left(\frac{[\text{NH}_4^+]}{M}\right) \left(\frac{[\text{OH}^-]}{M}\right)}{\left(\frac{[\text{NH}_3]}{M}\right) (1)} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} M^{-1}$$

(The solvent, $\text{H}_2\text{O}(\ell)$, is close enough to a pure liquid that its concentration is fixed and it has an activity of one.)

$$c. \quad Q_\alpha = \frac{\alpha_{\text{CHCl}_3(\text{g})}}{\alpha_{\text{CHCl}_3(\ell)}} = \frac{\left(\frac{P_{\text{CHCl}_3}}{\text{atm}}\right)}{1} = \frac{P_{\text{CHCl}_3}}{\text{atm}} \quad (\text{The pure liquid CHCl}_3(\ell) \text{ does not appear in the equilibrium expression.})$$

$$d. \quad Q_\alpha = \frac{\alpha_{\text{Cu}(\text{NH}_3)_4^{2+}} (\alpha_{\text{H}_2\text{O}(\ell)})^6}{\alpha_{\text{Cu}(\text{H}_2\text{O})_6^{2+}} (\alpha_{\text{NH}_3(\text{aq})})^4} = \frac{\left(\frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{M}\right) (1)^6}{\left(\frac{[\text{Cu}(\text{H}_2\text{O})_6^{2+}]}{M}\right) \left(\frac{[\text{NH}_3]}{M}\right)^4} = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{H}_2\text{O})_6^{2+}] [\text{NH}_3]^4} M^4 \quad (\text{Water is our solvent})$$

5. If a syringe containing $\text{COCl}_2(\text{g})$ in equilibrium with $\text{CO}(\text{g})$ and $\text{Cl}_2(\text{g})$ is quickly compressed at constant temperature, the partial pressure of each gas inside the container will rise by the same proportion, say by a factor of two. (We can choose any proportion we want, the qualitative answer we get to this qualitative question should be the same for any proportion.)

$$Q_\alpha = \frac{\alpha_{\text{CO}(\text{g})} \alpha_{\text{Cl}_2(\text{g})}}{\alpha_{\text{COCl}_2(\text{g})}} = \frac{\left(\frac{P_{\text{CO}}}{\text{atm}}\right) \left(\frac{P_{\text{Cl}_2}}{\text{atm}}\right)}{\left(\frac{P_{\text{COCl}_2}}{\text{atm}}\right)} = \frac{P_{\text{CO}} P_{\text{Cl}_2}}{P_{\text{COCl}_2}} \text{atm}^{-1} \Rightarrow \text{If each partial pressure goes up by a factor of two, } Q_\alpha \text{ will double.}$$

- By Le Châtelier's principle, the system will react (if possible) in such a way as to counteract what was done to Q_α . Q_α has gone up, so the system will try to bring it down again. That means consuming CO and Cl_2 (lowering these partial pressures) and producing COCl_2 (raising its partial pressure). In short, the reaction runs in reverse, causing the amount of CO present in the mixture to **decrease**.
- Equilibrium constants depend on temperature alone...so K_{eq} will **remain the same**. (To a good approximation, anyway!)
- Compressing the container causes all of the partial pressures to go up. But since the reaction reacts to increased pressure by further increasing the amount of $\text{COCl}_2(\text{g})$, we can be confident that the partial pressure of $\text{COCl}_2(\text{g})$ will **increase**. It would be much trickier to figure out what the net effect of compression would be on the partial pressures of the products!

6. These questions generally ask you apply Le Châtelier's principle – carefully! It's not as elementary as it seems, sometimes! I strongly suggest you start any problem like this by writing out Q_α . In this case, we have

$$Q_\alpha = \frac{(\alpha_{\text{CO}(\text{g})})^2}{\alpha_{\text{C}(\text{s})} \alpha_{\text{CO}_2(\text{g})}} = \frac{\left(\frac{P_{\text{CO}}}{\text{atm}}\right)^2}{(1) \left(\frac{P_{\text{CO}_2}}{\text{atm}}\right)} = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} \text{atm}^{-1}$$

- The partial pressure of CO_2 will go up while the other partial pressures remain the same, so Q_α will decrease. The system will respond by using up some of the $\text{CO}_2(\text{g})$, reacting it with $\text{C}(\text{s})$ to form more $\text{CO}(\text{g})$ and thus raising Q_α .
- The C is in solid form, and adding more of it will not change Q_α ! If the system is at equilibrium before more $\text{C}(\text{s})$ is added, it will still be in equilibrium after it is added. Nothing will happen!
- The partial pressures of the two gases will go up (in the same proportion), and since P_{CO} is squared in Q_α , the net effect will be an increase in Q_α . The system will respond by running in reverse, using up $\text{CO}(\text{g})$, so as to decrease Q_α again.

- d. This one is tricky! It's the first one where a "naive" reading of Le Châtelier's principle (encouraged by your textbook's approach) will lead you to the wrong answer. Adding an inert gas to a fixed volume does not change the partial pressure of the other gases in the system, even though it increases the total pressure of the system. Adding an inert gas at constant volume thus has no effect on Q_α , and the system won't do a thing, the amount of CO_2 , $\text{C}_{(s)}$, and CO in the container will stay just as they were before the inert gas was added.
- e. Here again, we need to think carefully. Now we are adding an inert gas at constant temperature and *pressure*, so the system volume will increase as we do this. If the moles of CO and CO_2 remain fixed, but the volume of the system doubles while the temperature remains constant, the ideal gas law tells us that the partial pressure of each of our gases will be cut in half. ($P_X = \eta_X RT/V$) This will cause Q_α to drop, again because P_{CO} is squared in the numerator but the partial pressure of CO_2 appears to only the first power in the denominator. To compensate, the reaction will try to increase Q_α by producing more CO and consuming CO_2 and $\text{C}_{(s)}$.
- f. A catalyst will speed up a system's approach to equilibrium, but it will not shift the position of the equilibrium unless the "equilibrium" is actually a "steady state" maintained by the constant input of something...like the constant input of photons in the case of stratospheric ozone. Thus a catalyst will speed up a system's approach to equilibrium, but it will not shift the position of the equilibrium. If the system is already at equilibrium, adding a catalyst will have no observable effect. (However, the rate of both the forward and reverse reactions will be increased!)
- g. As the total pressure of the system is held constant, the partial pressure of CO will go down while the partial pressure of CO_2 will go up. This decreases Q_α , and the system will respond by making more $\text{CO}_{(g)}$. It will consume some $\text{C}_{(s)}$ and $\text{CO}_{2(g)}$ in doing this.
- h. If CO is removed at constant volume, the partial pressure of CO will go down but the partial pressure of CO_2 will remain the same. ($P_X = \eta_X RT/V$, and η_X is not changing!) This will still lead to a decrease in Q_α and a concomitant shift in the reaction equilibrium such that more CO is produced. Again, some CO_2 and $\text{C}_{(s)}$ will be consumed in the process.

7. Here's a spreadsheet I set up that runs through the calculations:

Week	Dating Students	Breaking Up	New Daters	Single Students
1	400	40	350	1400
2	710	72	273	1090
3	911	92	222	889
4	1041	104	190	759
5	1127	112	168	673
6	1183	118	154	617
7	1219	122	145	581
8	1242	124	140	558
9	1258	126	136	542
10	1268	126	133	532
11	1275	128	131	525
12	1278	128	131	522
13	1281	128	130	519
14	1283	128	129	517
15	1284	128	129	516
16	1285	128	129	515
17	1286	128	129	514
18	1287	128	128	513
19	1287	128	128	513
20	1287	128	128	513

- a. Looks like equilibrium is reached after 18 weeks.
- b. At equilibrium, 128 people break up and 128 people hook up each week.

c. At equilibrium, $Q_\alpha = K_{eq}$, and here we have

$$Q_\alpha = \frac{\alpha_{\text{single}}}{\alpha_{\text{dating}}} = \frac{\left[\frac{\text{single people}}{\text{total people}} \right]}{\left[\frac{\text{dating people}}{\text{total people}} \right]} = \frac{\text{single people}}{\text{dating people}} = \frac{513}{1287} = 0.3986$$

So $K_{eq} = 0.3986$, which is dimensionless, as it should be (I didn't want to mess with sig figs on this one).

- d. The young lass has naught to fear! Equilibrium is a dynamic situation, and although there will remain 513 non-dating people on campus, now that equilibrium has been reached, they will not always be the same 513 people! Every week 128 random single people will enter into new relationships, and she could easily be one of those. Sure, new relationships aren't being formed as fast as they were at the start of the term, but she's not out of luck!