

1. Strictly speaking, NO system can be completely closed for example, hot liquid in the best thermos eventually cools down but for most purposes a system can effectively be "closed". How would you create a system which is more or less closed with respect to:

(a) heat loss?

(b) light?

(c) loss of mass?

2. Read the following observations and then answer the questions.

Two sealed glass tubes containing a mixture of a red-brown gas,  $\text{NO}_2(\text{g})$ , and a colourless gas,  $\text{N}_2\text{O}_4(\text{g})$ , are observed. The colour is an identical medium red-brown in each tube and there is no visible change in the colour of the contents as time passes.

One tube is placed in a beaker of boiling water for a minute. The contents of the tube become much darker red-brown in colour. Upon first placing the tube in the hot water, the colour gets continually darker, but after a few seconds the colour stops changing.

The second tube is placed in a beaker containing dry ice at  $-78^\circ\text{C}$ . The colour quickly disappears and the contents of the tube remain colourless. The hot and cold tubes are taken out of their beakers, placed side by side and allowed to come to room temperature. The tubes have an identical medium red-brown colour when they both are at room temperature.

- (a) The gases are involved in the reversible reaction:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ . What evidence exists that the forward and reverse rates are equal at room temperature?

(b) Can temperature changes affect an equilibrium reaction? How do you know this?

(c) What evidence shows that the forward and reverse reaction rates are equal at  $100^\circ\text{C}$ ? If the temperature were raised above  $100^\circ\text{C}$ , what would you expect to happen to the colour?

- (d) The balanced equation in part (a) should also include "energy". Consider what happened to the colour when a tube was heated. Is the reaction exothermic or endothermic, as written? Explain.
- (e) What gas was predominantly present at low temperatures? What gas was predominantly present at high temperatures? How would you describe the chemical composition in a tube when it was at room temperature?
- (f) If one tube were filled with pure  $\text{NO}_2(\text{g})$  and another tube with pure  $\text{N}_2\text{O}_4(\text{g})$ , what might be true of the colours you would expect to see in the tubes after they sit for a minute at the same temperature? What evidence do you have that your prediction should occur?
3. Water is boiling in a kettle at  $100^\circ\text{C}$ . Is the system at equilibrium? Explain.
4. Some liquid water is present inside a sealed flask at room temperature. Is water evaporating inside the flask? Is the system at equilibrium? Why?
5. A chemist wished to prepare pure phosgene,  $\text{COCl}_2(\text{g})$ , by reacting carbon monoxide,  $\text{CO}(\text{g})$ , and chlorine gas,  $\text{Cl}_2(\text{g})$ , according to the reaction  $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$ . Why will this reaction NOT produce pure  $\text{COCl}_2(\text{g})$ ? If the chemist could somehow obtain a sample of pure  $\text{COCl}(\text{g})$ , will it remain pure? Why?

6. Assume that the simple reaction  $A \rightleftharpoons B$  initially has:  $[A] = 1.200 \text{ M}$ ,  $[B] = 0.000 \text{ M}$ .  $K_{\text{forward}} = 0.50$ ,  $K_{\text{reverse}} = 0.10$ . The following results are produced.

Time (min)	RATE <sub>forward</sub>	RATE <sub>reverse</sub>	[A]	[B]
0	0.600	0.000	1.200	0.000
1	0.300	0.060	0.600	0.600
2	0.180	0.084	0.360	0.840
3	0.132	0.094	0.264	0.936
4	0.113	0.097	0.226	0.974
5	0.105	0.099	0.210	0.990
6	0.102	0.100	0.204	0.996
7	0.101	0.100	0.202	0.998
8	0.100	0.100	0.201	0.999
9	0.100	0.100	0.200	1.000
10	0.100	0.100	0.200	1.000

- (a) Plot the values of  $[A]$ -versus-time and  $[B]$ -versus-time on the same graph.
- (b) When does it appear that equilibrium finally occurs? How did you recognize that equilibrium was attained? What else occurs at equilibrium?
- (c) Is there a time when  $[\text{REACTANT}] = [\text{PRODUCT}]$ ? Is  $[\text{REACTANT}] = [\text{PRODUCT}]$  at equilibrium?
- (d) When is the forward rate greatest? What happens to the rate as the  $[A]$  decreases?
- (e) What is the numerical value of the ratio  $[\text{PRODUCT}] / [\text{REACTANT}]$  at equilibrium?

7. Now let's see what happens if the previous equilibrium is upset by ADDING an extra 0.6 M of B at the 11-th minute, so as to increase [B] from 1.0 M up to 1.6 M.

Time (min)	RATE <sub>forward</sub>	RATE <sub>reverse</sub>	[A]	[B]
11	0.100	0.160	0.200	1.600
12	0.130	0.154	0.260	1.540
13	0.142	0.152	0.284	1.516
14	0.147	0.151	0.294	1.506
15	0.149	0.150	0.297	1.503
16	0.150	0.150	0.299	1.501
17	0.150	0.150	0.300	1.500
18	0.150	0.150	0.300	1.500

- (a) Extend the graph you plotted in Exercise 6, part (a), to include the above data.
- (b) When is equilibrium re-established?
- (c) What is the numerical value of the ratio [PRODUCT] / [REACTANT] at equilibrium?
- (d) When equilibrium IS re-established, what has changed from the previous equilibrium? What remains unchanged?
8. In the reaction  $3\text{C}_2\text{H}_2(\text{g}) \rightleftharpoons \text{C}_6\text{H}_6(\text{g})$ , will the ratio of  $[\text{C}_2\text{H}_2(\text{g})]$  to  $[\text{C}_6\text{H}_6(\text{g})]$  at equilibrium be 3:1?

9. What things must be true at equilibrium?
10. Ozone ( $\text{O}_3$ ) and oxygen ( $\text{O}_2$ ) molecules can exist in equilibrium:  $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$ . If 2 mol of  $\text{O}_3$  react for every 2 mol of  $\text{O}_2$  reacting in a container, does equilibrium exist in the container? Why?
11. The following equilibrium occurs :  $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$ . A gaseous mixture of  $\text{NOCl}, \text{NO}, \text{Cl}_2$  is put in a container. After a few minutes it is found that two moles of  $\text{NOCl}$  react for every three moles of products which react. Is the mixture at equilibrium? Why?