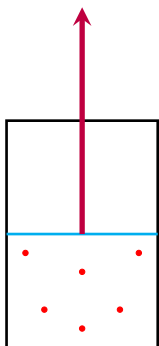
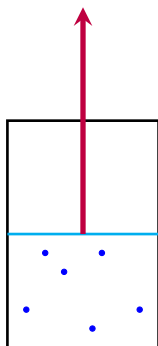


DALTON'S LAW OF PARTIAL PRESSURES

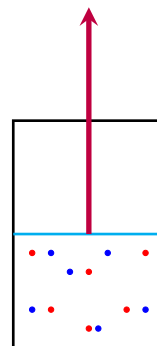
The pressure exerted by one gas in a mixture is independent of the other gases in the mixture.



Gas A with pressure P_A .



Gas B with pressure P_B .



Gas $A + B$ with pressure $P_A + P_B$.

In general,

$$P(\text{total}) = P_1 + P_2 + \cdots + P_k = \frac{(n_1 + n_2 + \cdots + n_k)RT}{V}$$

where

$$n(\text{total}) = n_1 + n_2 + \cdots + n_k$$

Consider a case in which two gases A and B are in a container of volume V :

$$P(A) = \frac{n(A)RT}{V} \quad P(B) = \frac{n(B)RT}{V}$$

where $n(A)$ and $n(B)$ are the number of moles of A and B respectively. Then

$$P(\text{total}) = P(A) + P(B)$$

Recall that the mole fraction is defined by

$$\chi = \frac{n}{n(\text{total})}$$

Then the mole fraction of A and B are defined by

$$\chi(A) = \frac{n(A)}{n(A+B)} \quad \chi(B) = \frac{n(B)}{n(A+B)}$$

Then the partial pressures can be calculated as follows:

$$P(A) = \chi_A \times P(\text{total}) \quad P(B) = \chi(B) \times P(\text{total})$$

In general,

$$P(k) = \chi(k) \times P(\text{total}) \quad \chi(k) = \frac{n(k)}{n(\text{total})} = \frac{P(k)}{P(\text{total})}$$

Example 4.1: Consider the composite system that is composed of He with 2.00 L and 1.50 bar, Ne with 3.00 L and 2.50 bar, and Xe with 1.00 L and 1.00 bar, which is held at 298 K. Assume ideal gas behavior, calculate the total pressure, and the partial pressure of each component if the barriers separating the compartments are removed. Assume that the volume of the barriers is negligible.

Solution: Fix $T = 298$ K. First, we calculate the amount of moles of each component.

$$\begin{aligned} n(\text{He}) &= \frac{P(\text{He})V(\text{He})}{RT} = \frac{(1.50 \text{ bar})(2.00 \text{ L})}{(0.08314 \text{ L bar/mol K})(298 \text{ K})} = 0.121 \text{ mol} \\ n(\text{Ne}) &= \frac{P(\text{Ne})V(\text{Ne})}{RT} = \frac{(2.50 \text{ bar})(3.00 \text{ L})}{(0.08314 \text{ L bar/mol K})(298 \text{ K})} = 0.303 \text{ mol} \\ n(\text{Xe}) &= \frac{P(\text{Xe})V(\text{Xe})}{RT} = \frac{(1.00 \text{ bar})(1.00 \text{ L})}{(0.08314 \text{ L bar/mol K})(298 \text{ K})} = 0.040 \text{ mol} \end{aligned}$$

and the total amount of moles is

$$n(\text{total}) = n(\text{He} + \text{Ne} + \text{Xe}) = 0.121 + 0.303 + 0.040 = 0.464 \text{ mol}$$

Next, we calculate the mole fraction for each component,

$$\begin{aligned} \chi(\text{He}) &= \frac{n(\text{He})}{n(\text{total})} = \frac{0.121}{0.464} = 0.261 \\ \chi(\text{Ne}) &= \frac{n(\text{Ne})}{n(\text{total})} = \frac{0.303}{0.464} = 0.653 \\ \chi(\text{Xe}) &= \frac{n(\text{Xe})}{n(\text{total})} = \frac{0.040}{0.464} = 0.086 \end{aligned}$$

Then the total pressure is

$$P(\text{total}) = \frac{n(\text{total})RT}{V(\text{total})} = \frac{(0.464 \text{ mol})(0.08314 \text{ L bar/mol K})(298 \text{ K})}{2.00 \text{ L} + 3.00 \text{ L} + 1.00 \text{ L}} = 1.92 \text{ bar}$$

Lastly, calculating the partial pressures of each component,

$$\begin{aligned} P(\text{He}) &= \chi(\text{He}) \times P(\text{total}) = 0.261 \times 1.92 \text{ bar} = 0.501 \text{ bar} \\ P(\text{Ne}) &= \chi(\text{Ne}) \times P(\text{total}) = 0.653 \times 1.92 \text{ bar} = 1.254 \text{ bar} \\ P(\text{Xe}) &= \chi(\text{Xe}) \times P(\text{total}) = 0.086 \times 1.92 \text{ bar} = 0.165 \text{ bar} \end{aligned}$$

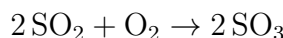
as required.

Example 4.2: Answer the following questions.

- Write a balanced equation for the formation of SO_3 from SO_2 and O_2 .
- At 310 K and 70 mbar, if 310 mL of O_2 reacts with 568 mL of SO_2 , determine the limiting reagent and the theoretical yield of the product SO_3 .

- (c) If after the experiment, 420 mL of SO_3 was collected, what is the percent yield?
- (d) In another experiment, an atmospheric chemist studying the pollutant SO_2 places a mixture of SO_2 and O_2 in a 2.00-L container at 800 K and 1.90 atm. When the reaction occurs, gaseous SO_3 forms, and the pressure falls to 1.65 atm. How many moles of SO_3 form?
- (e) What is the mole fraction of SO_3 in the final gas mixture?

Solution: (a) The balanced equation is as follows:



(b) The limiting reagent in this case is SO_2 because, if we have 310 mL of O_2 , we need 620 mL SO_2 , but we have SO_2 . Then,

$$n(\text{SO}_3)_T = n(\text{SO}_2) = \frac{PV(\text{SO}_2)}{RT} = \frac{(70 \times 10^{-3})(0.568)}{(0.08314)(310)} = 1.54 \times 10^{-4} \text{ mol}$$

Therefore, $n(\text{SO}_3)_T = 1.54 \times 10^{-4} \text{ mol}$. Then for the yield of the product,

$$m(\text{SO}_3)_T = n(\text{SO}_3)_T \times M(\text{SO}_3) = (1.54 \times 10^{-4})(80.6) = 0.123 \text{ g}$$

(c) We can find the percent yield using

$$\% \gamma = \frac{V_A}{V_T} = \frac{420}{568} = 73.9\%$$

(d) Let x be the pressure of SO_2 and y be the pressure of O_2 . Then initially, we have $P_1(x+y) = 1.90 \text{ atm}$, but $P_1(x)$ and $P_1(y)$ are unknown. Then if α is the change, then

$$P_2(x) = -2\alpha \quad P_2(y) = -\alpha \quad P_2(x+y) = 2\alpha$$

Then the final pressure is going to be

$$P_3(x) = x - 2\alpha \quad P_3(y) = y - \alpha \quad P_3(x+y) = 2\alpha$$

Then the sum of the final partial pressures must equal to $P_3(x+y)$, i.e.

$$P_3(x+y) = 1.65 = P_3(x) + P_3(y) = x + y - \alpha$$

Then since $P_1(x+y) = x + y = 1.90 \text{ atm}$,

$$1.65 = 1.90 - \alpha \Rightarrow \alpha = 0.25$$

So the change is 0.25 atm. Then $P_3(\text{SO}_3) = 2\alpha = 0.50 \text{ atm}$. Therefore, the number of moles is

$$n(\text{SO}_3) = \frac{(0.5)(2.00)}{(0.08206)(800)} = 0.052 \text{ mol}$$

(e) Then to find the partial pressures,

$$\chi(\text{SO}_3) = \frac{P(\text{SO}_3)}{P(\text{total})} = \frac{0.50 \text{ atm}}{1.65 \text{ atm}} = 0.303$$

See the table below for the reasoning in part (d).

$P(k)$	2SO_2	O_2	2SO_3
Initial	x	y	$x + y = 1.90$
Change	-2α	α	2α
Final	$x - 2\alpha$	$y - \alpha$	1.65

DEVIATIONS FROM IDEAL BEHAVIOR

The assumptions made in the kinetic molecular model break down at either *high pressure* and/or *low temperature*. That is, the postulates P2 and P3 break down.

P2. Volume of particles is negligible compared to the total volume occupied by gas.

P3. No attraction or repulsive forces between particles.

REAL GASES

The gas laws were obtained from experiments performed under "normal" conditions of temperature and pressure. Under more extreme conditions, we get deviations from the ideal gas law.

1. Effect of size: Although it was assumed in KMT that gas particles occupy very little space, their size does become more significant at higher pressures.
2. Effect of intermolecular force: When particles are found at small separations, intermolecular forces have to be taken into account.

At higher pressures, the gas particles occupy a significant portion of gas volume. The free volume (the one they can travel through) is reduced from the measured total volume V to an extent proportional to the number of molecules present and the volume they each exclude.

Modeling the relationship by taking the volume into account:

- Ideal Gas: V
- Real Gas: $V - nb$

where b is a constant that depends upon the gas,

$$V - nb = \frac{nRT}{P}$$

In ordinary pressure, the molecules of the volume are negligible, and at high pressure, the volume of molecules is significant.

At higher temperatures and lower pressures (even at STP), attractive forces between gas particles are very weak relative to their kinetic energy so these attractive forces have an insignificant effect on their collisions. However, at lower temperatures the kinetic energy of the gas particles decreases and the weak attractions between them become more significant.

Modeling the relationship by taking the effects of intermolecular forces into account:

- Ideal Gas: P
- Real Gas: $P + \frac{an^2}{V^2}$

where a is a constant that depends upon the gas.

Combining the effects of particle volume and intermolecular forces,

- Real Gas: $P + \frac{an^2}{V^2}$
- Real Gas: $V - nb$

We have the Van Der Waals Equation:

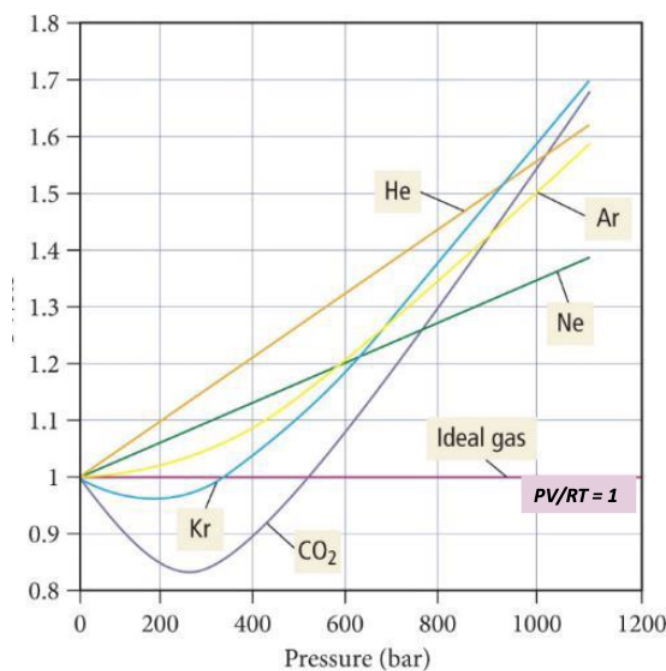
$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

This equation can be used to calculate the properties of a gas under non-ideal conditions. A gas that does not obey the ideal gas law is known as a real gas.

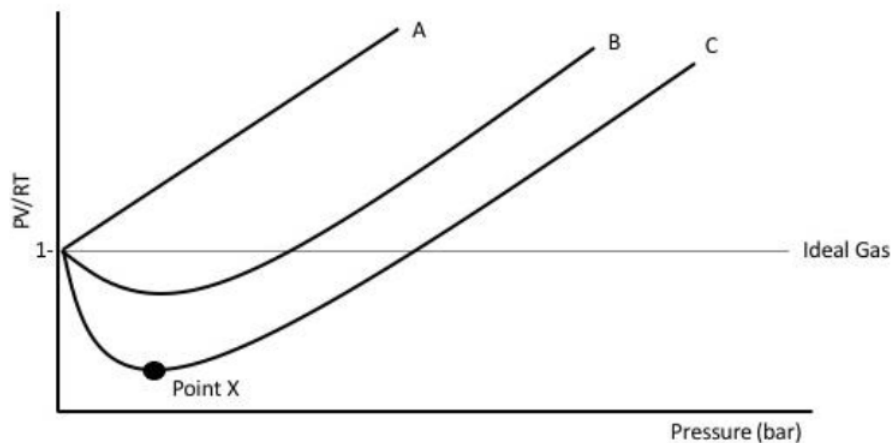
For an ideal gas, $PV = nRT$, and $n = \frac{PV}{RT} = 1$ (for 1 mole). For real gases, the ratio $\frac{PV}{RT}$ is greater or less than 1.

- When $n > 1$, the molecules having size and is quantified by the b factor.
- When $0 < n < 1$, the molecules having intermolecular forces and is quantified by the a factor.

What contributes to the different shapes and curves observed for He and CO₂?



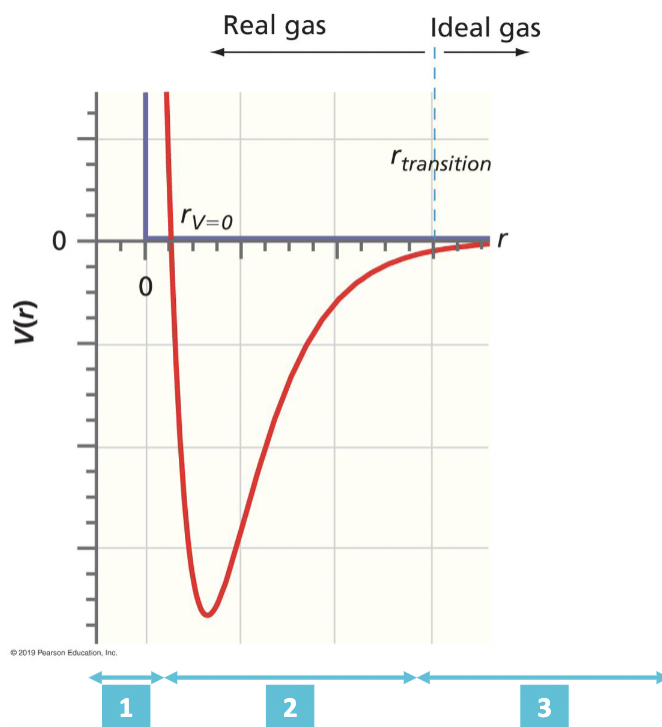
Question: A graph of PV/RT vs P for a series of real gases are shown below. Which temperature conditions (high or low) will result in the greatest deviation at point X?



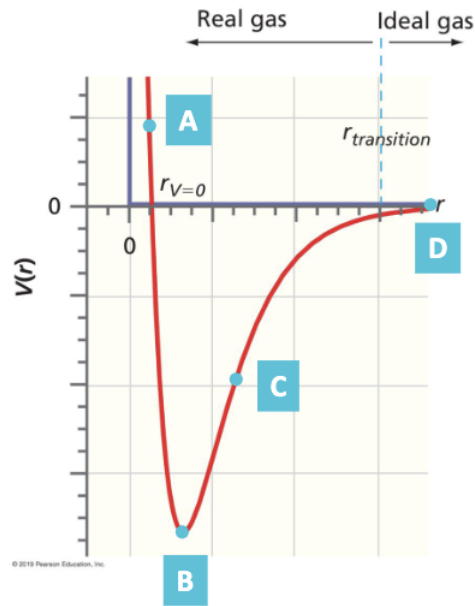
LOW TEMPERATURES

POTENTIAL ENERGY

1. If $r < r_{V=0}$ and $U = 0$, then we have repulsion.
2. If $r_{V=0} < r < r_{transition}$ and $U = 0$, then we have attraction.
3. If $r > r_{transition}$ and $U = 0$, then there is no interaction.



Question: Considering the potential energy of interaction of two molecules or atoms, at which point *A*, *B*, *C* or *D* does repulsion dominator over attraction?



A

Example 4.3: To synthesize ammonia using the Haber process, 2000 moles of N_2 are heated in a 800-L vessel to $625^\circ C$. Calculate the pressure of the gas if nitrogen behaves (a) as an ideal gas and (b) as a Van Der Waals gas.

Solution: Given that $n = 2000$ mol, $V = 800$ L, $T = 625^\circ C = 898$ K, $a = 1.35$ L² atm/mol² and $b = 0.0386$ L/mol, we want to determine the pressure in an ideal gas situation and in the real situation.

$$P_i = \frac{nRT}{V} = \frac{(2000)(0.08314)(898)}{800} = 187 \text{ bar}$$

Then in the real gas situation

$$P_V = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{(2000)(0.08314)(898)}{800 - (2000)(0.0386)} - \frac{(1.35)(2000)}{800^2} = 207 \text{ bar}$$

as required.