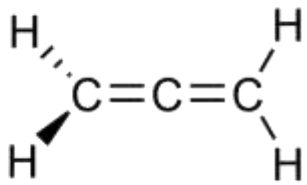
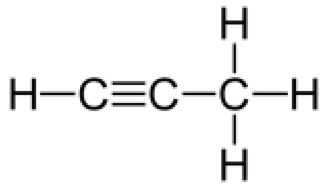
Simple Equilibrium with Multiple Reactions

The species C_3H_4 comes in three common isomers:



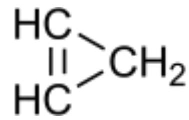
Allene (Propadiene)

A



Propyne (Methyacetylene)

B



Cyclo-Propene

C

If we buy a bottle of allene and heat it to 600 K, what is the composition of the gas? Assume P = 1 atm.

SOLUTION:

We have three possible reactions here: A↔B, B↔C, A↔C, but only two are independent, since we can write: A↔B + B↔C = A↔C. So we can choose any two of the three for our analysis. We'll select A↔B (call it reaction 1), and B↔C (reaction 2).

In this very simple case, we don't need to deal with advancements since our expressions for the equilibrium constant give us everything we need:

$$K_{p1} = \frac{P_B}{P_A} \qquad K_{p2} = \frac{P_C}{P_B}$$

and we also have the sum of pressures equals 1 atm. So we need to get the K_ps, and we'll be all set. For K_p, recall that:

$$K_p = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \exp\left(\frac{-\sum \mu_i^\circ \nu_i}{RT}\right) = \exp\left(-\sum \nu_i (\mu_i^\circ / RT)\right) = \exp\left(-\sum \nu_i \left(\frac{h_i}{RT} - \frac{s_i^\circ}{R}\right)\right)$$

In this form, it's easy to use the property coefficients directly to get the equilibrium constant. Here are the data from Kurucz:

```
H4C3 PROPYNE       T 2/90H   4C   3    0    0G   200.000  6000.000 1000.        1
 0.60252400E+01 0.11336542E-01-0.40223391E-05 0.64376063E-09-0.38299635E-13    2
 0.19620942E+05-0.86043785E+01 0.26803869E+01 0.15799651E-01 0.25070596E-05    3
-0.13657623E-07 0.66154285E-11 0.20802374E+05 0.98769351E+01 0.22302059E+05    4
C3H4 ALLENE        L 8/89C   3H   4    0    0G   200.000  6000.000 1000.        1
 0.63168722E+01 0.11133728E-01-0.39629378E-05 0.63564238E-09-0.37875540E-13    2
 0.20117495E+05-0.10995766E+02 0.26130445E+01 0.12122575E-01 0.18539880E-04    3
-0.34525149E-07 0.15335079E-10 0.21541567E+05 0.10226139E+02 0.22962267E+05    4
C3H4  cyPropene    T 7/11C  3.H  4.   0.   0.G   200.000  6000.000 1000.        1
 6.28078872E+00 1.12393798E-02-4.01957416E-06 6.46920405E-10-3.86433056E-14    2
 3.11629635E+04-1.11420363E+01 2.24666571E+00 5.76237942E-03 4.42080338E-05    3
-6.62906810E-08 2.81824735E-11 3.29498944E+04 1.33451493E+01 3.41487352E+04    4
```

We can make a simple spreadsheet to do the calculations for us using the low range coefficients (we're between 200 and 1000 K in this problem). Here's the spreadsheet:

	ALLENE	PROPYNE	cyPropene
a1	2.6804E+00	2.6130E+00	2.2467E+00
a2	1.5800E-02	1.2123E-02	5.7624E-03
a3	2.5071E-06	1.8540E-05	4.4208E-05
a4	-1.3658E-08	-3.4525E-08	-6.6291E-08
a5	6.6154E-12	1.5335E-11	2.8182E-11
a6	2.0802E+04	2.1542E+04	3.2950E+04
a7	9.8769E+00	1.0226E+01	1.3345E+01
T(K)	600	600	600
c_p/R	1.0970E+01	1.1091E+01	1.0953E+01
h/RT	4.1826E+01	4.2910E+01	6.1348E+01
s^o/R	3.6185E+01	3.5563E+01	3.5272E+01
μ^o/RT	5.6405E+00	7.3470E+00	2.6076E+01
K_p A → B	0.181501323		
K_p B → C	7.34911E-09		

So the pressure of B is 0.18 times that of A, and that of C is 7×10^{-9} times that of B. Some quick substitutions yield:

$P_{Allene} = .846$ atm $P_{Propyne} = .154$ atm $P_{Cyclo\text{-}Propene} = 1 \times 10^{-9}$ atm