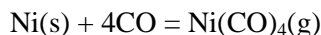# South Dakota School of Mines and Technology
Department of Materials and Metallurgical Engineering

Met 321   **Vapor Transport Reactions**

Mond (Nickel Carbonyl) Process

The reaction

$$Ni(s) + 4CO = Ni(CO)_4(g)$$

is EXOTHERMIC. One would guess it to be *endothermic* since the condensed phase Ni is going to a vapor phase but not so. This means the reaction is favored by *decreased* T. Therefore, the reaction is used to take up impure Ni a LOW temperature while pure Ni is dropped out at HIGH temperature. The Enthalpy and the Standard Gibbs energy change at selected temperatures are shown below.

```
O U T P U T   F R O M T H E R M O - C A L C
    2009. 4. 3 /15. 34. 4
    Reaction: 4C1O1+NI=C4NI1O4
        C1O1 stable as GAS
        NI stable as NI_S
        C4NI1O4 stable as C4NI1O4_L
```

```
*******************************************************************
```

T	Delta-Cp	Delta-H	Delta-S	Delta-G	
(K)	(Joule/K)	(Joule)	(Joule/K)	(Joule)	
```
*******************************************************************
```
298.15	6.10297E+01	-1.89669E+05	-5.00895E+02	-4.03274E+04	
300.00	6.11080E+01	-1.89556E+05	-5.00517E+02	-3.94011E+04	
320.00	6.18745E+01	-1.88326E+05	-4.96548E+02	-2.94307E+04	
340.00	6.25117E+01	-1.87082E+05	-4.92777E+02	-1.95378E+04	
360.00	6.30395E+01	-1.85826E+05	-4.89189E+02	-9.71843E+03	Makes Ni(CO)4 at std conditions[*]
380.00	6.34719E+01	-1.84561E+05	-4.85769E+02	3.08731E+01	Deposits Ni and releases 4CO[*]
400.00	6.38182E+01	-1.83288E+05	-4.82504E+02	9.71335E+03	
420.00	6.40839E+01	-1.82009E+05	-4.79383E+02	1.93320E+04	
440.00	6.42716E+01	-1.80725E+05	-4.76397E+02	2.88896E+04	
460.00	6.43806E+01	-1.79439E+05	-4.73538E+02	3.83887E+04	
480.00	6.44071E+01	-1.78151E+05	-4.70797E+02	4.78319E+04	
500.00	6.43433E+01	-1.76863E+05	-4.68169E+02	5.72213E+04	

* std conditions: pure Ni 1 atm CO and 1 atm Ni(CO)$_4$

There is nothing particularly magical about the temperature where the value of DG^o transition from positive to negative values. The primary feature to note is the shift in reaction favorability with T. However, the pressures of reactant and product gases both need to be significantly large to make kinetics substantial. This is going to be where the pressures are nearly the same: ergo Keq ~ 1 and Std Gibbs Energy ~ 0.

There are many such transport reactions. Two famous examples are the halogen light bulb and the carbon filament light bulb..

Halogen Light Bulbs: W-Cl System

A second nice example is the W-Cl system used in halogen high-intensity light bulbs:

```
O U T P U T F R O M T H E R M O - C A L C
    2009. 4. 3 /16.24.12
    Reaction: 3CL2+W=CL6W1<G>
        CL2 stable as GAS
        W stable as W_S
```

```
   *********************************************************************
   T        Delta-Cp       Delta-H        Delta-S        Delta-G
   (K)      (Joule/K)      (Joule)        (Joule/K)      (Joule)
   *********************************************************************
   1500.00  1.42319E+01    -4.73078E+05   -2.54061E+02   -9.19855E+04
   1600.00  1.36331E+01    -4.71684E+05   -2.53162E+02   -6.66252E+04
   1700.00  1.29444E+01    -4.70354E+05   -2.52355E+02   -4.13501E+04
   1800.00  1.21593E+01    -4.69098E+05   -2.51637E+02   -1.61512E+04
   1900.00  1.12718E+01    -4.67926E+05   -2.51003E+02    8.98012E+03
   2000.00  1.02767E+01    -4.66847E+05   -2.50450E+02    3.40521E+04
   2100.00  9.16873E+00    -4.65874E+05   -2.49975E+02    5.90727E+04
   2200.00  7.94327E+00    -4.65017E+05   -2.49576E+02    8.40496E+04
```

One can determine from this that the life of the W filament will be increased because W will be deposited on the any part of the filament that thins and gets hotter. The thicker (cooler part of the filament will supply the W. By this mechanism, the filament diameter remains constant. This continual "healing" prolongs the life of the filament by a factor of two to three times while operating at even higher temperatures than a normal bulb. The higher operating temperature makes halogen bulbs approximately 20 percent more efficient.

C Light Bulb Filaments

Another example arose from the days of C-filament (Edison's idea) light bulbs. If one laid half of the bulb in water, C was found to be deposited to the point of totally blackening the cold region. Why?

$$C_{(s)} + \tfrac{1}{2}\, O_2 = CO_{(g}$$
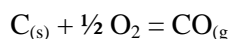
There is always a trace amount of O2 in the bulb. The reaction above is favored at high temperature. Think Ellingham Diagram: the C/CO line is the only one sloping downward. Therefore, CO is favored at high (filament) temperatures and less favored at low (cold bulb surface) temperatures. C will be transported to the cold surface by little CO trucks, which are never consumed. They just keep on trucking C from the filament to the wall. It is important for the bulb wall to be HOT to retard the transport thereby keeping the inner bulb surface clean.

Van Arkel – de Boer Process

The van Arkel – de Boer process is also known as the crystal bar process or iodide process. Anton Eduard van Arkel and Jan Hendrik de Boer discovered this vapor transport method in 1925. It was used to produce the first commercially pure ductile zirconium. It is possible to produce small ultra-pure quantities of both titanium and zirconium.

The process is based on the use of iodine gas in the following general reaction where M is either Ti or Zr

$$M_{(s} + 2I_{2(g)} = MI_{4\ (g)}$$
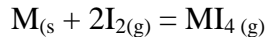
The endothermic reaction favors the formation of the metal tetraiodide at lower temperature while the metal is favored at high temperature.

Impure Ti or Zr in an evacuated vessel is heated with I_2 at 150^oC. The tetraiodide (TiI_4 or ZrI_4) vaporizes leaving all impurities behind. The tetraiodide is may be condensed and further purified by distillation or more simply kept within the same sealed vessel where it is formed and reduced to pure metal on a very hot (1400^oC) W filament. As metal deposits the filament requires more current to maintain a temperature great enough to promote the reduction reaction. The wire typically runs vertically along the centerline of a cylindrical vessel and the impure Ti or Zr is held along the outer wall within a mesh basket arrangement. The Kroll process replaced the van Arkel-de Boer process (circa 1945).

A similar process may be used to purify Al based on the formation of aluminum trichloride vapor according the reaction

$$2Al_{(l)} + AlCl_{3(g)} = 3AlCl_{(g)}$$
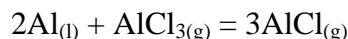
This reaction is more favorable at high temperatures making the deposition of pure Al favored at low temperature.

Physical properties:
$$TiI_{4,\ MP} = 150^oC, \quad TiI_{4,\ BP} = 377^oC$$
$$ZrI_{4,\ MP} = 499^oC, \quad ZrI_{4,\ BP} = 600^oC$$