

Effect of Heat of Intercalation on Graphite Temperature

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Introduction

During intercalation, the temperature of graphite will become higher than the surrounding temperature if the intercalation reaction is strongly exothermic. In this report an equation relating graphite temperature to heat of intercalation, reaction rate, reaction time, and graphite sample size are derived. The maximum temperature difference between graphite and its surrounding for some particular applications are then calculated and discussed.

Mathematical Modeling

From energy conservation, the rate of heat generated by intercalation is equal to the rate of heat accumulated by graphite plus the rate of heat loss from the graphite to its surroundings.

Let the percent completion of the reaction be $100(1-\exp(-kt))$ where t is reaction time, and k is a constant selected to fit the experimental data. If $-\Delta H$ is the heat generated by intercalation per mole of intercalant, W is the weight of pristine graphite to be intercalated, f is the fractional weight gain over pristine graphite for the completely intercalated compound, and M is the molecular weight of the intercalant, then the rate of heat generated by intercalation is:

$$q_1 = -\Delta H \left(\frac{Wf}{M} \right) ke^{-kt} \quad (1)$$

The rate of heat accumulated by graphite is:

$$q_2 = NC \left(\frac{dT}{dt} \right) \quad (2)$$

where N is the number of gram atom of graphite being intercalated, C is the heat capacity of the compound being intercalated per gram atom of graphite and T is the graphite temperature.

The rate of heat loss from graphite to its surroundings is:

$$q_3 = hA(T - T_0) = (h_r + h_c)A(T - T_0) \quad (3)$$

where A is the surface area for heat transfer, T_0 is the surrounding temperature, h is heat transfer coefficient between graphite and its surroundings and h_r and h_c are radiative

and convective components of h , respectively. For the radiative component:

$$h_r = (4 + n) \sigma \epsilon T_{avg}^3 \quad (4)$$

where σ is Stefan-Boltzmann constant, ϵ is emissivity and T_{avg} is the average temperature of graphite and its surrounding. For graphite below 600 K, ϵ is between 0.6 and 0.65 and n , a measure of the dependence of ϵ on temperature, is much smaller than 4.² Details to calculate h_c were lengthy. However, if the system is a horizontal long cylinder under natural convection, the relation between h_c and fluid properties are described in Table 1.

It follows that $q_1 = q_2 + q_3$, or

$$-\Delta H \left(\frac{Wf}{M} \right) ke^{-kt} = NC \left(\frac{dT}{dt} \right) + hA(T - T_0) \quad (5)$$

Initial condition for equation (5) is $T = T_0$, i.e., the initial graphite temperature is equal to the surrounding temperature.

Equation (5) with its initial condition and dimensionless variables has the following solution:

$$\frac{(T - T_0)}{T_0} = \left(\frac{K}{(1 - k')} \right) (e^{-k't'} - e^{-t'}) \quad (6)$$

Table 1. - Relation Between Convective Heat Transfer Coefficient and Fluid Properties For a System Where a Long Cylinder is Under Natural Convection

$\log \frac{D^3 \rho_f^2 g(T - T_0) C_f \mu_f}{T_0^2 \cdot k_f}$	4	2	0	-2	-4
$10 \log \frac{h_c D}{k_f}$	7	3.2	0	-1.8	-3.1

D : cylinder diameter; g : 9.8 m/sec^2 ; ρ_f : fluid density; μ_f : fluid viscosity; C_f : fluid heat capacity; k_f : fluid thermal conductivity

where $t' = \left(\frac{hA}{NC} \right) t$, (7)

$$k' = \left(\frac{NC}{hA}\right)k \quad (8)$$

$$\text{and} \quad K = (-\Delta H) \left(\frac{Wf}{M}\right) \frac{k}{hAT_0} \quad (9)$$

From equation (6), letting $dT/dt' = 0$, one has maximum temperature at $t'_{\max}$, where

$$t'_{\max} = \frac{(-\ln(k'))}{(1-k')}, \text{ or} \quad (10)$$

$$t_{\max} = \frac{NC}{hA} \frac{(-\ln(k'))}{(1-k')} \quad (11)$$

and the maximum temperature, $T_{\max}$, is

$$T_{\max} - T_0 = \left(\frac{T_0 K}{(1-k')}\right) \left(k'k'/1-k' - k'1/1-k'\right) \quad (12)$$

N, C, h, and A were treated as constants in this model. In reality, C, h, and A could change significantly during intercalation. Thus the temperature predicted from this model can only be regarded as an approximation, lower limit or upper limit when the values of C, A, and h used in this model are average value, upper limit or lower limit, respectively. It is also assumed in this model that the temperature in the graphite is uniform. This is believed to be a good approximation because the high thermal conductivity of graphite.

Results and Discussion

The model derived above was used to calculate the maximum graphite temperature in the following three different intercalation conditions. Values used in the calculations are described in Table 2.

(1) A Union Carbide P-100 graphite fiber (10 μ m diam, 1 cm long) was intercalated at 260 °C by ferric chloride with 1 atm chlorine gas. If the reaction was 50% complete at 5 sec after intercalation started ($t_{1/2} = 5$ sec) and the weight gain during intercalation was 190% over the pristine fibers to form C_7FeCl_3 , the maximum temperature increase ($\Delta T_{\max}$) was calculated to be 1.3 °C. The large surface to volume ratio and the high heat transfer coefficient for small sample were the reason why the graphite temperature increase was small despite the very high reaction rate.

(2) A strand of P-100 graphite fibers (2000 fibers), 1 ft long, was intercalated in a gas mixture containing equal amount of ferric chloride and chlorine at high temperature. If the strand had 1 mm diameter (and therefore 80 % porosity by volume), the reaction temperature was 360 °C and the total pressure could be less than 3 atm when $t_{1/2} = 5$ sec, the maximum temperature increase was calculated to be more than 52 °C. For such a large temperature increase this model became inaccurate because h is no longer a constant during intercalation. This result, however, indicated that $\Delta T_{\max}$ was large in this case.

(3) The P-100 fiber strand described in (2) was intercalated by bromine vapor at room temperature. If $t_{1/2}$ was 5 min and the weight gain during intercalation was 50 % over the pristine fibers, the maximum temperature increase was calculated to be 2.1 °C at 27 sec after intercalation reaction started.

Table 2. - Procedure to Calculate $\Delta T_{\max}$

Variables.	(a)	(b)	(c)	Unit
A	0.00314	15.05	15.05	cm ²
N	.00125	75	75	10 ⁻⁴ moles
T ₀	533	633	293	K
h _r (1)	5.1	8.66	0.82	10 ⁻⁴ cal (cm) ² (sec)
h _c (1)(2)	104.3	<14.3	1.34	
h	109.4	<22.9	2.16	
C(3)(4)(5)	8.23	8.23	2.74	*
-ΔH (6)(7)	18.9	18.9	10.9	**
W	.150	9000	9000	10 ⁻⁵ gm
f	1.92	1.92	.5	
t	5	5	300	sec
k ^{1/2}	139	139	2.32	10 ⁻³ /sec
k'	41.6	>2490	147	10 ⁻⁴
M	161	161	159.8	
ΔT _{max}	1.34	>52	2.1	K
t _{max}	.17	>3.3	27	sec

*cal/(mole carbon)(K)

**Kcal/(mole intercalant)

The above results suggested that for fast intercalation of a large amount of graphite fibers, the graphite temperature could increase significantly. Such temperature increase could be reduced by separating the individual fibers so that the surface area available for heat transfer is large. The problem could also be solved by using a heat sink, e.g., a reasonably thermal conductive mandrel for a spool of fibers. For producing pounds of intercalated graphite fibers, this model could be used to estimate the minimum efforts needed in applying heat sinks or increasing the surface area for heat transfer.

References

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