Kinetics of the Reaction of C_2H_6 , CH_4-CO_2 and $CO-CO_2-O_2$ Gases with Liquid Iron

Kazuto SEKINO, Tetsuya NAGASAKA¹⁾ and Richard J. FRUEHAN²⁾

Formerly Department of Materials Science & Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA, now at Kashima Works, Sumitomo Metal Industry Co. Ltd., Kashima, Japan.

1) Formerly Department of Materials Science & Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA, now at Department of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai, 980-8579 Japan.

2) The Center for Iron and Steelmaking Research, Department of Materials Science & Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA.

(Received on August 11, 1999; accepted in final form on November 30, 1999)

The kinetics of several gas-metal reactions relevant to bath smelting have been investigated. The rate of carburization of liquid iron by C_2H_6 gas was measured between 1 400 and 1 600°C under conditions in which partial pressure of C_2H_6 was in the range of 0.016 to 0.04 atm and sulfur content in the iron was in the range of 0.003 to 0.5 wt%. The experimental results indicate that the rate is controlled by the dissociation of C_2H_6 on the surface of iron and gas phase mass transfer in series. The gas phase mass transfer can be corrected with reasonable accuracy and the chemical rate constants were obtained. The rate was retarded by sulfur in liquid iron and there was evidence of a large residual rate at high sulfur contents. The rate of carburization of pure liquid iron ($a_s=0.01$) by CH_4-CO_2 gas mixture was measured at 1 600°C under conditions at which the rate is controlled by gas phase mass transfer and chemical reaction in series. The gas was 6 % CH_4 and up to 2.5 % CO_2 in Ar. It was concluded that CH_4 and CO_2 reached the surface of the iron before they reacted with each other and carburization by CH_4 and decarburization by CO_2 occurred independently for the present experimental conditions. The rate of decarburization of carbon saturated liquid iron by $CO-CO_2-O_2$ gas mixture was measured at 1 600°C. The partial pressure of O_2 in 90%CO/10% CO_2 gas was in the range of 0 to 0.03 atm and sulfur content in the metal was 0.1 wt%. The measured rate shows that the gases reached the surface of metal before they reacted with each other and decarburization by CO_2 and O_2 proceeded independently at a high gas flow rate (5 l/min), but there may have been some gas phase reaction at lower flow rate (2 l/min).

KEY WORDS: iron smelting; kinetics; carburization.

1. Introduction

In iron bath smelting, coal is used as an energy source and as the reducing agent. Since coal contains 10–35% volatile matter, considerable amount of gas (H_2 and hydrocarbon gas) should be generated from coal in the smelting furnace. Therefore, it is very important to study the reaction of these gases with liquid iron. The kinetics of the reactions between these gases (CO_2 , H_2O , CH_4 , etc.) and liquid iron have been studied by several investigators^{1–16)} and it was found that the rate of dissociation of these gases on the surface of iron control the rate of the carburization or decarburization of iron. In a previous paper,¹⁵⁾ rate of reaction of CH_4 , which is the most important hydrocarbon gas with liquid iron, has been investigated and the dissociation of CH_4 molecule on the surface of liquid iron was found to be a rate-determining step. It was also observed that the rate was retarded by sulfur in liquid iron and there was a significant rate at high sulfur contents.

In this paper, the kinetics of reaction for another volatile

species (C_2H_6) and a simulated mixed volatile gas mixture (CH_4-CO_2) on the surface of liquid iron were studied. In addition, the rate of reaction of a $CO-CO_2-O_2$ gas mixture with carbon saturated iron was measured. In the experiments using C_2H_6 gas, the effect of sulfur and carbon contents in the iron, partial pressure of C_2H_6 and temperature on the rate of carburization by C_2H_6 gas was investigated. The energy efficiency of the bath smelting process relies on the post combustion of CO and H_2 from the bath. However, several reactions could occur to reduce the degree of this post combustion. For example, the reaction CO_2 with the released volatile matter such as CH_4 or C_2H_6 . Therefore, these reactions should be studied to clarify the reaction mechanism of these gases generated from coal with liquid iron. Furthermore, CO_2 and H_2O could also react with iron droplets reducing post combustion and possible oxidizing iron. These reactions have been studied^{2,3,5,7,11,13,14)} and are reasonably understood. However, since oxygen (O_2) is used in the process, it should be known whether (1) O_2 will react with CO and simply increase the CO_2 content or (2) react

directly with carbon in iron.

It is known that the rate of direct reaction of O_2 (2) is much faster than for CO_2 , so that this would have a greater effect. Therefore, the combined reactions of $\text{CO}_2\text{--CH}_4$ and $\text{CO--CO}_2\text{--O}_2$ with Fe–C melts were also studied in the present work.

2. Experimental Technique

The general experimental technique was the same as that described in a previous paper.¹⁵⁾ The metal samples (about 20 g) were prepared prepawl from pure iron ($S=0.0006\%$) and premelted to prepare master alloys (Fe–S–C alloys). The reaction gas mixture was jetted onto the surface of the inductively heated metal, which was held in an alumina crucible (ID 2 cm), through a coaxially placed alumina tube of 3 mm ID, held about 10 mm above the surface of the metal. In the experiments of carburization by C_2H_6 and $\text{CH}_4\text{--CO}_2$ gases, some carbon (0.4%) was initially added in the metal to eliminate the effect of dissolved oxygen on the rate of reaction. In the experiments of decarburization by $\text{CO--CO}_2\text{--O}_2$ mixed gas, a graphite disk (1.5 to 2.0 g) was cemented to the bottom of the inside of the alumina crucible using high purity alumina refractory cement to maintain carbon saturation of the iron. This technique has been used by several investigators.^{2,3,10,13,14)} The sample was slowly heated to the aim experimental temperature (from 1 400 to 1 600°C) in a quartz reaction chamber under a high Ar flow rate, about 200 ml/min. The temperature was measured by an infrared two-color optical pyrometer and controlled within $\pm 10^\circ\text{C}$ during the experimental runs by manual adjustment of the power supply. After keeping the experimental temperature constant, for about 5 min, the Ar gas was switched to the reaction gas. The gas flow rate was controlled by the calibrated mass flow meter. For the experiments of carburization by C_2H_6 gas and $\text{CH}_4\text{--CO}_2$ gas mixture, the gas flow rate was maintained at 10 l/min. Flow rates of 2 and 5 l/min were used in the experiments of decarburization by the $\text{CO--CO}_2\text{--O}_2$ gas mixture. The rate of carburization and decarburization were determined by the weight change of the iron sample during experimental runs. Sulfur and carbon contents in the iron were also analyzed for the experiments of carburization after the experiments. The sulfur content of iron decreased by about 10% the input amount during experiments. The activity of sulfur for these experiments of carburization was calculated at average carbon and sulfur concentration during experimental runs using the data of Ban-ya and Chipman.¹⁷⁾

3. Rate Equations

3.1. Gas Phase Mass Transfer

If the rate is controlled by gas phase mass transfer for a dilute species i , the rate is given by:

$$(dn_i/dt)/A = (k_g/RT)(p_i^b - p_i^s) \text{ (mol/cm}^2\text{ s)} \dots\dots\dots(3)$$

where, k_g , p_i^b and p_i^s are mass transfer coefficient in the gas

phase, partial pressure of species i in bulk and in surface layer, respectively. The mass transfer coefficient (k_g) can be estimated from the empirical Eq. (4) proposed by Kikuchi *et al.*¹⁸⁾ It was verified in previous experiments (CH_4 and H_2O reaction)^{13–15)} using the same experimental apparatus that the gas phase mass transfer coefficient can be calculated with reasonable accuracy using this equation:

$$\text{Sh} = (0.27 + 0.07)(r_s/d)^{-1.5} \text{Re}^{0.76} \text{Sc}^{0.5} \dots\dots\dots(4)$$

where, Sh=apparent Sherwood number ($k_g d/D$), Sc=Schmidt number ($\mu/\rho D$), Re=Reynolds number ($du\rho/\mu$), d =diameter of the nozzle (cm), D =gas diffusivity (cm^2/s), μ =viscosity of the gas (g/cm s), ρ =density of the gas (g/cm^3), u =average gas velocity (cm/s) and r_s =radius of the crucible (cm).

3.2. Chemical Reaction

If the rate is controlled by the dissociation of species i on the surface of liquid iron, the rate is given by:

$$(dn_i/dt)/A = k_c(p_i^b - p_i^e) \text{ (mol/cm}^2\text{ s)} \dots\dots\dots(5)$$

where, k_c is the chemical rate constant of dissociation of species i and p_i^e is the species i pressure in equilibrium with the melt. If there are any surface active elements in the iron, such as oxygen and sulfur, the chemical rate constant is related to the bare surface rate constant k_c as a function of activity of surface active elements as follows:

$$k_c = k^o / \left(1 + \sum K_j a_j\right) \dots\dots\dots(6)$$

where, K_j and a_j are the adsorption coefficient and the activity of surface active element j respectively. If the rate is controlled by the dissociation of species i , the should be retarded with the surface active elements in iron and the rate constant should approach zero with activity of species j increasing. However, the rate does not become infinitely slow but approaches a finite value for many chemical reactions such as N_2 , CO_2 and CH_4 .^{2–4,8,10,13–15)} This is known as the residual rate phenomena and two possible explanations have been proposed as discussed previously in detail.¹⁵⁾

Briefly, a gaseous molecule can dissociate only on the surface not covered by a surface active element and all of the surface can not be covered by it even at high concentration of the surface active element in the metal. The chemical rate constant is given by:

$$k_c = k^o / \left(1 + \sum K_j a_j\right) + k_r \dots\dots\dots(7)$$

Another possibility is that the molecule can also dissociate on the surface covered by a surface active element and this rate may be smaller than the rate on pure metal. The chemical rate constant is given by:

$$k_c = k^o / \left(1 + \sum K_j a_j\right) + k_r \sum K_j a_j / \left(1 + \sum K_j a_j\right) \dots\dots\dots(8)$$

As discussed previously, the values of k^o , k_r and K_s can be determined for the limiting cases. If only one surface active element such as sulfur exists in the metal and the concentration of sulfur is high $K_s a_s$ as must be much larger than unity. Therefore, Eqs. (7) and (8) can be approximately:

$$k_c = (k^o/K_s)(1/a_s) + k_r \dots\dots\dots(9)$$

From Eq. (9), the rate constant should increase linearly with $1/a_s$ at high sulfur contents. k^o/K_s and k_r can be obtained from the slope and intersection of this relation respectively. On the other hand, at low sulfur contents, the rate constant should approach k^o . Therefore, Eqs. (7) and (8) can be approximated by:

$$1/k_c = (K_s/k^o)a_s + 1/k^o \dots\dots\dots(10)$$

From Eq. (10), $1/k_c$ should increase linearly with a_s and k^o can be obtained from the intercept at low sulfur concentrations.

3.3. Mixed Control

If the rate is controlled by both processes (gas phase mass transfer and chemical reaction) in series and the rate is first order with respect to the partial pressure of species i , the rate is represented by mixed control model as follows:

$$(dn_i/dt)/A = k_m(p_i^b - p_i^e) \dots\dots\dots(11)$$

where, k_m is the overall rate constant given by:

$$1/k_m = 1/k_c + RT/k_g \dots\dots\dots(12)$$

3.4. Liquid Phase Mass Transfer

Liquid phase mass transfer of carbon from the surface to the bulk liquid is given by:

$$d[\%C]/dt = m_l(A/V)(C^b - C^s) \dots\dots\dots(13)$$

where, m_l , A , V , C^b and C^s are mass transfer coefficients in liquid, area of interface, volume of sample, carbon concentration in bulk and carbon concentration in surface, respectively. For the present experimental conditions, C^s is essentially equal to the concentration of carbon saturated iron. In Eq. (13), the rate of carburization should be first order with respect to carbon concentration if liquid phase mass transfer is dominant. For the present experimental conditions, the calculated liquid phase mass transfer of carbon is much faster than gas phase mass transfer of reaction gases (C_2H_6 , CH_4 , CO_2 , etc.) as discussed previously.¹⁵⁾ Therefore, liquid phase mass transfer can be neglected.

4. Results and Discussion

4.1. Carburization by C_2H_6 gas

4.1.1. Rate Controlling Step and Order of Reaction

The reaction between C_2H_6 and liquid iron can be written as:

The rate of carburization by C_2H_6 gas can be controlled by the following rate determining steps.

- (1) Gas phase mass transfer of C_2H_6 from the bulk to the surface of the iron.
- (2) Dissociation of C_2H_6 on the surface of the iron.
- (3) Dissolution of carbon into the liquid iron.
- (4) Liquid phase mass transfer of carbon from the surface to the bulk.

If step (1) or (2) is dominant, the rate of carburization should depend on $p_{C_2H_6}$ and be independent of carbon con-

Fig. 1. Rate of carburization of iron by 4% C_2H_6 gas.

Fig. 2. Effect of $p_{C_2H_6}$ on the rate of carburization of iron at 1600°C.

tent in the iron. In addition, if sulfur in the iron decreases the chemical rate, step (2) should be one of the rate determining steps. On the other hand, if step (3) or (4) is dominant, the rate should be first order with respect to carbon content in the iron. However, liquid phase mass transfer is much faster than gas phase mass transfer for the present experimental conditions. Therefore, step (4) can be neglected. **Figure 1** shows the rate of carburization by 4% C_2H_6 gas at very low sulfur activity ($a_s=0.007$). Carbon in iron increased linearly with time and the measured rate is about one third of the rate calculated for gas phase mass transfer. For these experimental conditions, the rate is clearly independent of carbon content in the iron. **Figure 2** shows the effect of pressure of C_2H_6 in gas phase on the rate of carburization. The rate is clearly first order with respect to $p_{C_2H_6}$. From these results it appears that the rate is controlled by the dissociation of C_2H_6 on the surface of iron and gas phase mass transfer in series and the rate equation is given by Eq. (11). For these experimental conditions $p_{C_2H_6}^e$ is essentially equal to zero. The chemical rate constant of dissociation for C_2H_6 can be obtained reasonably accurately using the mixed control model. For the chemical rate constant (k_c) used in the following sections, the effect of gas phase mass transfer was corrected using Eqs. (11) and (12).

Fig. 3. Effect of sulfur activity on the rate constant for dissociation of C_2H_6 on liquid iron.

Fig. 4. Relationship between k_c and $1/a_s$ for the carburization of iron by C_2H_6 .

The correction for gas phase mass transfer was up to 37% at 1600°C at the lowest sulfur content.

4.1.2. Effect of Sulfur in iron on the Rate Constant

The effect of sulfur activity in iron on the chemical rate constant between 1400 and 1600°C is shown in **Fig. 3**. Sulfur decreases the rate but the chemical rate constant approaches a finite value at high sulfur activities. The residual rate phenomenon was also observed for the CO_2 , H_2O and CH_4 reactions,^{2-4,8,10,13-15} the residual rate is about half of the bare surface rate in present work. This phenomenon is very similar to that in the CH_4 reaction¹⁵) and C_2H_6 may dissociate not only on the surface which is not covered by sulfur, but also on the surface covered by sulfur. Therefore, Eq. (8) may be applied to this reaction to represent the chemical rate constant as a function of sulfur activity in iron. **Figure 4** shows the relationship between k_c and $1/a_s$ from 1400 to 1600°C at high sulfur activity above 0.065. Within the experimental scatter, k_c increased linearly with $1/a_s$. k_r and k^0/K_s were obtained from the intersections and slopes of these relations for each temperature. **Figure 5** shows the relationship between $1/k_c$ and a_s from 1400 to 1600°C at low sulfur activity, below 0.13. The results for each temperature are in accord with a linear dependence of $1/k_c$ on a_s and the values of k^0 were obtained from the in-

Fig. 5. Relationship between $1/k_c$ and a_s for the carburization of iron by C_2H_6 .

Fig. 6. Effect of temperature on the chemical rate constants (k^0 pure iron, k_r residual rate) for the carburization of iron by C_2H_6 .

Fig. 7. Effect of temperature on the adsorption coefficient K_s of sulfur on iron.

tersections for each temperature.

4.1.3. Effect of Temperature

The values of k^0 , k_r and K_s obtained from 1400 to

Fig. 8. Comparison of the dissociation rates of C_2H_6 , H_2O ,^[13] CO_2 ,^[2,10,14] CH_4 ^[15] and N_2 ^[19] as a function of sulfur content in liquid iron at 1600°C.

1600°C are represented in Figs. 6 and 7 as a function of reciprocal temperature. From these linear relations, the temperature dependency of k^o , k_r and K_S is given by:

$$\log k^o = -4860/T - 0.705 \dots \dots \dots (15)$$

$$\log k_r = -3960/T - 1.55 \dots \dots \dots (16)$$

$$\log K_S = 5560/T - 1.37 \dots \dots \dots (17)$$

The activation energies of k^o and k_r are evaluated from Eqs. (15) and (16) as 92.9, 75.7 kJ/mol, respectively. The value of K_S for this reaction is about 40 at 1600°C. For ideal Langmuir adsorption, the value of K_S should be same for all reactions. However, different values have been obtained for each reaction by several investigators. For example, The values of K_S have been found to be about 60,^[12] and 130,^[6,9] 100^[15] for CH_4 , 50^[2] for CO_2 and 60^[13] for H_2O , respectively. Considering the scatter in the values of K_S obtained from the different reactions, the value obtained from present results is reasonable.

The rate constants from 1400 to 1600°C were calculated by Eqs. (8), (15), (16) and (17). The calculated rate constants are indicated in Figure 3 as solid lines and the measured rates are in accord with the calculated rates. This supports that the residual rate phenomenon for the C_2H_6 reaction comes from the dissociation of gas molecule on the adsorbed sulfur. The dissociation rate of C_2H_6 is compared with that of other gas molecules^[10,14,15] as a function of sulfur content in liquid iron at 1600°C and presented in Fig. 8. It is seen that the dissociation rate of C_2H_6 is faster than that of CH_4 and slightly slower than that of CO_2 .

4.2. Reaction between CH_4 - CO_2 Gas and Liquid Iron

In a CH_4 - CO_2 gas mixture, if the CO_2 reacts with CH_4 at high temperature, this reaction is given by:

The rate of reaction of iron with CH_4 - CO_2 depends on

Fig. 9. Effect of CO_2 on the rate of carburization by CH_4 gas at 1600°C.

whether Reaction (18) could occurs.

Case I: If Reaction (18) is very fast, almost all of the CO_2 in the gas should react with CH_4 before reaching the surface of the iron and the gas on the surface may consist of CH_4 - CO -Ar. Since the equilibrium CO_2 pressure of Eq. (18) is much lower than that of Eq. (19) in these experimental conditions, carburization of iron by CO (Reaction (19)) can occur. However, since the CO_2 pressure of Reaction (19) in equilibrium with the Fe-C melt is very low (about 10^{-6} atm for 1% C iron), this reaction must be controlled by gas phase mass transfer of the produced CO_2 leaving from the surface and the rate of this reaction is very slow. Therefore, the effect of Reaction (19) on the overall rate will be negligible and CO_2 can be considered simply to reduce the pressure of CH_4 by Reaction (18). In this case, the melt should be carburized by the remaining CH_4 in the gas mixture on the surface and the rate of carburization should decrease with CO_2 pressure.

Case II: If the mass transfer of CO_2 is faster than the rate of Reaction (18), CO_2 may reach the surface of the iron before Reaction (18) occurs. Therefore, carburization by CH_4 and decarburization by CO_2 may occur independently. Both reactions should be controlled by gas phase mass transfer and their chemical reaction in series^[2,3,5,10,15] for these experimental conditions. In this case, the net rate of carburization should also decrease by adding CO_2 since CO_2 is decarburizing the metal. CO_2 will slow down the overall rate of carburization more rapidly than in Case I. The previously measured rate of decarburization^[2,3,10] was deducted from the previously measured rate of carburization by CH_4 ^[15] correcting in each case for gas phase mass transfer. The computed rate is shown in Fig. 9.

Figure 9 shows the effect of pressure of CO_2 on the rate of carburization by 6% CH_4 at a flow rate of 10 l/min and the solid lines in Fig. 9 are the calculated rates for each case. The measured rate was in good agreement with the calculated line for Case II. This result indicates that CO_2 reached the surface of iron before it reacted with CH_4 and carburization by CH_4 and decarburization by CO_2 proceed-

Fig. 10. Effect of O_2 on the rate of decarburization by CO-CO₂ gas at 1600°C.

ed independently. The calculated line for Case II is not simply curve fitting but uses the previously independent measured rates for the CH₄ and CO₂ reactions.

4.3. Reaction between CO-CO₂-O₂ Gas and Liquid Iron

In a CO-CO₂-O₂ gas mixture, O₂ could react with CO and this reaction is given by:

The equilibrium partial pressure of oxygen in Eq. (20) is essentially equal to zero. The rate of decarburization in a CO-CO₂-O₂ gas mixture could be controlled by one of the following two mechanisms.

Case I: If Reaction (20) is very fast, all of the O₂ should react with CO before reaching the surface of the liquid iron and the gas on the surface should not contain O₂. Therefore, the rate of carburization should be controlled by dissociation of CO₂ on the surface of the iron.^{2,3,5,10,14} In this case, the rate should increase slightly due to the increase of CO₂ by Reaction (20).

Case II: If the mass transfer of O₂ in the gas phase is faster than Reaction (20), O₂ may reach the surface of the iron before it reacts with CO. Therefore, decarburization will occur by both the reaction of CO₂ and O₂, the rate of decarburization may be controlled primarily by chemical kinetics of CO₂ and by gas phase mass transfer of O₂. In this case, the rate of decarburization should increase significantly with adding O₂.

Figure 10 shows the effect of the pressure of oxygen on the rate of decarburization by 90%CO-10%CO₂ and the solid lines in Fig. 10 are the calculated rates for each case. At a flow rate of 5 l/min, the rate increased significantly with increasing p_{O_2} and the measured rate was in good agreement with the calculated rate for Case II. However, as the flow rate was 2 l/min, the rate also increased by the addition of O₂, but the rate was intermediate between the calculated rates for Case I and Case II. This result indicates that some of the O₂ may react with CO before it reaches the surface of the iron at low flow rates.

4.4. Gas Phase Reactions

In these experiments using a gas mixture of CO-CO₂-O₂ and CH₄-CO₂, the gases did not react with each other at high flow rates. For these experimental conditions, the gas velocity on the metal surface was very fast ($u=75$ m/sec at 1600°C, at 10 l/min) and the gas was heated only by the metal. Therefore, temperature of these gases before they reach the metal surface must be relatively low and the reaction rate between gas species could be slow. However, because the gas generated from the coal in a furnace must be already heated, and the gas velocity may be much slower in an actual process than in these experiments, the gas species could react before they reach the metal surface. These reactions should be considered in more details for actual flow conditions existing in an actual process.

5. Summary and Conclusion

The rate of carburization of liquid iron by C₂H₆ gas was studied between 1400°C and 1600°C under conditions where a reasonable correction for the effect of gas phase mass transfer can be made. The rate was measured in the range of $p_{C_2H_6}$ from 0.016 to 0.04 atm and sulfur contents in liquid iron from 0.0006 to 0.5 wt%. The measured rates indicate that the rate of carburization was controlled by the dissociation of C₂H₆ on the surface of liquid iron. Sulfur decreases the rate and the residual rate phenomenon was observed. The residual rate for this reaction may come from the dissociation of C₂O₆ on the metal surface covered by sulfur. The rate constant was presented by bare surface rate constant, residual rate constant and adsorption coefficient for sulfur, which were determined as functions of temperature.

The rate of carburization of liquid pure iron ($a_s=0.01$) by a CH₄-CO₂ gas mixture was studied at 1600°C for a gas flow rate of 10 l/min. It was found that the gas reached the metal surface before reacting with each other, then, carburization by CH₄ and decarburization by CO₂ occurred independently for the experimental conditions in this study.

The rate of decarburization of carbon saturated iron containing 0.1 wt% sulfur was studied for a CO-CO₂-O₂ gas mixture at 1600°C, at gas flow rates of 2 and 5 l/min. At the high flow rate (5 l/min), the gas reached the metal surface without any reaction. Therefore, the rate of decarburization was controlled by gas phase mass transfer of O₂ and the dissociation of CO₂ on the metal surface independently. However, at a low flow rate (2 l/min), some of the O₂ may have reacted with CO and the gas composition changed before reaching the metal surface.

Acknowledgments

The authors wish to thank the AISI Direct Steelmaking Project, of which 77% was funded by the Department of Energy for support. The authors also thank Sumitomo Metal Ind. for support of K. Sekino for his stay at Carnegie Mellon University and Mrs. M. Lesko (Carnegie Mellon University) for the preparation of these manuscript.

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